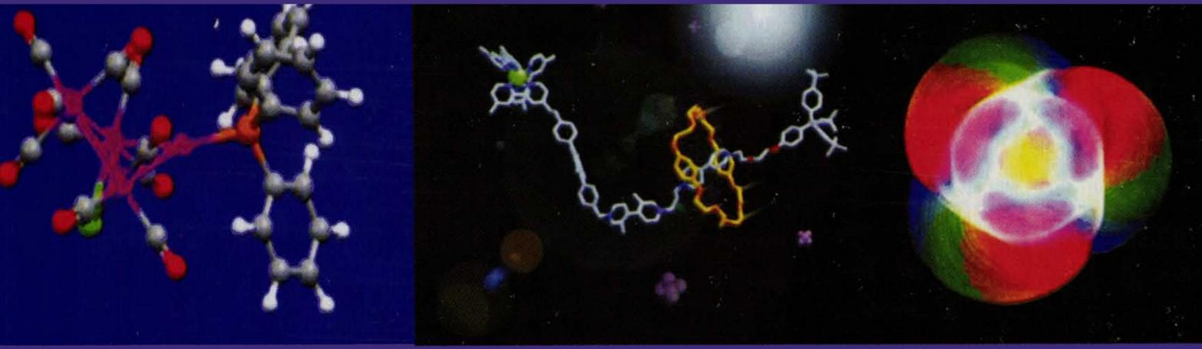

PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY

VINAY PRABHA SHARMA
RAKESH KUMAR

A Pragati Edition

Pragati's

PERICYCLIC REACTIONS
and
ORGANIC PHOTOCHEMISTRY

VINAY P. SHARMA
M.Sc., Ph. D.
Department of Chemistry,
J.V. (P.G.) College, Baraut (U.P.)

RAKESH KUMAR
M.Sc., Ph. D.-Scholar
Department of Chemistry,
J.V. (P.G.) College, Baraut (U.P.)

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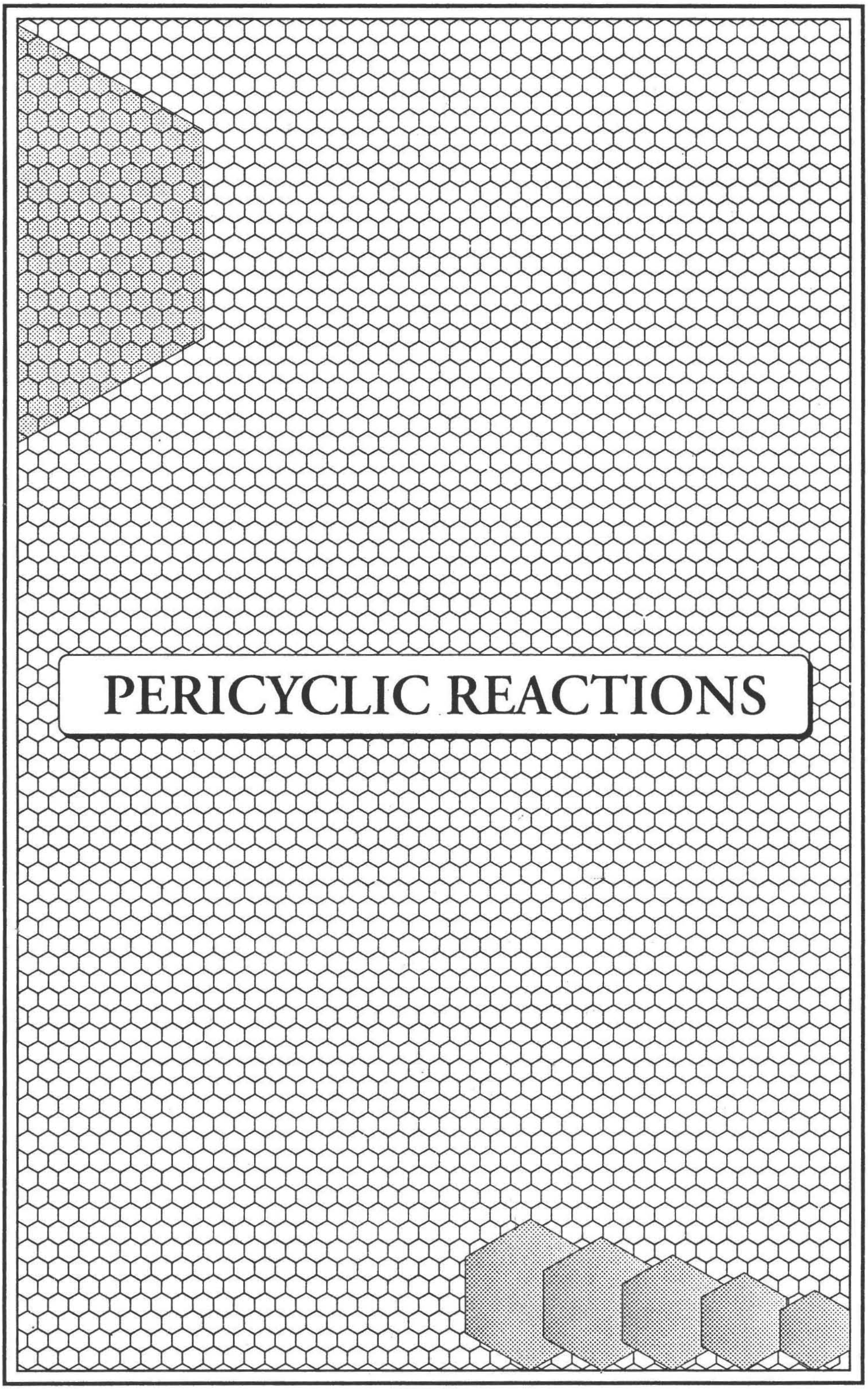

PERICYCLIC REACTIONS

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UNIT

1

INTRODUCTION

1.1 GENERAL INTRODUCTION

A large number of chemical reactions of unsaturated organic compounds (both olefinic as well as acetylenic) are such that they proceed without any involvement of intermediates like carbonium ion, carbanion or free radical, rather they involve cyclic transition state (T.S.). As they involve cyclic T.S., hence they are known as pericyclic reactions. These reactions were discovered by Woodward and Hoffmann in 1965. Their characteristics are :

(i) They are insensitive to the presence or absence of catalysts and solvents.

(ii) They are feasible both thermally as well as photochemically.

(iii) Products through thermal and photochemical transformations are generally different in their stereochemistry.

(iv) Most important observation about them is that during their occurance symmetry properties of orbitals are conserved, *i.e.*, a symmetric orbital transforms into a symmetric orbital and an asymmetric orbital is transformed into an asymmetric orbital.

(v) They occur in a concerted manner, *i.e.*, bond making and bond breaking both are synchroneous.

(vi) They always follow lowest energy path even if difference between symmetry allowed or symmetry forbidden transition is very small; otherwise they will not occur in concerted manner.

An interesting example of pericyclic reaction is cyclization of precalciferol to steroisomeric I and II under thermal condition; both of which are *cis*-products. Similar reaction under photochemical conditions, *i.e.*, upon irradiation gives ergsterol(III), which is *trans*-product. Thus pericyclic reaction may result is different products under thermal and photochemical conditions.

These reactions are generally equilibrium reactions. The extent of equilibrium is governed by entropy and enthalpy of reacting systems. Though these reactions are not affected by catalyst, but some transition metals such as Pt(II), Pd(II), Ag(I), Ir(I), Rh(I) and Ni(I) etc., sometime catalyse these reactions in unusual way. However, they are unaffected by acids and bases.

Under thermal condition activation energy required for pericyclic reactions is supplied by increasing the reaction temperature as a result of which most of the molecules have nearly same amount of energy and the molecules which have

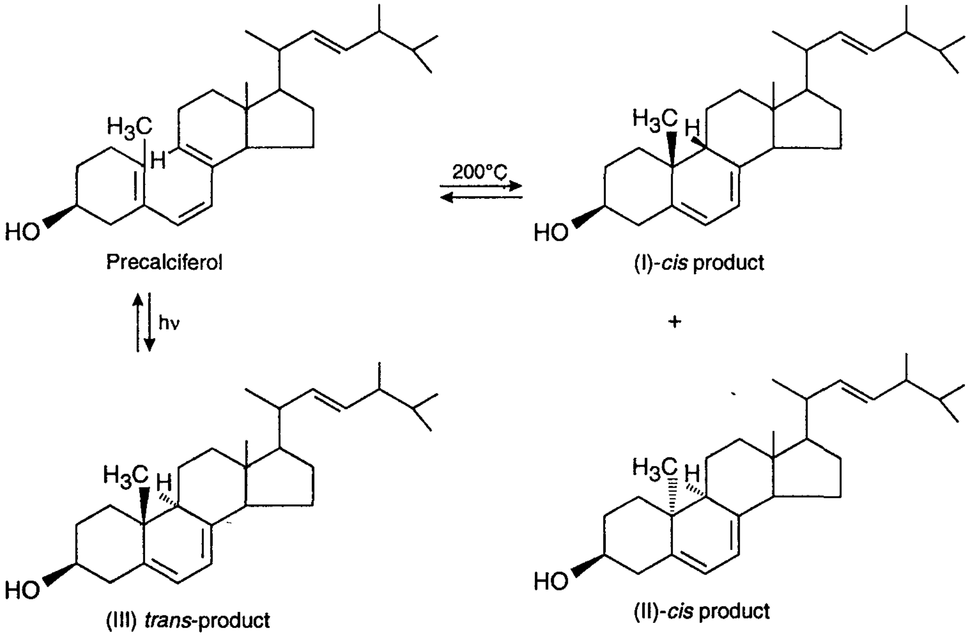


Fig. 1.1. Stereochemistry of thermal and photochemical reactions.

acquired sufficient energy result in the formation of product. At normal temperature and pressure vibrational, rotational and translational energies of molecules are higher than as expected from Maxwell and Boltzmann's law.

On the other hand energy for photochemical reactions come from ultra-violet and visible (U.V. visible) electromagnetic radiations. By absorbing these radiations molecules jump into excited state. Energy of radiation depends upon its frequency and is given by expression, $E = h\nu$. E is energy, h = Plank's constant and ν = frequency of radiation. Excited molecules and ground state (G.S.) molecules undergo chemical reactions in different manner, *i.e.*, why products of photochemical and thermal reactions are different. Thus, course of reaction can be changed by switching over from thermolysis to photolysis and vice-versa. Photochemical reactions are useful in synthesising highly-strained and thermodynamically unstable compounds, which cannot be synthesised by thermal methods. U.V.-visible radiations have enough energy to bring electronic excitation and to break chemical bond. Their energy ranges from 38–71 K. cals/mole.

Absorption of U.V. visible radiations causes promotion of electron from bonding to antibonding orbitals. Antibonding orbitals are described by putting star as superscript on corresponding bonding orbital. The order of energies of some bonding and antibonding molecular orbitals is given in Fig. 1.2.

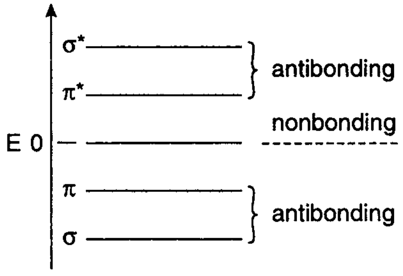
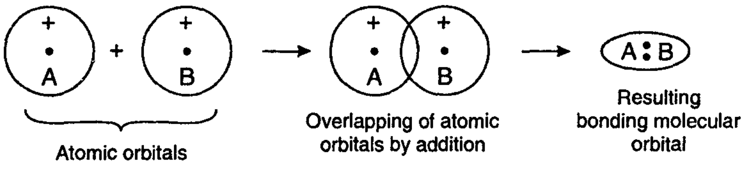


Fig. 1.2. Relative energies of bonding and antibonding molecular orbitals.

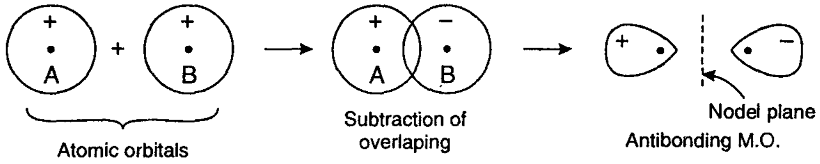
Molecular orbitals (M.Os.), represented by linear combination of atomic orbitals (LACO) are formed either by addition of overlap or by subtraction of overlap. M.Os. formed by addition of overlap are called bonding molecular orbitals; whereas subtraction of overlap of atomic orbitals results in the formation of antibonding molecular orbitals. In addition of overlap both the overlapping waves have same sign and as in this case maximum electron density lies in the region between atoms as well as extent of overlap is maximum, this results in lowering of energy of system and gives rise to bonding molecular orbitals which are more stable than overlapping atomic orbitals. This occupies both the electrons of m.o. formed by two A.O. in ground state.



$\psi = \phi_A + \phi_B$; ψ = m.o.

Fig. 1.3. Formation of bonding molecular orbital.

In Linear combination of atomic orbital (LACO) by subtraction of overlap wave functions of atomic orbitals are of opposite sign. This combination results in cancellation of electron density and hence probability of finding electrons in the region of overlap is practically zero. Due to small charge density in the region of overlap, repulsion between nuclei is high which results in destablization of molecular orbital and oppose the bond formation. The M.O. thus formed is called antibonding molecular orbital. This remains vacant in ground state.



$\psi = \phi_A - \phi_B$; ψ = m.o.

Fig. 1.4. Formation of antibonding molecular orbital.

Energy of bonding molecular orbital is lower than the energy of the overlapping atomic orbitals, whereas the energy of antibonding molecular orbital is higher. Doubly occupied M.O. has higher energy as compared to vacant bonding orbital due to interelectronic repulsion, *i.e.*, why doubly occupied M.Os. show unequal splitting with respect to energy level of A.Os. Hence $E_2 > E_1$.

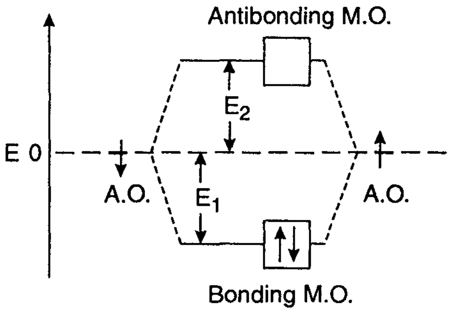


Fig. 1.5. Relative energies of atomic orbitals, bonding molecular orbitals and antibonding molecular orbitals in ground state.

1.2 SINGLET AND TRIPLET STATES

Excitation from ground state (G.S.; bonding molecular orbital) to first excited state (antibonding M.O.) can occur in two ways : (i) With retention of electronic spin, *i.e.*, electronic spins are still paired, this is represented as $S_0 \rightarrow S_1$ transition. (ii) With inversion of electron spin; now the electronic spins are parallel, the transition is represented as $S_0 \rightarrow T_1$ transition.

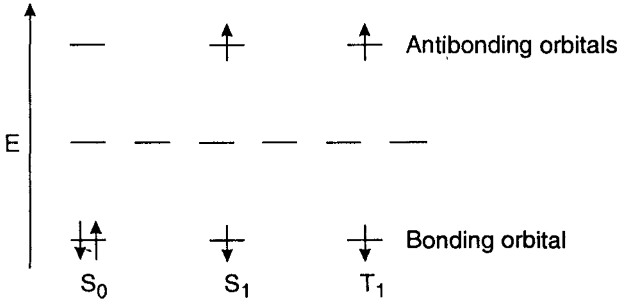


Fig. 1.6. Singlet and triplet excited states.

In G.S. normal covalent compounds have all their spins anti-parallel, *i.e.*, molecule is in singlet state. So, upon excitation electrons still have opposite spins to give the first excited singlet state S_1. Upon excitation electrons can also become of parallel spins. This state is known as triplet state (T_1). These two excited states (E.S.) differ in their multiplicities in magnetic field. While singlet state does not split, triplet state may split in three possible energy states. However, according to **Hunds rule** of multiplicities; a system of highest multiplicities has lowest energy and is more stable in comparison to system without multiplicities. Therefore, triplet state is more stable than singlet state.

1.3 CLASSIFICATION

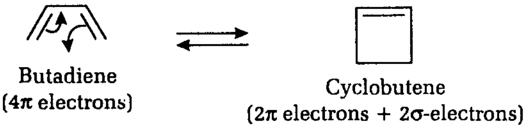
Pericyclic reactions may be ring-opening, ring closing or rearrangements and are classified in three major categories which are :

(i) Electrocyclic reactions
(ii) Cycloaddition reactions
(iii) Sigmatropic rearrangements

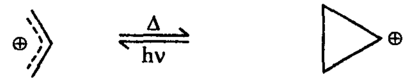
1.3.1 Electrocyclic Reactions

These are concerted reactions in which polyolefines containing n_π electrons cyclize to give products with $(n\pi - 2)\pi$ electrons $+2\sigma$-electrons, *i.e.*, 2π electrons of linear partner form one σ-bond in cyclization process or the reverse of it in which ring opening takes place as a results of which two electrons of σ-bond get converted into π bond electrons. For example :

(i)



(ii)



These were first concerted (pericyclic) reactions to be discovered by Woodward and Hoffmann in 1965 and in them ring opening and ring closure may take place by two modes : viz conrotation or disrotation. If both the involved orbitals rotate in the same direction (either clockwise or anticlockwise) it is known as **conrotation** and when involved orbitals rotate in the opposite directions, *i.e.*, one rotates clockwise and other anticlockwise it is known as **disrotation**.

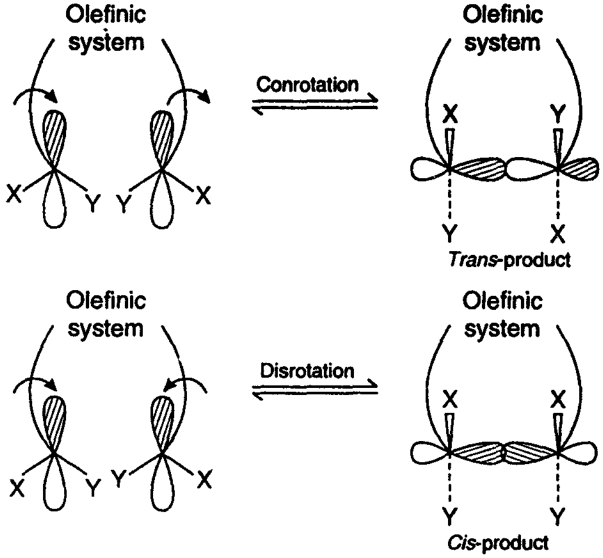
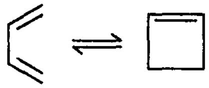
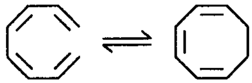
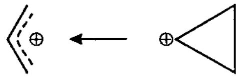
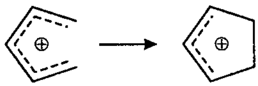
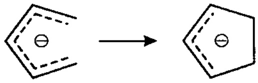


Fig. 1.7. Conrotation and disrotation.

Electrocyclic reactions are possible in two types of π-systems : 4*n* π-systems and (4*n*+2)π-systems (Here *n* is an integer). In either case reactions occur either thermally or photochemically, *i.e.*, reactions are either thermally allowed and photochemically forbidden or photochemically allowed and thermally forbidden and cyclization either takes place by conrotatory or disrotatory mode. Selection rule predicting mode of rotation of orbitals in both the systems can be diagramatically represented as follows :

Reaction	**Thermal conditions**	**Photochemical condition**
 (4*n* system)	Conrotatory	Disrotatory
 [(4*n* + 2) system]	Disrotatory	Conrotatory

Reaction	Thermal conditions	Photochemical condition
 (4*n* system)	Conrotatory	Disrotatory
 [(4*n* + 2) system]	Disrotatory	Conrotatory
 (4*n* – system)	Conrotatory	Disrotatory
 (4*n* – system)	Conrotatory	Disrotatory
 [(4*n* + 2) – system]	Disrotatory	Conrotatory

Selection rules may be summed up as :

System	Thermally allowed	Photochemically allowed
4*n*	Conrotatory	Disrotatory
4*n* + 2	Disrotatory	Controtatory

It is important to note that after rotation of molecular orbitals either by conrotation or disrotation (in ring closure as well as ring opening) rehybridization of molecular orbitals takes place; only then formation of σ-bond during ring-closure and formation of π-bond during ring-opening is possible. This can be illustrated as follows :

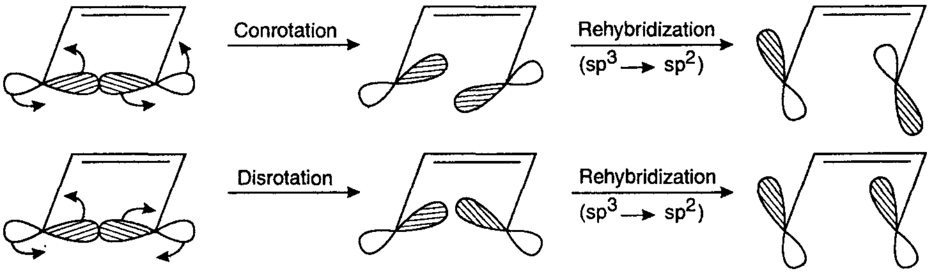


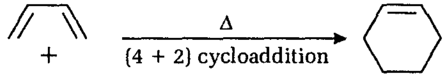
Fig. 1.8. Ring-opening by conrotation and disrotation.

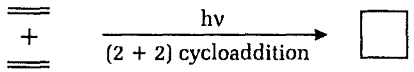
Thus, during ring-opening rehybrization changes, from sp^3-sp^2. But during ring closure $sp^2 \rightarrow sp^3$ hybrization occurs. Rehybridization leads to orientation of M.Os in such a way that it can be followed by overlapping of orbitals leading to σ or π-bond formation. As with the rotation of orbitals other groups attached to central atom also rotate it decide stereochemistry of product.

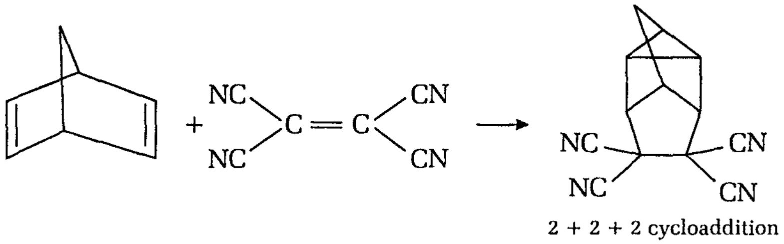
1.3.2 Cycloadditions

In these reactions a system with $m\pi$ electrons adds to a system with $n\pi$-electrons to give a cyclic molecule having $(m-2)+(n-2)\pi$ electrons. 4π-electrons are used up in the formation of 2σ-bonds.

For example :

(i) 

(ii) 

(iii) 

These reaction are classified as $(m+n)$ cycloaddition reactions, *e.g.*,

(i) is (4+2) cycloaddition

(ii) is (2+2) cycloaddition and

(iii) is (2+2+2) cycloaddition.

Suprafacial and Antarafacial Processes : These are two stereochemical modes of cycloaddition. Here two systems containing double bonds add up, therefore it is logical to expect that addition occurs either at the same side of opposite side of the system. As both the π-systems are undergoing addition, it is

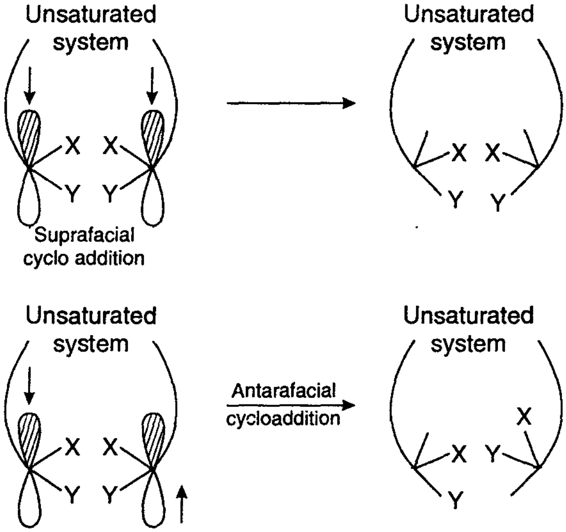


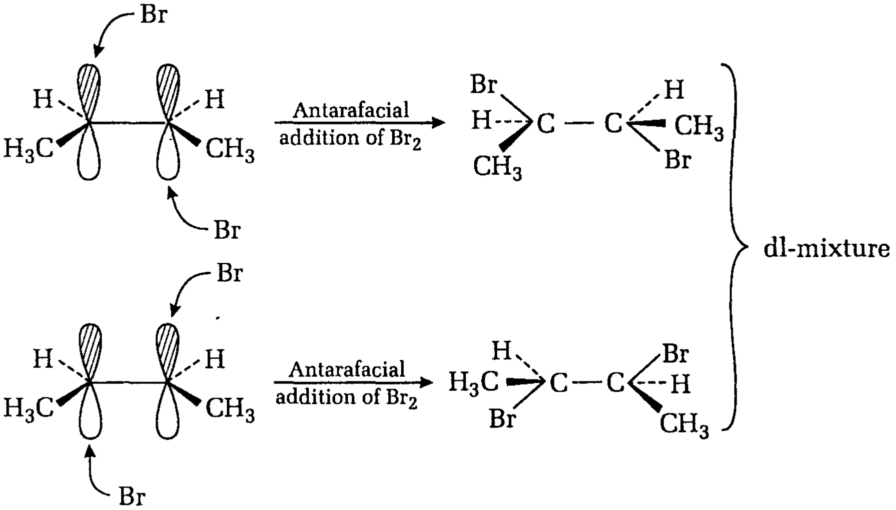
Fig. 1.9. Suprafacial and antarafacial cycloadditions.

essential to specify these modes of addition with respect to each of them. When addition is on the same side of double bond, it is termed as suprafacial addition and when addition occurs on the opposite side process is named as antarafacial addition.

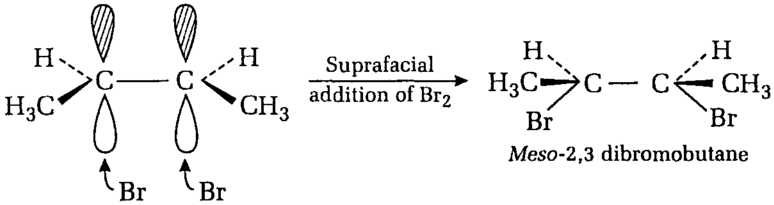
Suprafacial and **antarafacial** cycloadditions have their definite stereochemical consequences which can be made clear through the following examples :

It has been observed that antarafacial addition of bromine to *cis*-2-butene yields *dl*-2, 3-dibromobutene and it is expected that suprafacial addition of the same will produce *meso*-2, 3-dibromobutane.

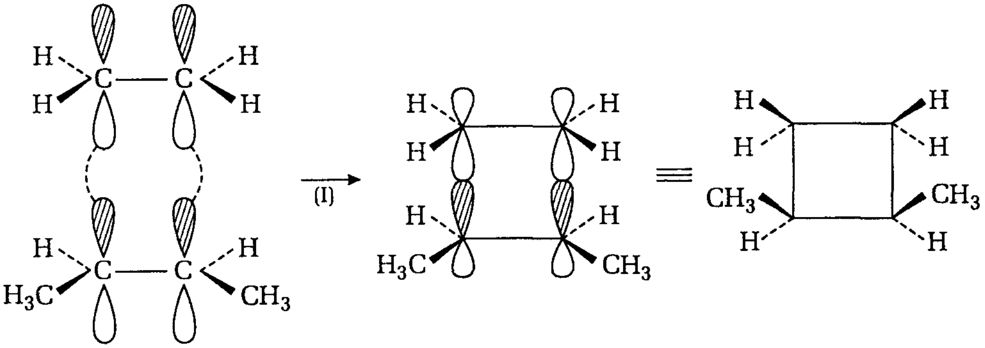
(i)

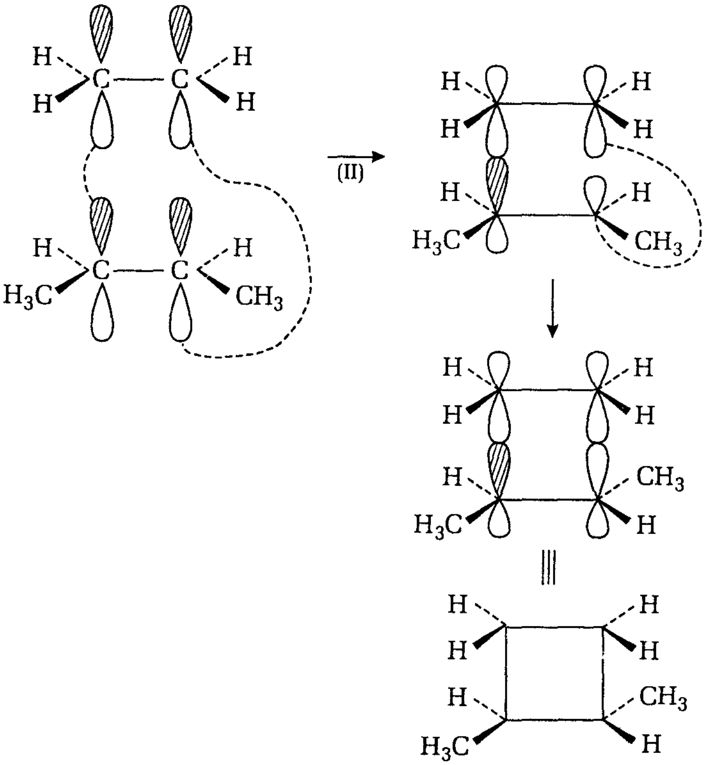


(ii)



During cycloaddition originally *cis* groups become *trans* if addition is antarafacial. Cycloaddition supra with respect to ethylene and supra w.r.t. *cis*-2-butene(I) results in the formation of *cis*-1, 2-dimmethylcyclobutane, but





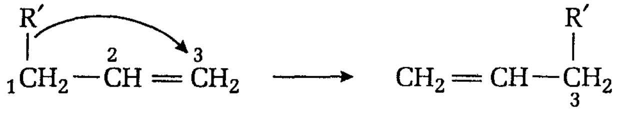
cycloaddition involving ***supra*** addition w.r.t. to ethylene and **antara** w.r.t. *cis*-2-butene(II) gives *trans*-1, 2-dimethylcyclobutane.

Selection Rules for ($m+n$) Cycloadditions

$m + n$ (Number of electrons involved)	Thermally allowed, photochemically forbidden	Photochemically allowed, thermally forbidden
$4q$	$m_s + n_a$ $m_a + n_s$	$m_s + n_s$ $m_a + n_a$
$4q + 2$	$m_s + n_s$ $m_a + n_a$	$m_s + n_a$ $m_a + n_s$
q is an integer; a = antarafacial; s = suprafacial		

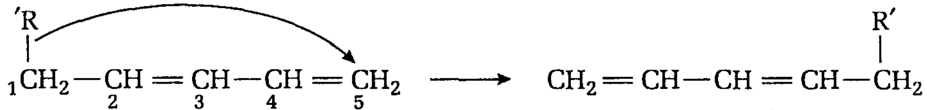
1.3.3 Sigmatropic Rearrangements

Sometimes thermal or photochemical reactions involve rearrangements in which a σ-bond flanked by one or more π-electrons are transferred to new positions i to j. They are known as **sigmatropic rearrangements** of the order (i, j). Here the system (i, j) is numbered by starting with atoms from which σ-bond is to be migrated, *i.e.*, i represents initial position of σ-bond, whereas, j represents the position to which bond has migrated. For example :



$$\overset{R'}{{}_1CH_2}-\overset{2}{CH}=\overset{3}{CH_2} \longrightarrow CH_2=CH-\overset{R'}{\underset{3}{CH_2}}$$

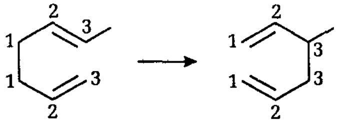
[1,3] shift



$$\underset{1}{\overset{'R}{CH_2}}-\underset{2}{CH}=\underset{3}{CH}-\underset{4}{CH}=\underset{5}{CH_2} \longrightarrow CH_2=CH-CH=CH-\overset{R'}{CH_2}$$

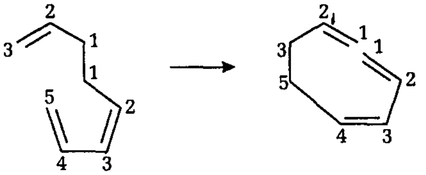
[1,5] shift

If σ-bond moves across two-parts of a polyene system numbers of two terminal ends constitute *i* and *j*. For instance, following is an example of [3, 3]-sigmatropic rearrangements :



1,5-pentadienyl system

An example of 3, 5-sigmatropic rearrangement is cited below :



1,3,7-octatriene

Suprafacial and Antarafacial Process is Sigmatropic Rearrangements : Sigma bond migrates across a conjugated system of π-bonds in sigmatropic rearrangements. New bond may form either on same or opposite face of π-system and the processes are accordingly termed as suprafacial and antarafacial, respectively. Migration through suprafacial modes is more feasible. However, when conjugated system is long enough antarafacial process may also take place. This stereochemistry of migration is digramatically illustrated in Fig. 1.10.

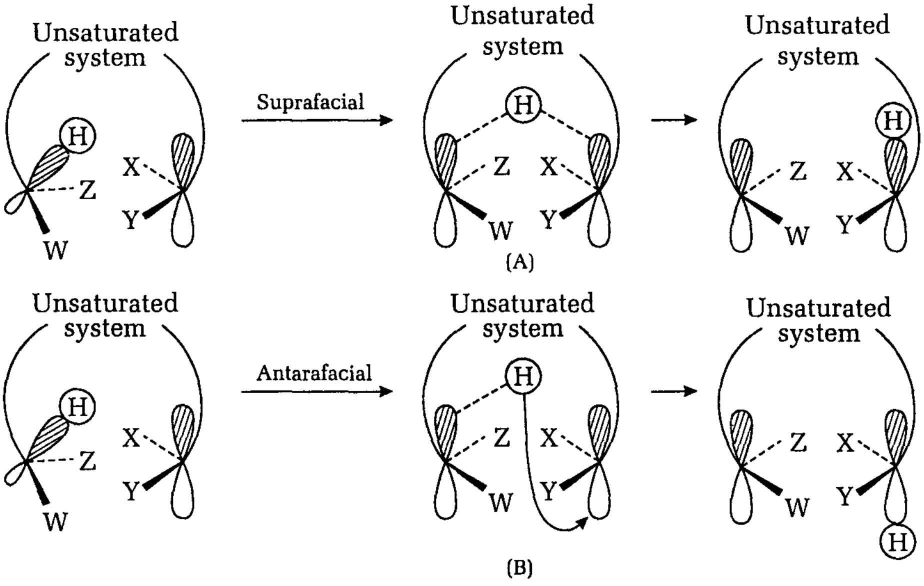
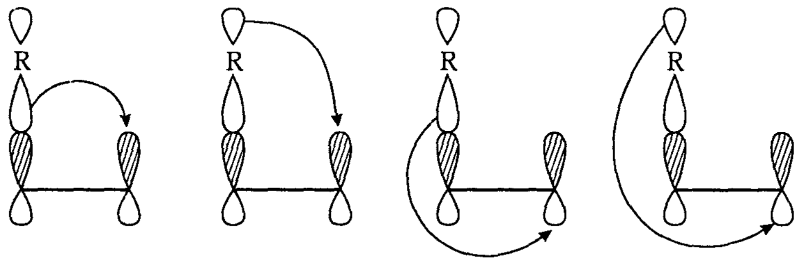


Fig. 1.10. Suprafacial (A) and antarafacial (B) migrations of hydrogen.

Suprafacial as well as antarafacial migrations may be either with retention or inversion at migratory centres. These four possibilities may be illustrated as follows :



(1) (2) (3) (4)

(1) Suprafacial with retention (2) Suprafacial with inversion
(3) Antarafacial with retention (4) Antarafacial with inversion

Although, there is enough crowding at transition state, still inversions are possible. For sigmatropic rearrangements also selection rules have been formulated. For instance, suprafacial 1, 5-sigmatropic hydrogen shift is thermally feasible. For this $i+j=1+5=6$. This is $(4n+2)$ system. Suprafacial 1, 3-sigmatropic shift is thermally forbidden, but is photochemically feasible. It has $i+j=1+3=4$. It is $4n$ system. Predictions through these rules are in conformity with experimental facts.

Rules for H-migration

System	**Thermally feasible; but photochemically forbidden**	**Photochemically feasible; but thermally forbidden**
$4n$	Antarafacial	Suprafacial
$4n+2$	Suprafacial	Antarafacil

Here n is an integer.

Rules for Sigmatropic Rearrangement if i, $j>1$

System $(i+j)$	**Thermaly allowed; photochemically forbidden**	**Photochemicaly allowed; thermally forbidden**
$4n$	Antara-supra or supra-antara	Supra-supra or antara-antara
$4n+2$	Supra-supra or antara-antara	Supra-antara or antara-supra

Stereochemistry of migration mentioned above is determined by the number of electrons involved in migration. For instance, in 1, 5-sigmatropic shift $1+5=6$ electrons are involved; two of which are σ-electrons and four are π-electrons.

❑❑❑

UNIT

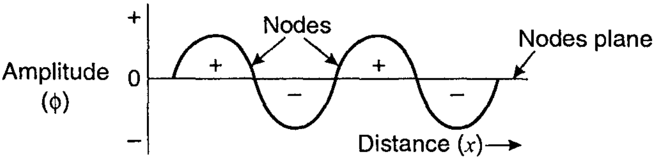
2

MOLECULAR ORBITAL, ORBITAL SYMMETRY AND FRONTIER MOLECULAR ORBITALS

2.1 MOLECULAR ORBITAL

Molecular structure is best represented in terms of quantum mechanics. Quantum mechanical calculations are quite difficult. Therefore, approximation methods have been evolved which are result of mathematical simplifications. Molecular orbitals are centered around all the nuclei present in the molecule. Relative stabilities of molecules depend upon how electrons are distributed in them. In order to understand molecular symmetry; it is essential to understand wave equations, phases of waves originated by the movement of electrons if we consider them as waves and also what are bonding and antibonding molecular orbitals.

Phase : Electrons not only behave as particles but as waves as well, *i.e.*, they have dual nature. A stationary wave can be represened as follows.



The vertical displacement of wave is known as **amplitude** which increases in one direction to the maximum, then decreases to zero and then again increases in opposite direction. The points of zero amplitude are known as nodes which lie is nodel plane perpendicular to the plane of paper. Upward and downward displacements are opposite **phases**, to distinguish between them we assign them positive and negative signs respectively.

Wave nature of electrons can be expressed in terms of **wave equation** which describes amplitude, ϕ, as a function of distance (x). Such function is known as wave function. It is important to note that electron waves are similar to string waves. When wave function gives the amplitude (ϕ) as a function of three co-ordinates it is known as **orbital**. In case of orbital lobes of opposite phases are given plus (+) and minus (–) signs or one of them is shown by shaded area; between two lobes lies nodal

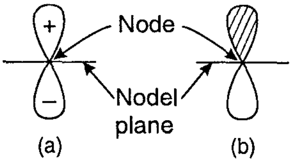


Fig. 2.1. Representation of *p*-orbital (a) by (+) and (–) signs (b) by shading.

plane. These (+) or (–) sign have nothing to do with charge. They indicate amplitude of electron wave is of opposite sign is two lobes. The amplitude or wave function, ϕ, is the orbital. It is actually ϕ^2 and not ϕ which have some meaning and gives the actual probablity of finding the electron is space. ϕ may be either (+) or (–) but ϕ^2 is always positive indicating that probability can not be zero.

2.2 MOLECULAR ORBITAL SYMMETRY

When we think of symmetry of orbitals we mean relative disposition of phase of two lobes in space. In pericyclic reactions only *p*-orbitals of alkenes are involved; therefore, we consider only symmetries of *p*-orbitals (σ-skeleton is often ignored). For a system with $n\pi$-electrons *n*-molecular orbitals will be there; $\frac{n}{2}$ bonding orbitals and $\frac{n}{2}$ antibonding orbitals. In other words, we can say that in a system with $n\pi$-electrons *n*-approximation sets of *p*-orbitals will be there, all of which differ in regard to their energies. Half of them with lower energies will be bonding molecular orbitals and other half with higher energies will be antibonding molecular orbitals.

Each of the approximation set of *p*-orbitals, *i.e.*, molecular orbital have either mirror plane symmetry (*m*) or c_2-axis of symmetry (c_2). A molecular orbital is having *m*-symmetry if a line drawn perpendicular to the plane of molecule divides it in two equal halves which are mirror images of each other. On the other hand a molecular orbital is said to possess c_2-axis of symmetry if rotation around its axis perpendicular to mirror plnane by $\frac{360°}{2}$, *i.e.*, 180° gives the arrangement identical to the original one.

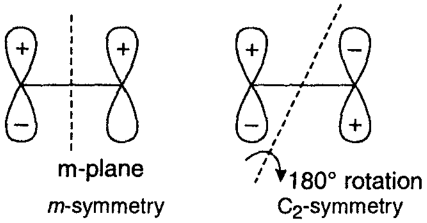
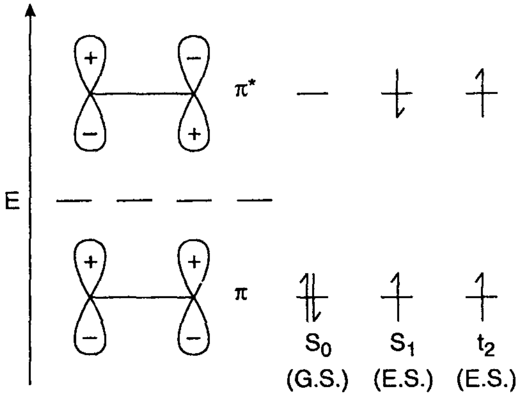


Fig. 2.2. Mirror plane (*m*) and two fold (C_2) symmetries.

Symmetry properties of *p*-molecular orbitals of some important systems are discussed below :

Ethylene : In ethylene, there are only two π-electrons, therefore, it has only two molecular orbitals : π-bonding and π-antibonding (π^*). Symmetry properties of both the orbitals are different. Ground state (G.S.) orbital is symmetric (*S*) with respect to mirror plane (*m*) and antisymmetric (A) w.r.t. the rotational axis (c_2). On the other hand antibonding orbital π^* of ethylene is antisymmetric w.r.t. *m* plane and symmetric with respect to c_2-axis (Fig. 2.3).

1, 3-Butadiene : The four *p*-orbitals in butadiene molecule and their combinations will give us four molecular orbitals ψ_1, ψ_2, ψ_3 and ψ_4 in the increasing order of their energies out of which ψ_1 and ψ_2 are bonding orbitals which contain all the four π-electrons, as they are lowest energy molecular orbitals and are filled first similar to the filling pattern of atomic orbitals. ψ_3 and ψ_4 are antibonding orbitals and are vacant. Ground state of butadiene is



m.o.	m	C_2
π*	A	S
π	S	A

Fig. 2.3. Symmetry properties of ethylene molecule.

represented by S, whereas excited states by S_1 (singlet) and t_2 (triplet) symbols. In S_1 electron from highest occupied molecular orbital (HOMO) has jumped to lowest unoccupied molecular orbital (LUMO, antibonding) and have opposite spins as but in t_2 their spins are same.

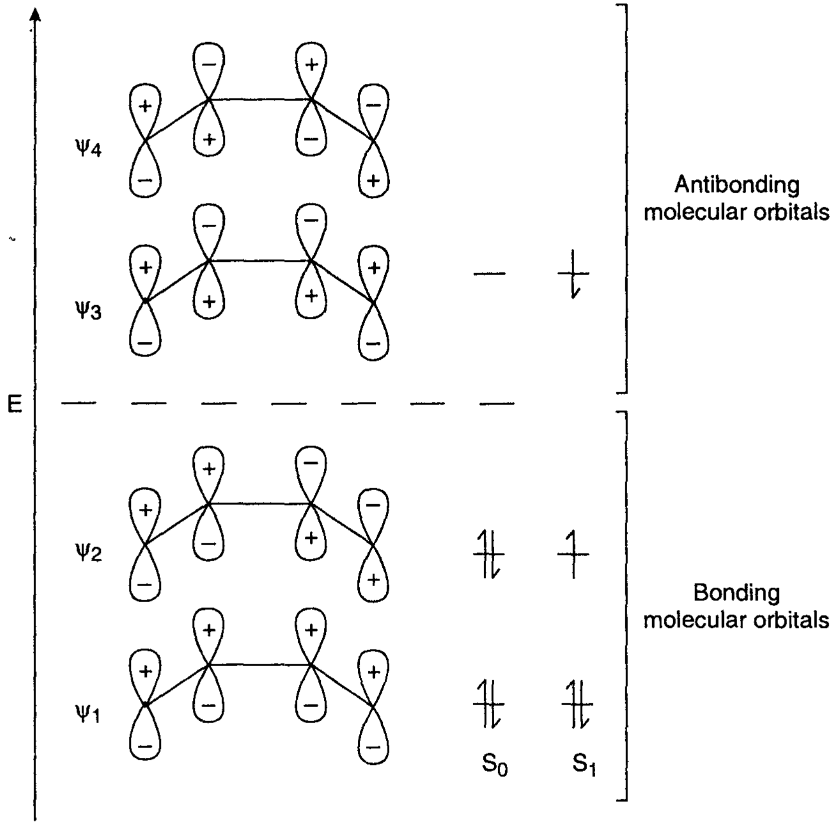


Fig. 2.4. Molecular orbitals of 1, 3-butadiene.

Symmetry properties of π-molecular orbitals of 1, 3-butadiene can be summarized in tabular form as given below :

Molecular orbital	*m*	c_2
ψ_4	A	S
ψ_3	S	A
ψ_2	A	S
ψ_1	S	A

1, 3, 5-Hexatriene : The six π-electrons of hexatriene are accomodated in first three molecular orbitals ψ_1, ψ_2 and ψ_3; while remaining three molecular

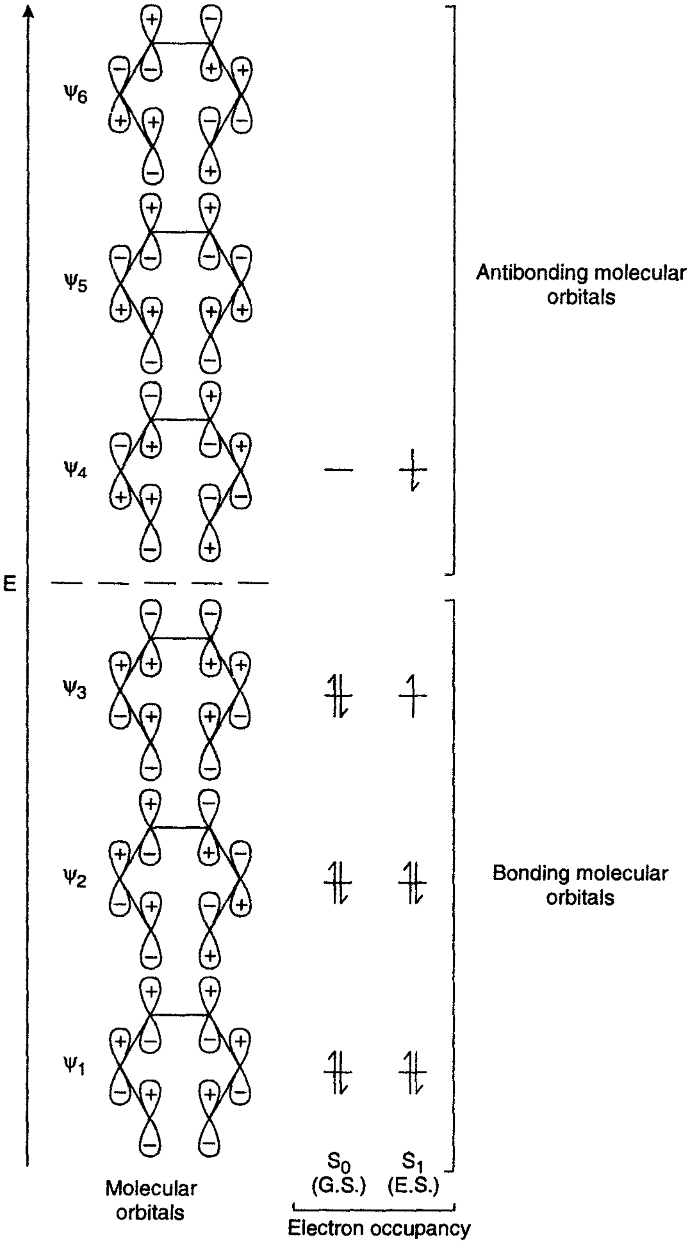


Fig. 2.5. Representation of molecular orbitals and electron occupancy of 1, 3, 5-hexatriene.

orbitals ψ_4, ψ_5 and ψ_6 are unoccupied. Symmetry properties of 1, 3, 5-hexatriene along with their electron occupancy in ground state and excited state are described in Fig. 2.5.

Tabular representation of symmetry properties of molecular orbitals of 1, 3, 5-hexatriene :

Molecular Orbital	m	c_2
ψ_6	A	S
ψ_5	S	A
ψ_4	A	S
ψ_3	S	A
ψ_2	A	S
ψ_1	S	A

Symmetry properties of a linear conjugated molecular orbital ψ_n can be predicted on the basis of number of nodes in it. A ψ_n m.o. has $(n-1)$ nodes. If $(n-1)$ is zero or even integer molecular orbital is symmetrical w.r.t. mirror plane and antisymmetrical w.r.t. two fold axis. On the other hand if $(n-1)$ is odd integer m.o. is antisymmetric with respect to mirror plane but contains c_2-axis of symmetry.

Node $(n-1)$	Symmetry w.r.t. m	Symmetry w.r.t. c_2
0 or even number	S	A
odd integer	A	S

A C—C covalent molecular orbital possess m-symmetry as well as c_2-axis of symmetry; because rotation about its mid-point brings same σ-orbital. An antibonding sigma orbital (σ*) is antisymmetric w.r.t. mirror plane as well as c_2-axis.

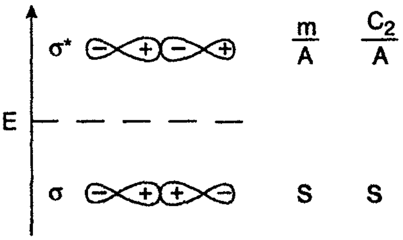


Fig. 2.6. Symmetry properties of σ-molecular orbital and σ*-molecular orbitals.

Allylic Systems : For conjugated systems with an even number of carbon atoms such as butadiene or 1, 3, 5-hexatriene, the nodes occur between carbon atoms. But in conjugated systems with odd number of C-atoms, nodes can coincide with one or more of C-atoms. Same is the case with allylic systems. The middle non-bonding orbital; which is singly occupied in allyl radical and doubly occupied in anion has a single nodal plane which precludes any contribution of 2p-orbital at central carbon atom. The orbital of highest energy possess two nodes. Nodes falling on carbon atom may be represented by a dot (•) and those falling between carbon atom by broken lines (⁝). Symmetry properties of allylic systems are described in Fig. 2.7, 2,8, 2.9 and 2.10.

It has been found that unbranched conjugated cations, anions and free radicals possess odd number of carbon atoms. Two such simplest systems are allylic systems and 2, 4-pentadienyl systems. One important characterstic of

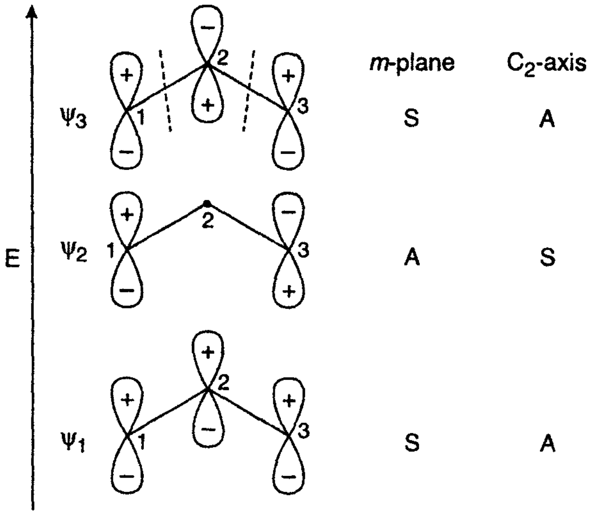


Fig. 2.7. Symmetry properties of allylic system.

these systems is that corresponding cations, anions and free radicals though have same number of molecular orbitals with same symmetry properties; but they differ in electron occupancy. Secondly, in some of their molecular orbitals nodes lie on one or more C-atoms. Occupancy characterstics of allylic cation, anion and free radicals are as follows :

(a) **Allylic cation :**

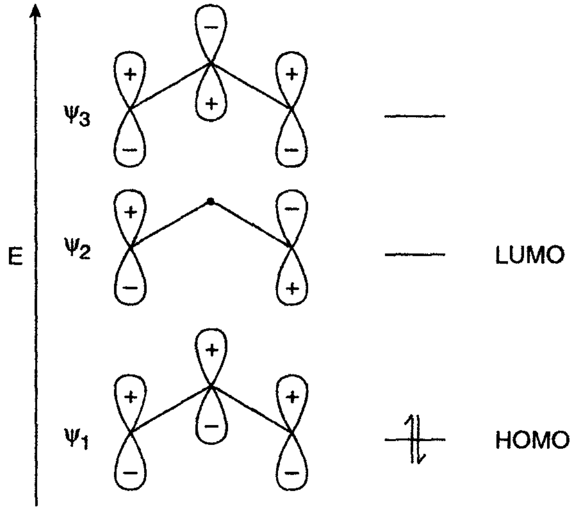


Fig. 2.8. Electronic occupancy of allylic cation.

Allylic cation has three isolated *p*-orbitals and only one π-bond :

$$CH_2{=}CH{-}\overset{\oplus}{C}H_2$$ Allylic cation

(b) Allylic anion contains one π-bond and one *p*-orbital with lone pair of electrons :

$$CH_2{=}CH{-}\underset{\bullet\bullet}{\overset{\ominus}{C}}H_2$$ Allylic anion

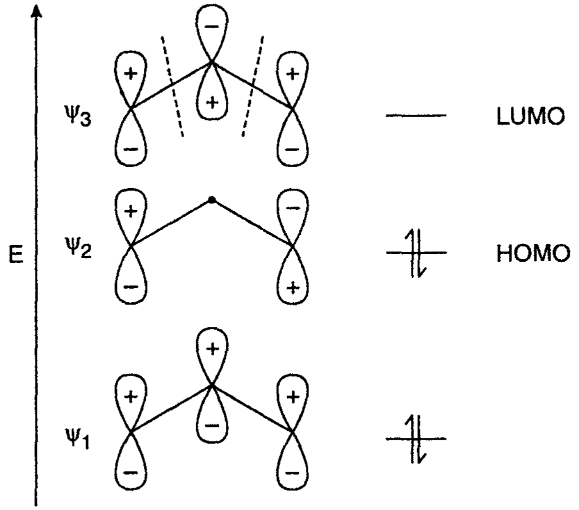


Fig. 2.9. **Electronic occupancy of allylic anions.**

(c) Allylic free radical possess three *p*-orbitals; out of which two form one π-bond and third one contains one electron.

$CH_2{=}CH{-}\dot{C}H_2$ Allylic free radical

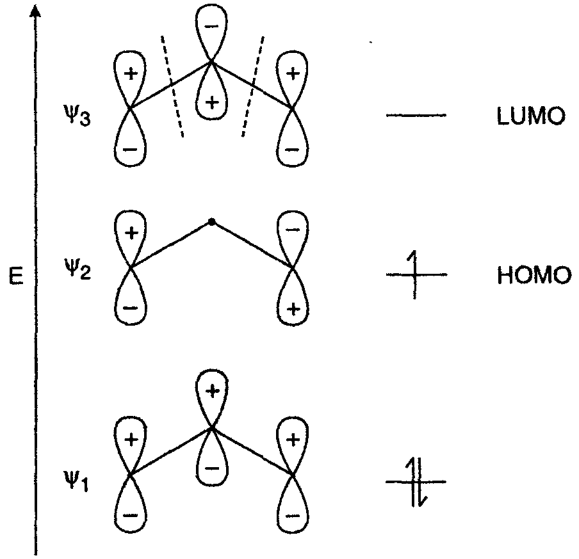


Fig. 2.10. **Electronic occupancy of allylic free readical.**

2, 4-Pentadienyl System : 2, 4-pentadienyl system possesses five molecular orbitals. Their symmetry properties and electron occupancies are given in Fig. 2.11.

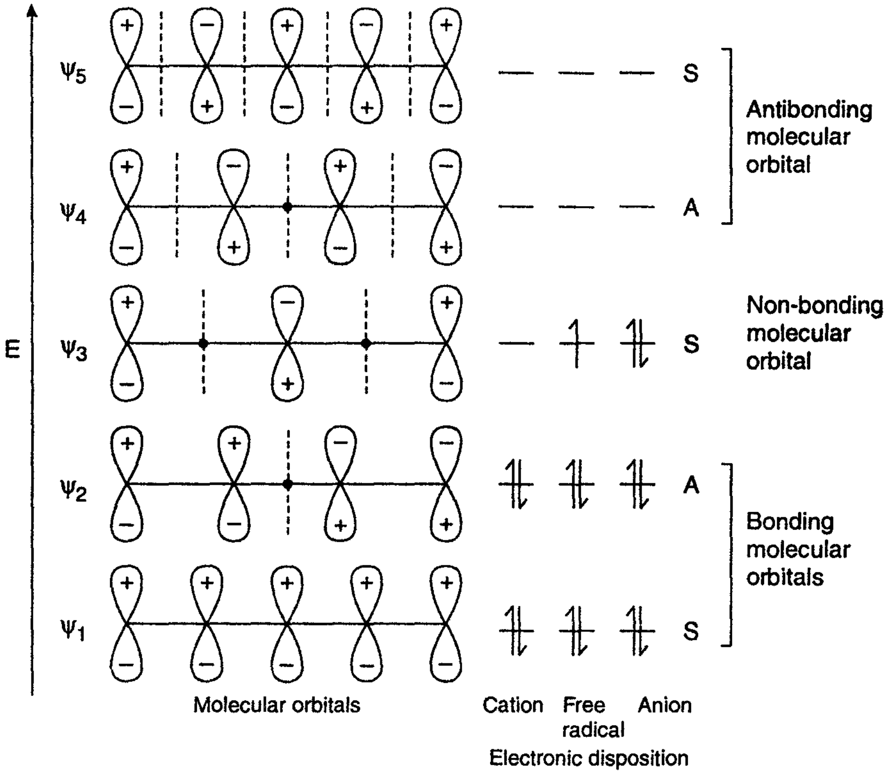


Fig. 2.11. Symmetry properties and electronic occupancy of pentadienyl system.

2.3 FRONTIER MOLECULAR ORBITALS (FMO)

Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are frontier molecular orbitals. They are different for different olefins as well as depend upon species, *i.e.*, whether it is cation, free radical or anion. For example :

(i) In ethylene HOMO is π and LUMO is π^*.

(ii) In 1, 3-butadiene ψ_2 is HOMO, whereas ψ_3 is LUMO. But is excited state ψ_3 becomes HOMO and ψ_4 LUMO.

(iii) For 1, 3, 5-hexatriene ψ_3 is HOMO and ψ_4 is LUMO; but upon irradiation ψ_4 becomes HOMO and ψ_5 LUMO.

(iv) HOMO and LUMO of allylic systems have already been discussed in previous article.

(v) HOMO and LUMO of 2, 4-pentadienyl systems are diagramatically represented in fig. 2.15.

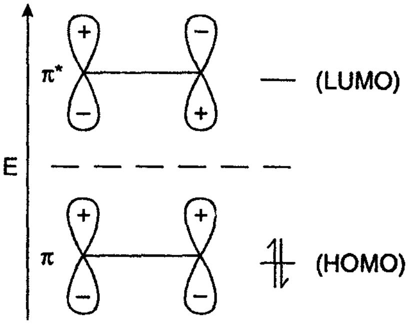


Fig. 2.12. HOMO and LUMO of ethylene.

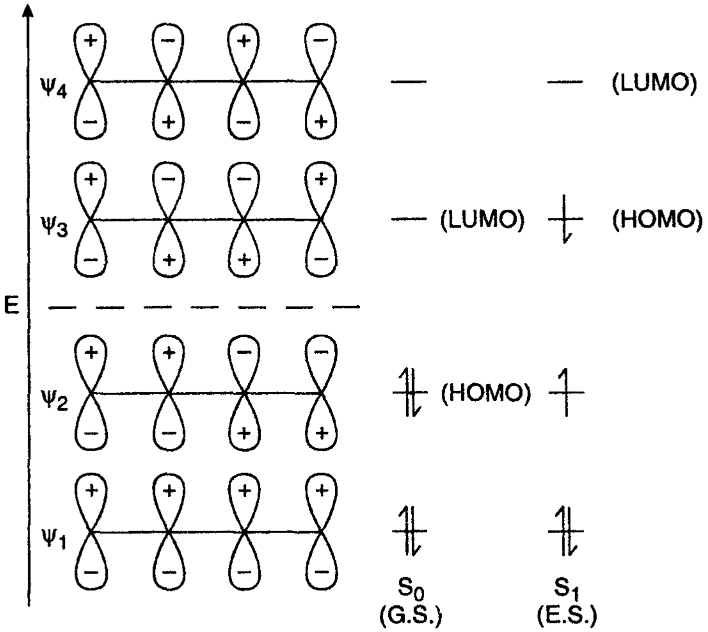


Fig. 2.13. HOMO and LUMO of 1, 3-butadiene.

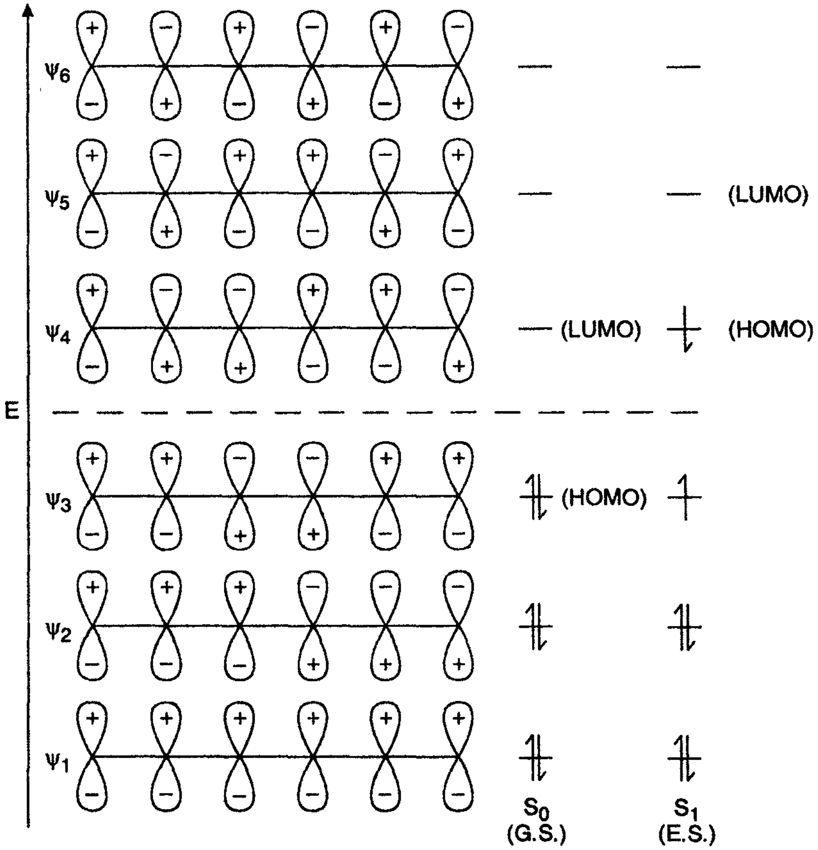


Fig. 2.14. HOMO and LUMO of 1, 3, 5-hexatriene in ground state and excited state.

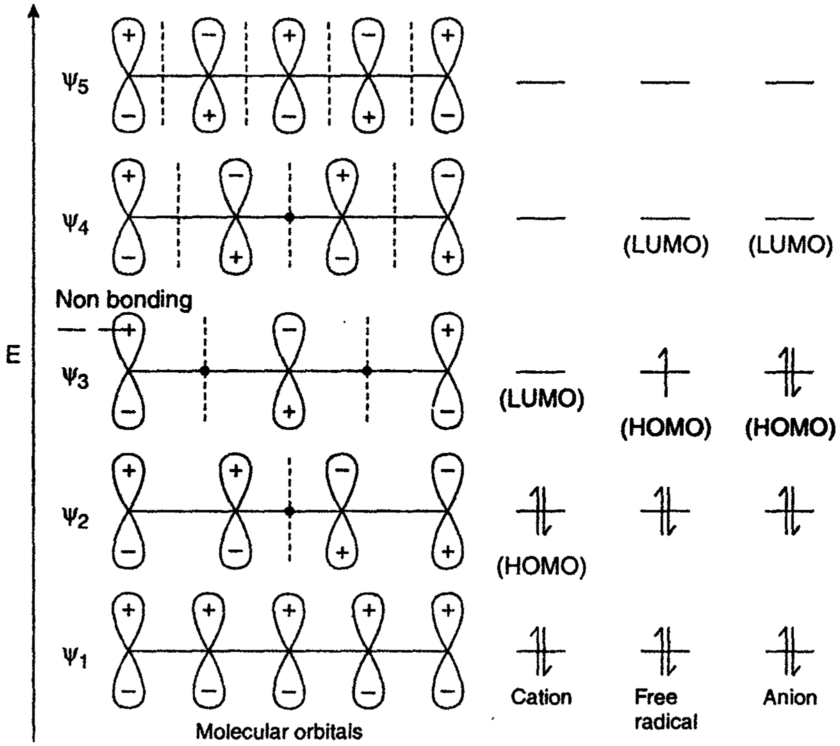


Fig. 2.15. HOMO and LUMO of 2, 4-pentadienyl cation, free radical and anion.

❑❑❑

UNIT

3

PREDICTIONS ABOUT FEASIBILITIES OF PERICYCLIC REACTIONS

As already discussed pericyclic reactions take place under thermal as well as photochemical conditions and stereochemistry of products generally differs under these two conditions. It is also well known that out of possible stereoisomers a particular stereomer is more active than other or one have activity and other does not. Hence, prediction about the fact that which stereoisomer will form under which condition is important for the preparation of particular isomer, which, is important from the point of view of its applications. There are three different approaches to predict conditions for a particular pericyclic reaction which are :

(1) Woodward-Hoffmann correlation diagram approach.
(2) Frontier molecular orbital (FMO) approach.
(3) Perturbational molecular orbital (PMO) approach.

First method takes into account symmetry properties of reactants and products; second is based upon FMOs; but in third forecasts can be made without considering symmetries of molecular orbitals.

3.1 WOODWARD-HOFFMANN CORRELATION-DIAGRAM APPROACH

Most important observation about pericyclic reactions is that, in them molecular orbital symmetry is conserved, *i.e.*, symmetrical orbitals are converted into symmetrical orbitals; whereas asymmetric orbitals are transformed to antisymmetric orbitals. We can predict whether a reaction is feasible thermally or photochemically by constructing correlation diagram in which molecular orbitals of similar symmetry of reactants and products are matched. If they are matched in ground state, the reaction is feasible thermally. On the other hand if molecular orbitals of reactants in G.S. are matched to excited state of products or vice-versa the reaction is allowed under photochemical conditions. For constructing correlation diagram first step in writting the symmetry properties of reactants as well as products with respect to mirror plane (m) or c_2-axis, keeping in view which symmetry is being conserved during the reaction. Which type of symmetry is being conserved is determined by assuming how molecules are approaching each other. The molecular orbital correlation diagram also yields important information about transition state. It is important to mention here that molecular orbitals are arranged in the increasing order of energies.

The approximate energies of molecular orbitals can be obtained by adding and subtracting all the bonding and antibonding molecular orbitals of the molecules from which molecule under invetigation is fromed' in every possible way. The approximation set with no **node** will be of minimum energy and as the number of nodes increases the energy of approximation set also increases. An important observation is that energy separation between π and π^* M.Os is approximately 5 electron volts; whereas between σ and σ^* of the same combination is of the order of 10 electron volts. In between bonding and antibonding orbitals lies non-bonding m.o. Arrangement of approximation sets in the increasing order of energies on the basis of number of nodes for butadiene formed by two ethylene molecules is given below :

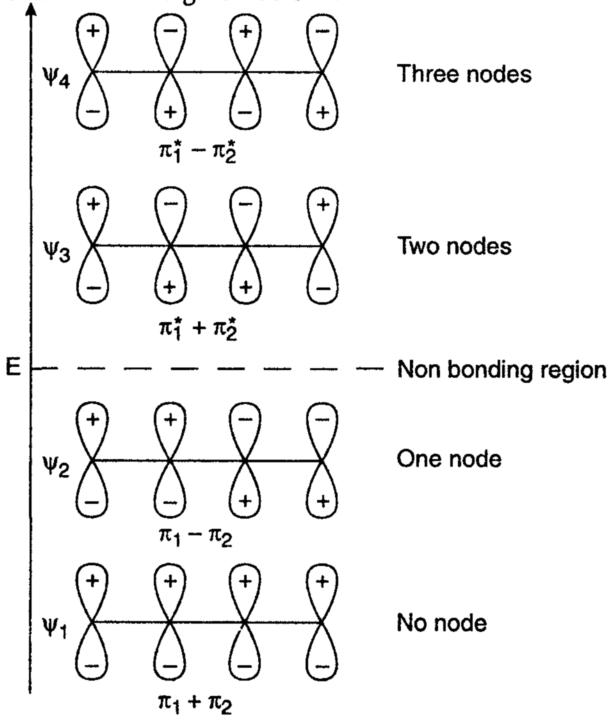


Fig. 3.1. Order of M.O. energies on the basis of number of nodes in them.

(In above figure π_1 and π_2 or π_1^* and π_2^* orbitals are molecular orbitals of two ethylene molecules which combine to give butadiene molecule.)

After arranging the m.os. of reactants and products in the increasing order of energies and writting their symmetries we simply match the orbitals of similar symmetries. If matching is possible in G.S. reaction is feasible thermally otherwise photochemically.

A simple example to predict feasibility of reaction conditions by this method is 1, 3-butadiene $\rightleftharpoons$ cyclobutene interconversion which is discussed below :

The molecular orbitals (m.os.) of butadiene involved in transformation are ψ_1, ψ_2, ψ_3 and ψ_4; whereas that of cyclobutene are σ, π, π^* and σ^*. This statement does not means that other lower energy σ-orbitals have no effect upon energy

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* If wave signs of two neighbouring orbitals of an approximation set are opposite it is said to have a node.

requirements of cyclization. σ-bonded orbitals also participate in the bond angle deformation during cyclization. For the electrocyclic ring closure of butadiene there is twisting (rotation) about $C_1—C_2$ and $C_3—C_4$ bonds. Hence, it may be said that *p*-orbitals are most involved orbitals. For interconversion to occur two orbitals move either is same direction or in opposite direction which are termed as **conrotation** and **disrotation**, respectively. To predict feasibility of butadiene-cyclobutene interconversion by these two processess following considerations are made :

(A) During conrotation two fold axis of symmetry (c_2) is conserved through out the process (Fig. 3.2). For the preparation of correlation diagram

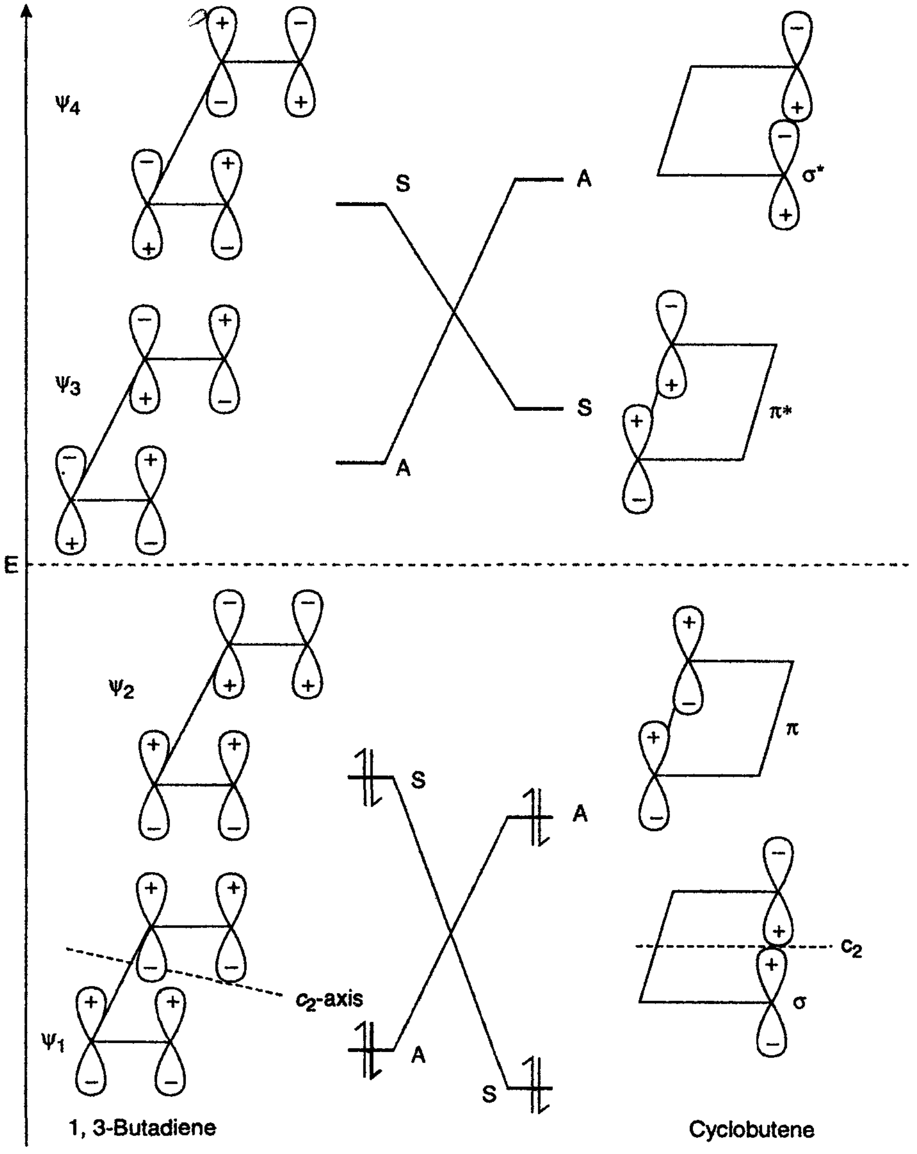


Fig. 3.2. **Correlation diagram to predict feasibility of 1, 3-butadiene-cyclobutene interconversion by conrotatory mode.**

(i) symmetry properties of the molecular orbital ψ_1, ψ_2, ψ_3 and ψ_4 as well as molecular orbitals σ, π, π^* and σ^* are written in increasing order of energy as well as are written their symmetries towards C_2-axis.
(ii) Then molecular orbitals of like symmetries are matched. The matching takes place in ground state; therefore reaction through conrotatory mode is feasible thermally.

(B) For disrotatory ring closure mirror plane (*m*) symmetry is conserved. Correlation diagram is prepared for it in the same manner as for

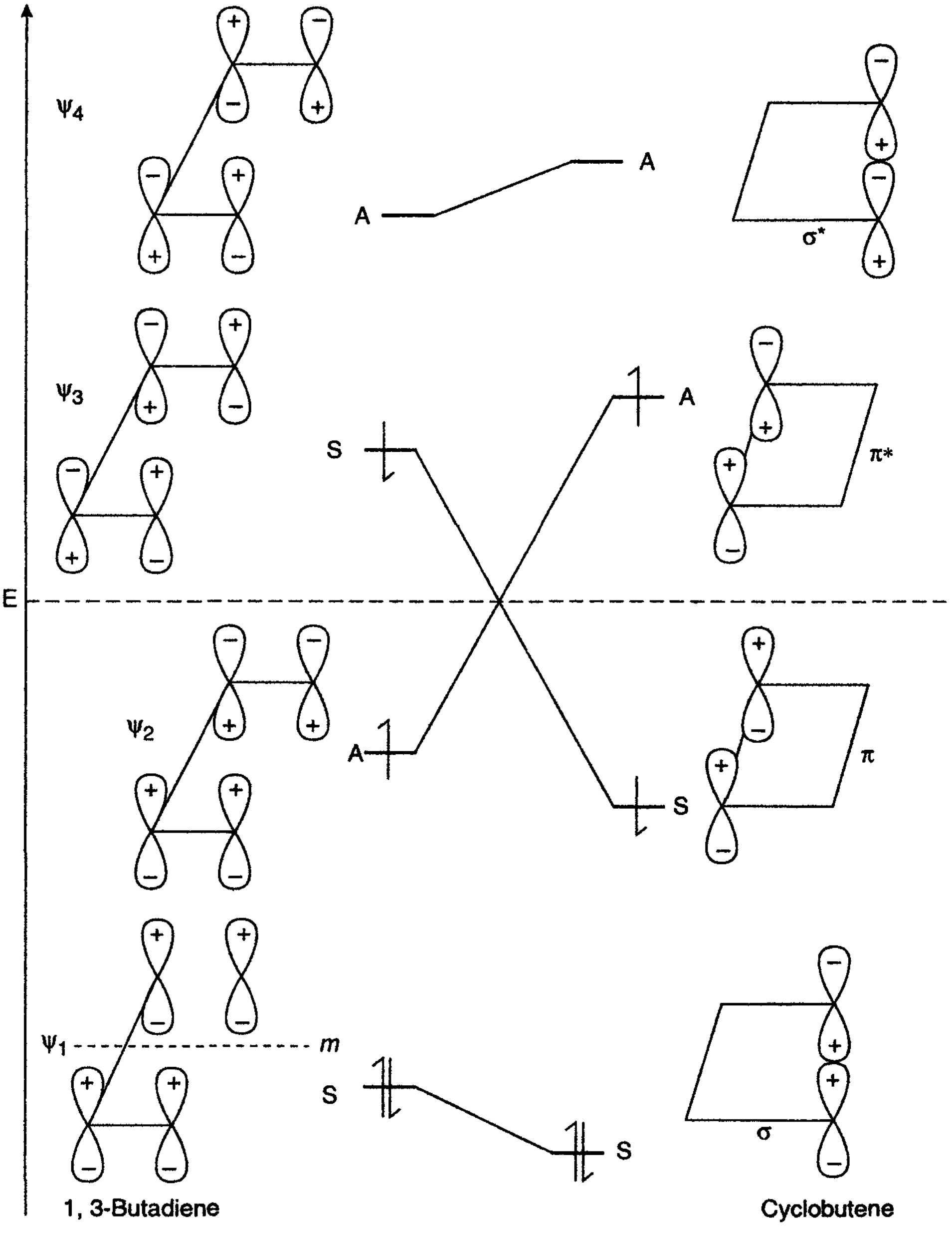


Fig. 3.3. Correlation diagram to predict feasibility of 1, 3-butadiene-cyclobutene interconversion by disrotatory mode.

conrotatory interconversion. Here LUMO matches HOMO in excited state, *i.e.*, singly occupied asymmetric ψ_2 with respect to mirror plane matches singly occupied π * of cyclobutene (excited state) and singly occupied ψ_3 of butadiene matches (excited state) with π-m.o. of cyclobutene. As matching is feasible in E.S. reaction is photochemically feasible.

3.1.1. Precautions in the Construction of Correlation Diagrams :

(1) Each basic process must be isolated and analysed separately. Otherwise the superposition of two forbidden but independent processes will be there and we will reach to **erroneous** conclusion.

(2) The symmetry elements chosen for operation should bisect M.O. being formed or M.O. being broken. Choosing such symmetry element with respect to which all the molecular orbitals are either symmetric or anti symmetric is of no use, because conclusion reached this way will be that reaction is always symmetry allowed, which will be wrong one. On the other hand if symmetry elements do not divide the bond formed or broken in two halves again correlation diagram formed will show that process is symmetry allowed either ways.

(3) If there are heteroatoms in polyene component; they are to be replaced by their isoelectronic carbon groupings. Heteroatoms offer the possibility of new reactions by the non-bonding pair of electrons or by the availability of low-lying unoccupied orbitals. This type of interactions should be considered cautiously.

(4) Quantum mechanical non-crossing rule, which states that the only levels of unlike symmetry should be allowed to cross must be observed in constructing correlation diagram. This is because of electronic repulsion.

3.2 FRONTIER MOLECULAR ORBITAL (FMO) APPROACH

In correlation diagram method to approach feasibility of concerted reactions transformational energy changes of each orbitals are carefully analysed. It is also possible in many cases to arrive at same conclusion by frontier molecular orbital method as by other methods. The frontier orbitals are highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO). LUMO are also known as lowest vacant molecular orbitals (LVMO). These orbitals often contribute to overall energy changes during the transformations. This approach can be applied to electrocyclic reactions, cycloadditions as well as sigmatropic rearrangements and is based upon the assumption that bonding interactions are possible only between the HOMO of one reactant and LVMO of the other; because energy barrier is minimum then (Fig. 3.4 and 3.5). An illustrative example of analysis of cycloaddition is discussed below :

Whether a cycloaddition reaction is allowed, depends upon the symmetry properties of HOMO of one reactant and LVMO of other under the reaction condition. A favourable bonding interaction takes place when wave signs of interacting atomic orbitals of HOMO and LVMO are same. $\pi_s^2 + \pi_s^2$ cycloaddition

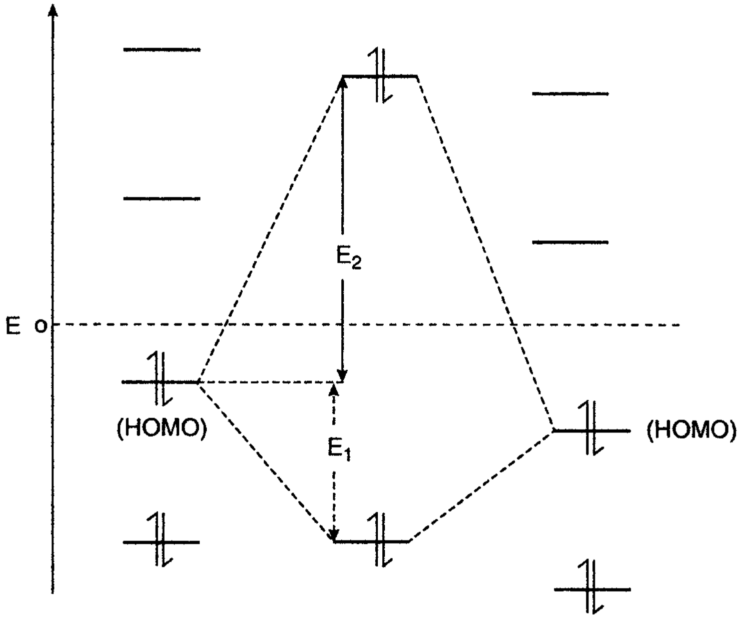


Fig. 3.4. HOMO-HOMO interaction $E_2 > E_1$ (endothermic *i.e.*, energy increasing); destablizing.

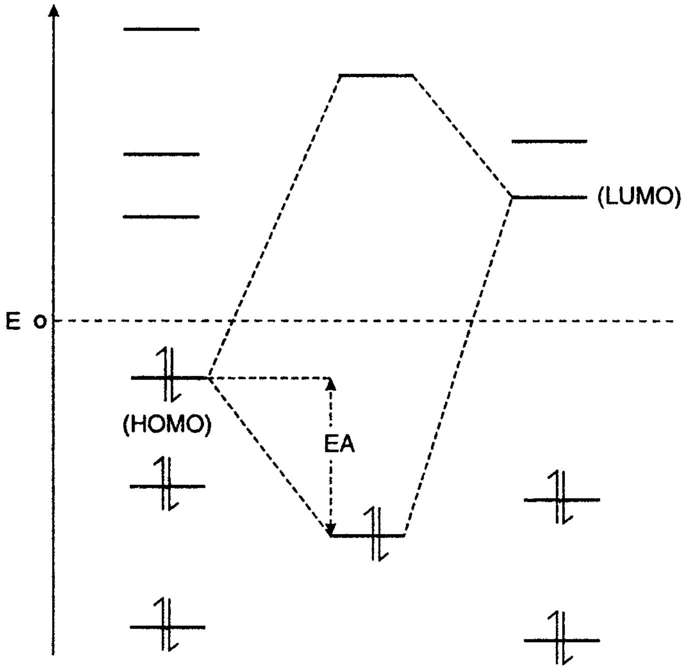
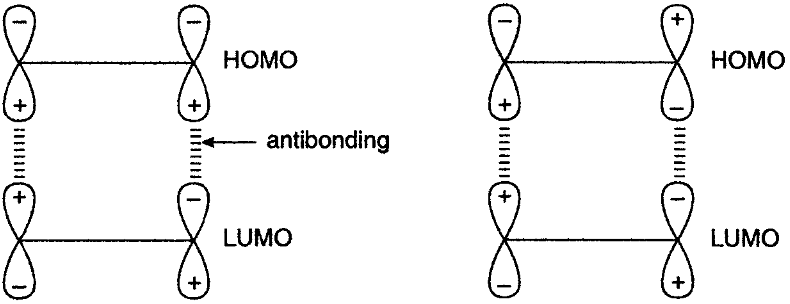


Fig. 3.5. HOMO-LUMO interaction (energy lowering).

of ethylene to give cyclobutane shows that the phases of atomic orbitals of HOMO of one molecule and LUMO of other are not same; hence reaction is thermally forbidden. On the other hand upon irradiation one electron is promoted to π *-orbital; which becomes HOMO (SOMO); now and the signs of wave functions of HOMO of one ethylene matches to LUMO of other (unexcited ethylene molecule), therefore, now reaction proceeds photochemically.



Ground state reaction; thermally forbidden

Excited state reaction; Photochemically allowed

Fig. 3.6.

In case one ethylene moiety is allowed to react with another is suprafacial-antarafacial manner (on the opposite side of olefin); $\pi_s^2 + \pi_a^2$, the reaction becomes symmetry allowed in ground state.

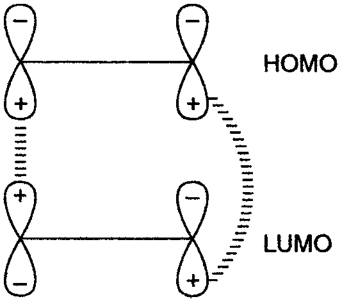


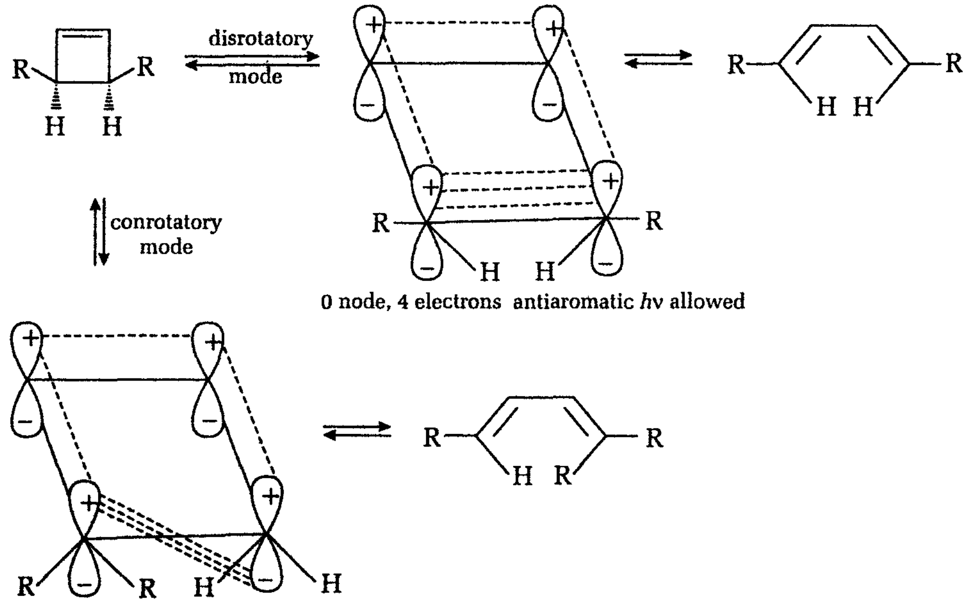
Fig. 3.7. Ground state reaction; thermally allowed in $\pi_s^2 + \pi_a^2$ manner.

3.3 PERTURBATIONAL MOLECULAR ORBITAL (PMO) APPROACH

This approach was developed by M.J.S. Dewar and too leads to similar conclusion about pericyclic reactions as above two methods without taking into account symmetry of molecular orbitals.

According to Hückel's rule of aromaticity a planer conjugated system with $(4n+2)\pi$-electrons is aromatic; therefore, stable in ground state. On the other hand, a system with $(4n)\pi$-electrons is antiaromatic and hence, unstable in ground state. Calculations have shown that these rules are reversed in presence of a node or odd number of nodes in arrangement of atomic orbitals. Therefore, a system with $(4n+2)\pi$-electrons and one node is antiaromatic in G.S. Conversly, $(4n)\pi$ system with one node is aromatic is G.S. These rules when applied to concerted reactions lead to conclusion that thermal reactions proceed through aromatic transition state and photochemical reactions involve antiaromatic transition states. A cyclic transition state is aromatic or isoconjugate with related aromatic system if the number of the conjugated atoms and that of the π-electrons involved are same as in the related aromatic system. On the other hand, cyclic transition state is antiaromatic or isoconjugate with related antiaromatic system if the number of conjugated atoms and the π-electrons involved are same as in the related antiaromatic system. It is important to note that for this approach only cyclic array of aromatic orbitals which undergo change in transition state are considered. The atomic orbitals are assigned signs in the best possible way of overlapping. Aromaticity of transition state is assigned on the basis of number of nodes and involved electrons in it. Alternatively it may be said that in this method we choose basic set of *p*-orbitals [$(4n+2)\pi$ or $(4n)\pi$ systems] and look for sign inversion in the transition state. Even number of sign inversion or zero sign inversion give rise to Hückel system and odd number of sign inversion are in Möbius system. Application of this approach to predict the allowed mode in electrocyclic reaction is dissussed below :

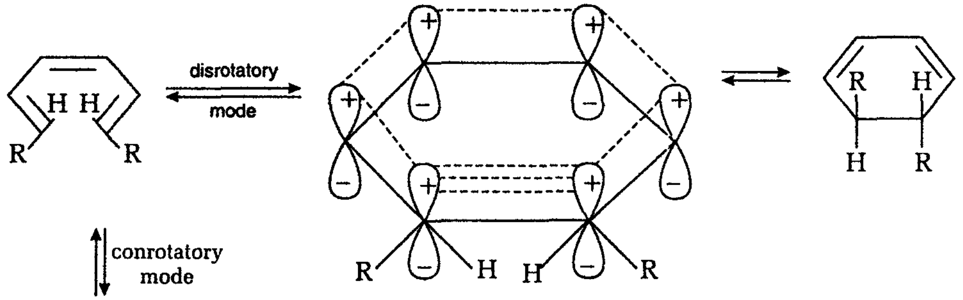
(a) Cyclobutene $\rightleftharpoons$ 1, 3-butadiene system



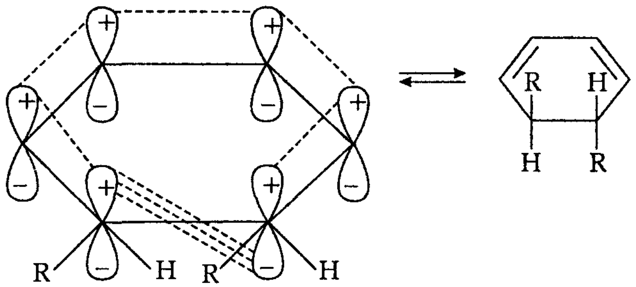
0 node, 4 electrons antiaromatic *h*ν allowed

1 node, 4 electrons aromatic, Δ allowed

(b) 1, 3, 5-Hexatriene $\rightleftharpoons$ cyclohexadiene



T.S. for disrotatory process, 0 node, 6 electrons, aromatic (Hückel system) thermally allowed



T.S. for conrotatory process, 1 node, 6 electrons, antiaromatic (Mobius system) *hν* allowed.

Mathematical approach to PMO method can be described as follows :

Perturbational molecular orbital approach is used in calculating the π-energy differences between closely related systems. This method is based upon localized bond models for sigma and isolated double bonds as well as Hückel's molecular orbital (HMO) method for the treatment of delocalized systems. While comparing closely related systems change in energy of localized bonds in ignored. When we are comparing energy of two conjugated systems difference in their energy is taken in terms of difference in energy of π-electrons and contribution of stretching and bending of σ-bonds is ignored. Difference in energy of two closely related systems is given by

$$\Delta E = \Delta E_\sigma + \Delta E_\pi$$

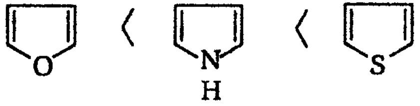
ΔE is the difference is energy of two systems A and B in context to their σ-electrons and ΔE_π is difference in their π-energy. ΔE_σ can be used from the tables of bond energies. Method of calculation involves :

(i) Calculation of difference in electronegativities from the changes in coulomb integral (α).

(ii) Difference in strength of one or more bond of systems under consideration is given by π-resonance integral (β). β according to Hückel approximation is constant for covalently linked atoms and is equal to 0 between two atoms which are not linked by covalent bond. Thus difference between π-energies of two closely related structures is calculated either in terms of one or both the fundamental constants α and β.

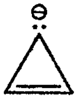
(iii) For the calculation of π-energy of a new π-system if wave function for a similar π-system are known; calculations for the wave function of new system according to HMO-method are not needed. Then only thing we need is to consider is perturbation in new system. Suppose **hamiltonian operator** for unperturbed system A is H and for perturbed system A' is H', then $H' = H + P$. Here P is **hamiltonian operator** for perturbation. Perturbation may be of first order or second order. A noteworthy thing is that as calculations of unperturbed wave functions are made on the basis of crude. Hückel molecular orbital method, therefore, accurate calculations of second order perturbation are not needed except when first order perturbation is insignificant. A perturbation may be intermolecular as well as intramolecular.

Relative chemical stabilities of aromatic systems can be ascertained by **intramolecular perturbation.** For instance, chemical stabilities of pyrrole, furan and thiophene can be compared considering perturbation due to increase in electronegativity of heteroatoms. Increase in electronegativity of one of the annular atoms decreases mesomeric stabilization. Order of electronegativities of heteroatoms oxygen, nitrogen and sulphur is O > N > S.



This is order of Chemical stabilities of pyrrole, furan and thiophene is Furan < Pyrrole < Thiophene as given above.

π-Energies difference may also be explained in terms of inductive effect as in case of cyclopropenyl anion and azacyclopropene.



Cyclopropenyl anion

Azacyclopropene

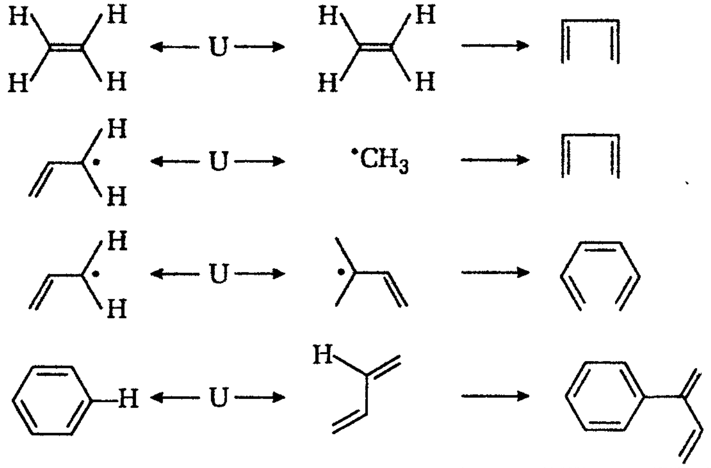
The coulombic integral (α_N) and resonance integral (β_{CN}) for nitrogen can be expressed in terms of values of carbon.

$$\alpha_N = \alpha + h_\beta, \quad \beta_{CN} = k_\beta$$

The values of h and k can be calculated.* If $\beta_{CN} = \beta$. Then $\Delta E_\pi = q_N \ \Sigma\delta a_i$

It is easy to calculate the π-energy difference between the two systems if we know values for q_N and δa_1. Because these two systems are isoconjugate, q_N should be same as for carbon and therefore π-energy difference is given by $\Delta E_\pi = \delta a_i = \alpha_N - \alpha = h_\beta$.

On the other hand **intermolecular perturbation** is a simple method to determine the relative stabilities of conjugated π-systems and it can be used for the direct analysis of pericyclic reactions. π-energy difference in intermolecular perturbation can be determined by applying concept of '**union**' in PMO approach. Union (← U →) combines π-systems to give larger π-systems.



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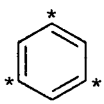
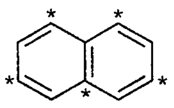
* A. Streitweiser, Molecular Orbital Theory of Organic Chemist, John-Wiley, 1961.

Sigma bonds are broken or formed during the process and corresponding energy changes (ΔE_σ) are calculated in terms of these bond energies. However, these are π energy changes (ΔE_π) with which we are concerned.

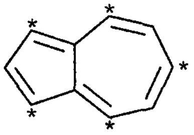
Union of two allyl units yields 1,3, 5-hexatriene, but not biallyl. According to Dewar π-energy changes can be calculated for benzenoid aromatic systems too. For instance, union of methyl and pentadienyl systems at the terminus gives 1, 3, 5-hexatriene and at both the ends yields benzene. If difference in π-energy by the two methods can be made we can determine if benzene is aromatic or not.

Aromatic hydrocarbons may be alternant as well as non-alternant. Alternant hydrocarbons possess two types of atoms (starred and unstarred) arranged in such a way that no two similar atoms are directly linked as in case of benzene and naphthalene. In even attachment hydrocarbon number of starred and unstarred atoms is same.





In non-alternant hydrocarbons two starred or unstarred atoms are directly linked as in case of azulene.

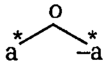


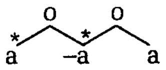
Azulene

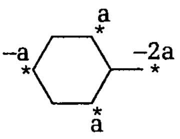
Odd alternant hydrocarbons, those having odd number of conjugated atoms, should occur as carbonium ions, radicals and carbanions. They have a non bonding m.o. of zero binding energy besides usual number of bonding and anti-bonding molecular orbitals. Calculation of π-energy of a compound obtained by the union of odd-alternant radicals is quite easy. In them sum of coefficients of atoms linked to unstarred is zero in non-bonding molecular orbitals (NBMO). Coefficients at unstarred atoms is also zero. The change in energy of two odd alternant hydrocarbons (AH's) R and S is given by

$$\Delta E_\pi = \Sigma 2a_{or}b_{os}\beta_{rs}$$

Here a_{or} and b_{os} are coefficient in NBMOs of atoms in systems R and S, respectively.

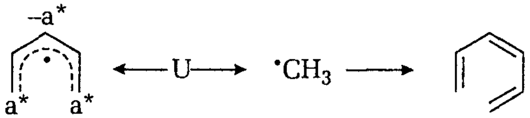






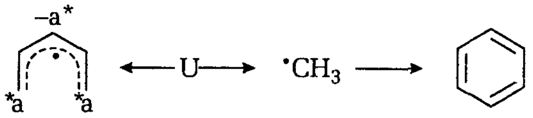
In case π-energy change for cyclic structure is greater than acyclic analogue former is aromatic. If π-energy for both is same cyclic structure is non-aromatic.

In third case cyclic structure is antiaromatic. ΔE_π for 1, 3, 5-hexatriene is calculated as given below :



$$\Delta E_\pi = 2\beta(1+a) = 2a\beta$$

(Non-bonding M.O. coefficient for CH_3 group is 1)
ΔE_π for benzene is



$\Delta E_\pi = 2\beta\ (1.a + 1a) = 4a\beta$

Since π-energy is greater for the formation of benzene is comparison to 1, 3, 5-hexatriene, former is aromatic. Cyclobutadiene is antiaromatic on the same grounds.

$\Delta E_\pi = 2\beta\ (1a) = 2a\beta$

$\Delta E_\pi = 2\beta\ [1.a + 1.(-a)] = 0$

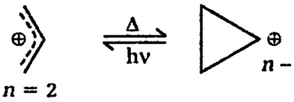
❑❑❑

UNIT

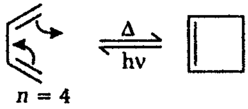
4

ELECTROCYCLIC REACTIONS

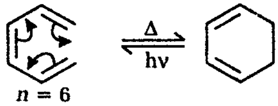
In electrocyclic reactions as already mentioned there is ring-opening or ring-closure of polyenes. In these reactions an open chain conjugated olefinic system with $n\pi$-electrons undergoes ring-closure to a system with $(n-2)\pi$-electrons + one σ-bond and converse of this process is also feasible under changed reaction conditions. Some examples of electrocyclic reactions are cited below :

(i) 

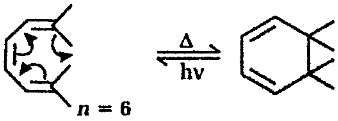
$n-2 = 0\pi e^-$s + one σ-bond

(ii) 

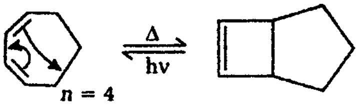
$n-2 = 2\pi e^-$s + one σ-bond

(iii) 

$n-2 = 4\pi e^-$s + one σ-bond

(iv) 

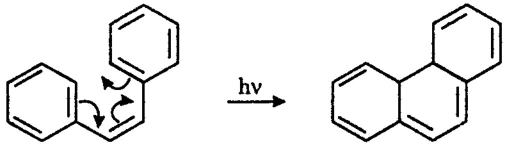
$n-2 = 4\pi e^-$s + one σ-bond

(v) 

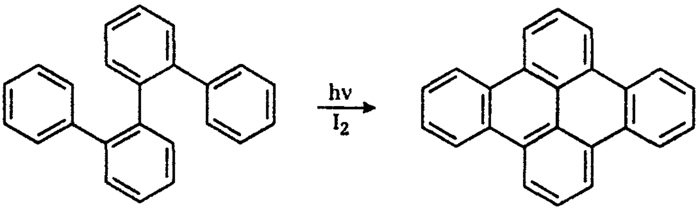
$n-2 = 2\pi e^-$s + one σ-bond

(vi) 

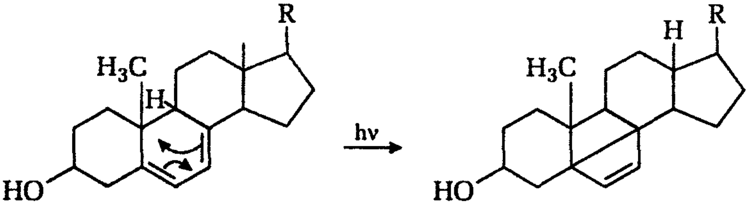
Norcardiene Cycloheptatriene

(vii) 

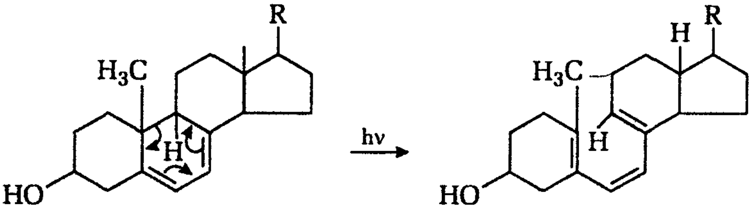
(viii)



(ix)

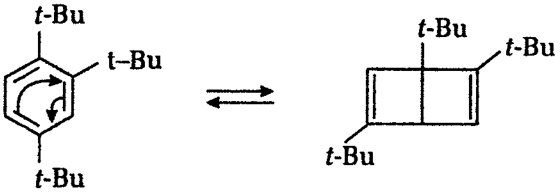


(x)

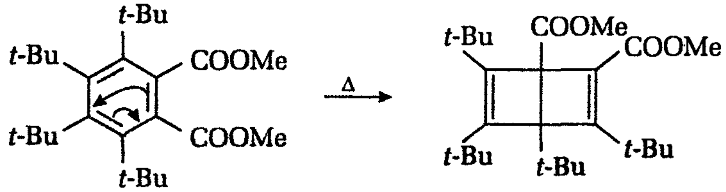


Thermal reactions are generally not reversible (although there are some exceptions). Some cyclobutenes can be converted to 1, 3-diene by heating to 100–200°C. Photochemical reaction can be carried out in either direction. Some 1, 3-dienes can be converted to cyclobutenes rather than reverse reaction. Cyclohexadiene to 1 3, 5-trienes conversions cause thermal ring closure rather than photochemical ring opening. These reactions are highly stereospecific.

1, 3-Diene to cyclobutene interconversion can be carried out in benzene rings too. For instance, photolysis of 1, 2, 4-tri-*t*-butyl benzene gives 1, 2, 5-tri-*tert*-butyl [2, 2, 0] hexadiene (Dewar benzene).

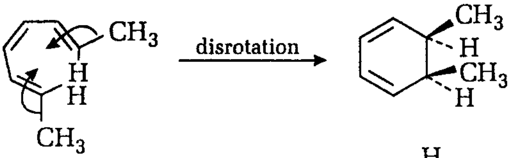


Dewar benzene is more stable than benzene. The rearrangement is given below :

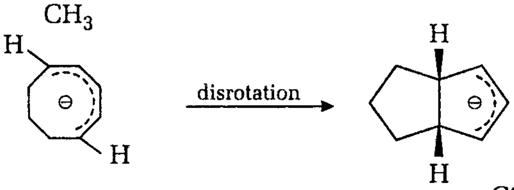


Some other example are :

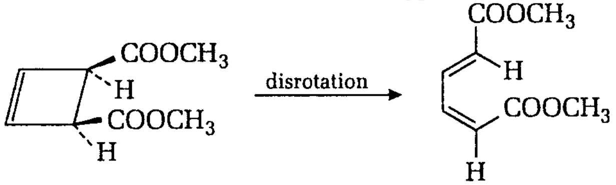
(a)



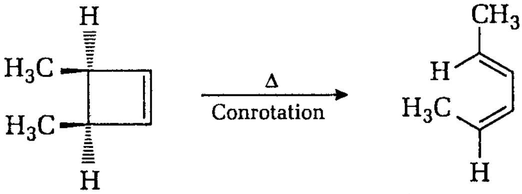
(b)



(c)



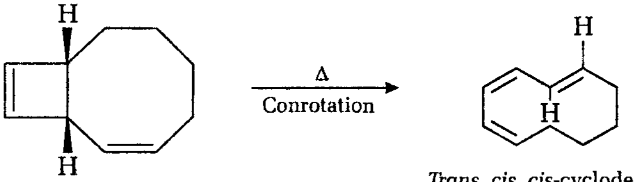
(d)



Cis-3,4-dimethyl cyclobutene

Cis, trans-2,4-hexadiene

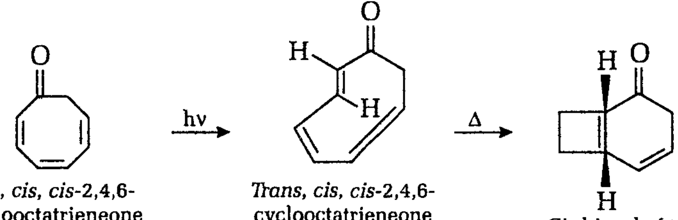
(e)



Cis-bicyclo
[6,2,0] deca-2,9-diene

Trans, cis, cis-cyclodeca-
1,3,5-triene

(f)

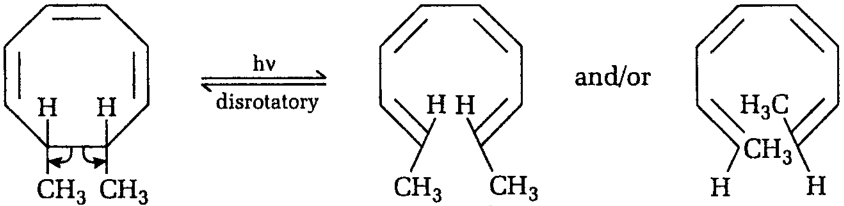


Cis, cis, cis-2,4,6-
cyclooctatrieneone

Trans, cis, cis-2,4,6-
cyclooctatrieneone

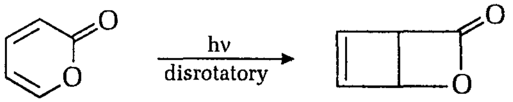
Cis-bicyclo [4,2,0]-
octa-3,6-diene-2-one

(g)



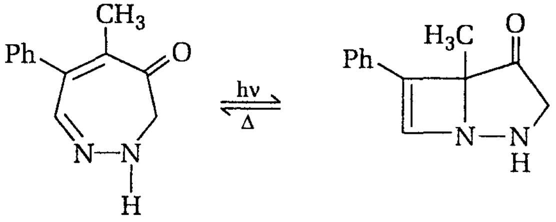
(Favoured)

(h)



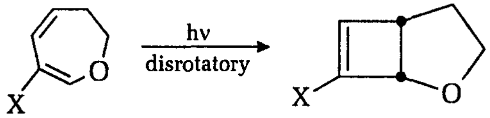
Ref. 1

(i)



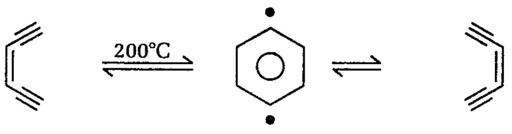
Ref. 2

(j)



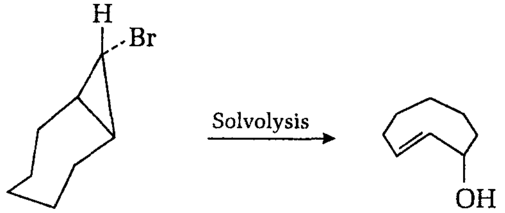
Ref. 3

(k)



Ref. 4

(*l*)



Ref. 5

1. R. Huisgen and H. Seidal, **Tetrahedron letters**, 3381 (1964).
2. W.J. Theuer and J.A. Moore, **Chem. Commun.**, 468 (1965).
3. E.J. Corey and J. Streith, **J. Amer.Chem.Soc.**, 86, 950 (1964).
4. S.K. Kundu, T. Das Gupta, S.Das and A. Praminak, **Indian J. Chem, 42,** 1716 (2003).
5. G.H. Whitbam and M. Wright, **Chem. Commun**, 294 (1967).

4.1 PREDICTIONS OF FEASIBILITY

All the three methods viz correlation diagram method, Frontier molecular orbital (FMO) method as well as perturbational molecular orbital (PMO) method can be used to predict feasiblity of electrocyclic reactions.

4.1.1 Correlation Diagram Method

Prediction of electrocyclic reactions has been discussed in unit III. Prediction by correlation diagram method has been done through the example of butadiene $\rightleftharpoons$ cyclobutene interconversion. One important thing noted there is that energies of some molecular orbitals increase (upward slope), but those of

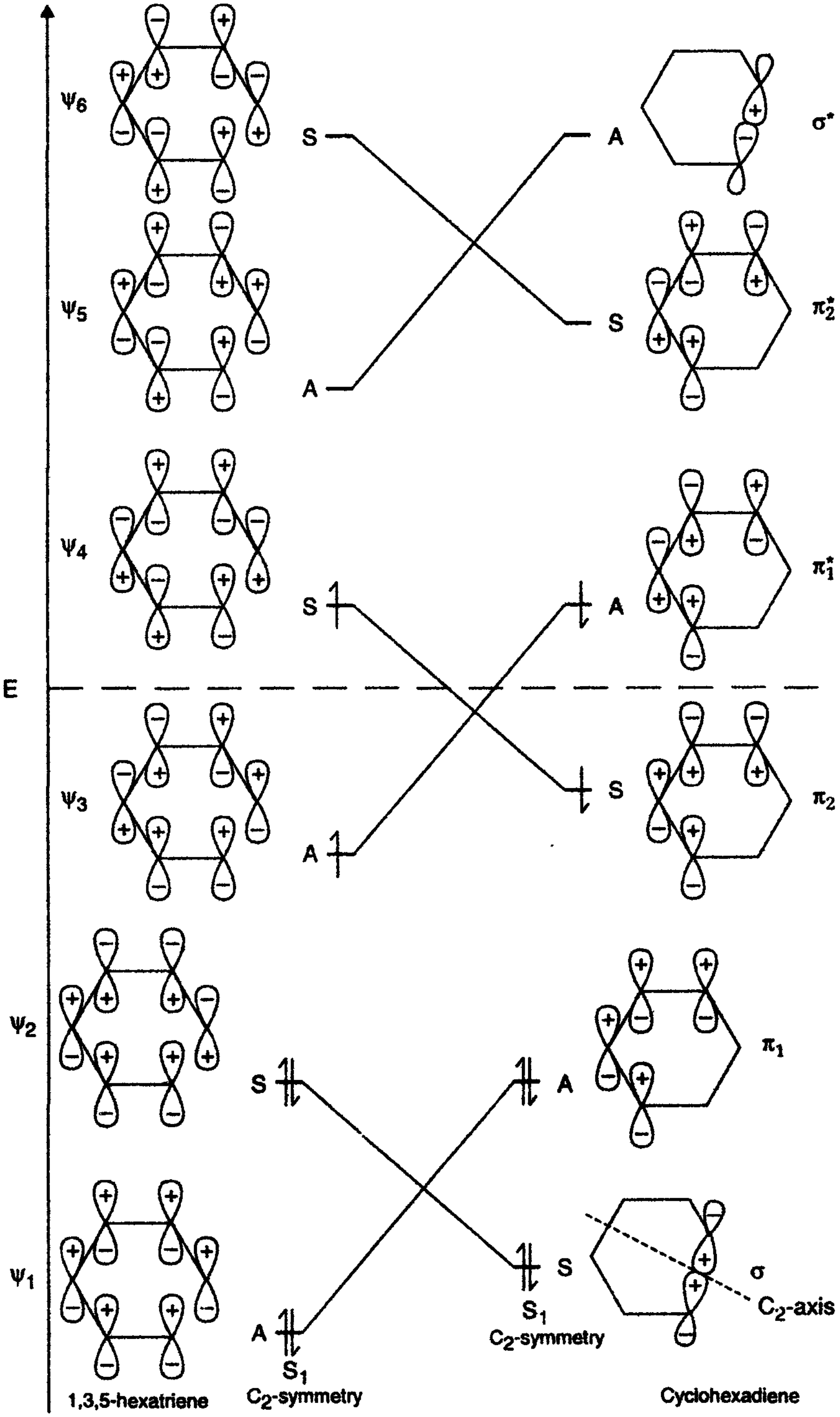


Fig. 4.1. c_2-axis of symmetry is conserved during conrotatory ring closure which is feasible photochemically. *Indicates antibonding; (A) Asymmetric; (S) symmetric.

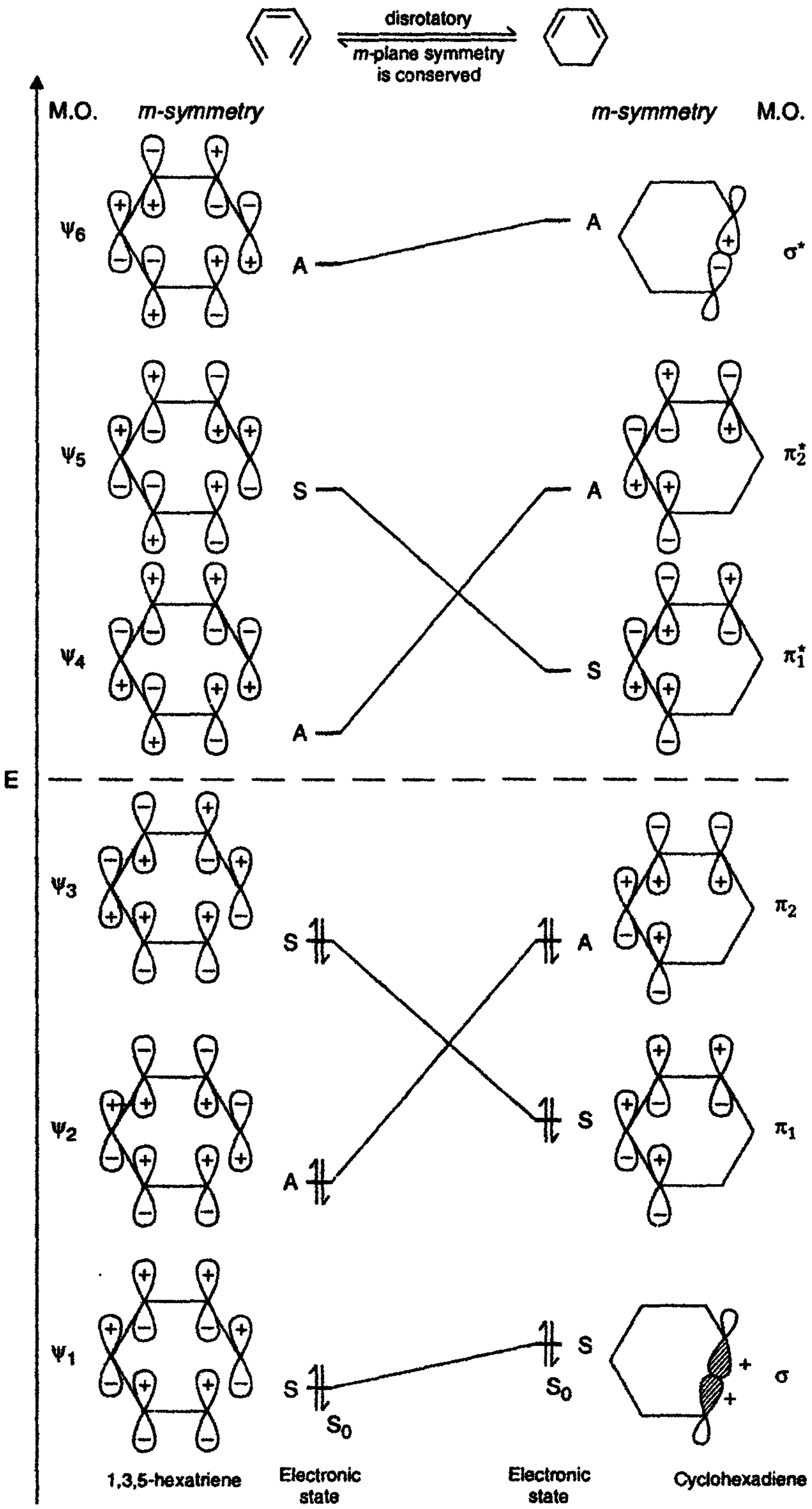


Fig 4.2. Thermal reaction is feasible by disrotatory mode in 1, 3, 5-hexatriene ⇌ cyclohexadiene interconversion.

other molecular orbitals decrease (downward slope) as the reaction proceeds. The reason can be traced by the mode of interaction of terminal lobes during conrotatory ring closure of ψ_1 and ψ_2. For ψ_1 as reaction proceeds an antibonding interaction takes place at terminal lobes as a result of which energy increases with the progress of reaction. But for ψ_2, interaction at terminal lobes is bonding, resulting in decrease in energy as reaction proceeds. Likewise, energy of ψ_3 will increase and that of ψ_4 will decrease.

In case of unsymmetrical 1, 3-dienes; for example 2-methyl-1, 3-butadiene, *i.e.*, isoprene, reaction same type of interactions are involved. Additional methyl group does not affects much to the coefficients of molecular orbitals.

Predictions for 1, 3, 5-Hexatriene $\rightleftharpoons$ cyclohexadiene interconversions : These predictions can be made on the similar grounds as for 1, 3-butadiene $\rightleftharpoons$ cyclobutene interconversion. Photochemical reaction is feasible by conrotatory mode; whereas thermal reaction follow disrotatory mode of ring closure as is explainable by Fig. 4.1. and Fig. 4.2, respectively.

4.1.2 Frontier Molecular Orbital (FMO) Method

In FMO-method symmetry of HOMO of open chain partner is important and decisive. If HOMO of open chain partner has c_2-symmetry, reaction follows conrotatory path. On the other hand presence of *m*-symmetry in HOMO of open chain partner causes the reaction to take disrotatory course. It is well known that symmetry of molecular orbital depends upon the number of nodes. If number of nodes is zero or an even integer, the orbital is symmetrical with respect to mirror plane and antisymmetric with respect to c_2. But, symmetry properties are reversed if number of nodes is an odd integer. For instance, in ground state of butadiene during 1, 3-butadiene to cyclobutene interconversion; ψ_2 is HOMO; it has one node, therefore, possesses c_2-axis of symmetry and during thermal ring-closure, conrotatory mode of ring closure is followed. Upon irradiation, one electron jumps from ψ_2 to ψ_3 which now becomes HOMO (or SOMO). ψ_3 with two nodes thus possesses *m*-symmetry, therefore, disrotatory mode is followed for ring-closure under photochemical condition. These explanations are based upon the facts that overlapping of wave functions of same phase is essential for bond formation (Fig. 4.3).

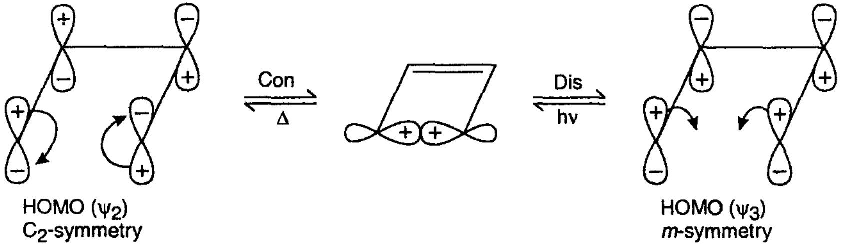


Fig. 4.3. FMO-approach for 1, 3-butadiene-cyclobutene interconversion.

In 1, 3, 5-hexatriene $\rightleftharpoons$ cyclohexadiene interconversion contrary to above transformation thermal ring-closure is disrotatory and photochemical

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* I. Flemming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, London New York (1976).

ring-closure is conrotatory. This is again explained by the fact that in thermal ring-closure. HOMO is ψ_3 which is symmetric with respect to *m*-plane which can be conserved only through disrotation. But, during photochemical process ψ_4 with c_2-axis of symmetry is HOMO which can be conserved only through conrotation, hence, upon irradiation conrotatory path is followed (Fig. 4.4).

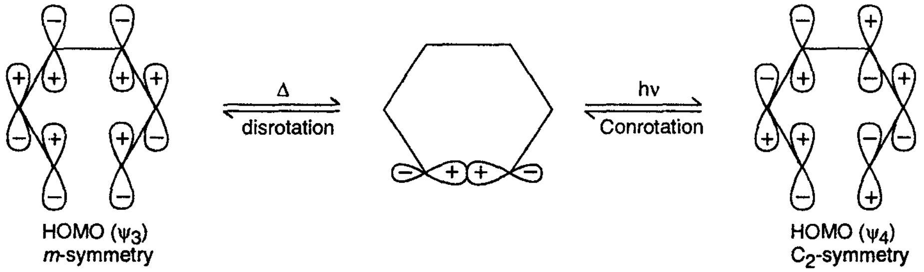


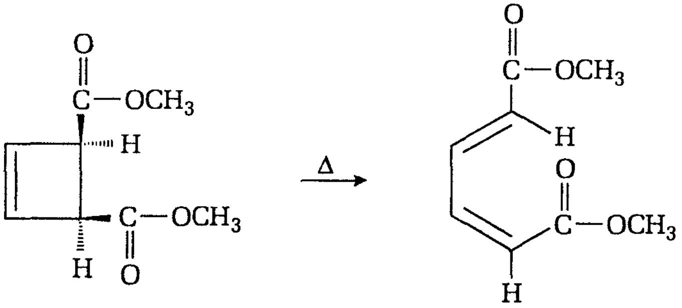
Fig. 4.4. FMO-approach for 1, 3, 5-hexatriene-cyclohexadiene interconversion.

Both conrotations as well as disrotations of *n*π-conjugated polyenes to (*n* − 2)π cyclopolynes and vice versa can take place in both directions; but always sterically less hindered product formation is favoured.

4.1.3 Stereochemical Outcome of Electrocyclic Reactions

During electrocyclic ring-opening as well as electrocyclic ring-closure of a polyene system there are two possibilities due to symmetry of the system. One possibility may be disallowed on account of molecular geometry or steric factor operational during transtional state. Stereochemical outcomes for different membered polyene systems are discussed below :

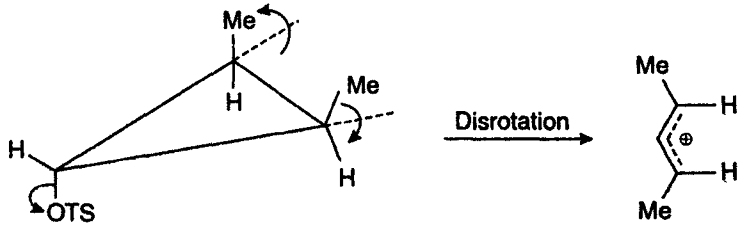
(A) Four-membered Rings : Electrocyclic ring-opening of cyclobutene to 1, 3-butadiene is thermally conrotatory and photochemically disrotatory. Reverse reaction, *i.e.*, ring-closure of 1, 3-butadiene is not thermodynamically favoured due to greater stability of butadiene over cyclobutene by the factor 50 kJ mol^{-1}. These two reactions occur with high degree of **stereoselectivity**. For instance, dimethyl-*cis*-3-cyclobutene-1, 2-dicarboxylate upon heating to 140°C, yields dimethyl (2*Z*, 4*E*)-2, 4-hexadienedioate due to the fact that ring strain of double bond in cyclobutene and conjugation of double bond in acyclic member with carbonyl group stablize diene to greater extent. The reaction may be thermally feasible at this relatively low temperature.



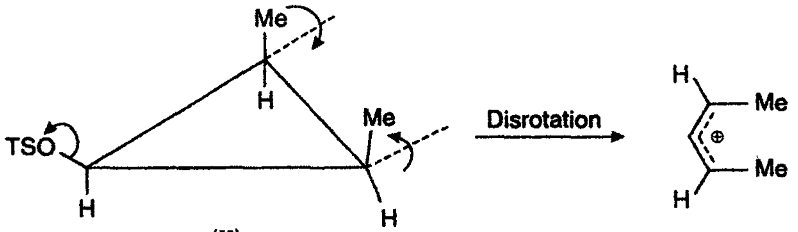
Dimethyl-*cis*-3-cyclobutene-1,2-dicarboxylate

Dimethyl (2Z, 4E)-2,4-hexadienedioate

(B) Three-membered Rings : In contrast to even-membered rings where molecule undergoing ring opening are neutral molecules, for electrocyclic ring opening in three-membered as well as other odd-membered ring systems species must be cations, anions or free radicals. A cyclopropyl cation upon thermal ring opening follows disrotatory mode (2π-system)*; cyclopropyl anion gives allyl anion through conrotatory mode under thermal conditions [4π-system]*. Disrotatory ring openings of two isomers of cyclopropyl tosylate give isomers of different types and occur at different rates (solvolysis). In fact, ring opening involves rupture of σ-bond. In case of cyclopropane with axial tosylate group (I) **anchimeric assistance** enhances rate of reaction than in case of the substrate with equatorial tosyl group (II) (4500 : 1) [Fig. 4.5].



(I)



(II)

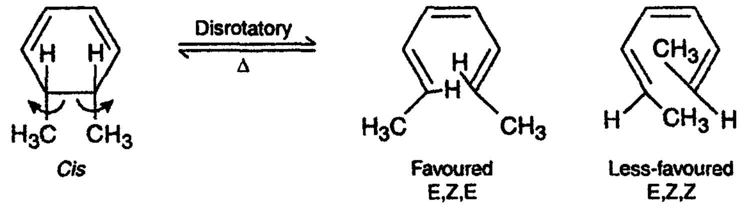
Fig. 4.5. Disrotatory ring openings of cyclopropyl tosylates.

In compound (I) outward movement of two methyl groups is easy and therefore rate of reaction rate is high; but in compound(II) methyl groups move inwardly which is difficult as steric hinderance is there.

(C) Six-membered Rings : Hexatriene ⇌ cyclohexadiene interconversion [(4n+2)π system] involves conrotatory mode under photochemical conditions and disrotatory process occurs under thermal conditions. Always sterically less hindered product is major product.

For instance,

(a) (i)



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* (1) R.B-Woodward and R. Hoffmann, "The conservation of Orbital Symmetry", Verlag-Chemie, Academic Press, New York (1970)

(2) G.B. Gill and M.R. Willis; "Pericyclic Reactions," Chapman and Hall, London (1974).

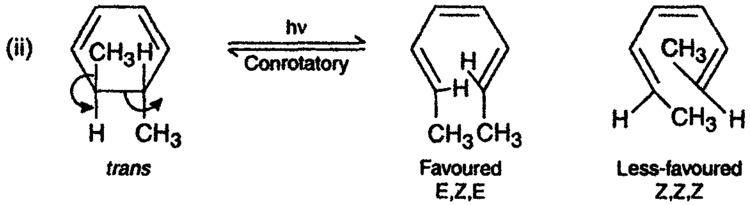
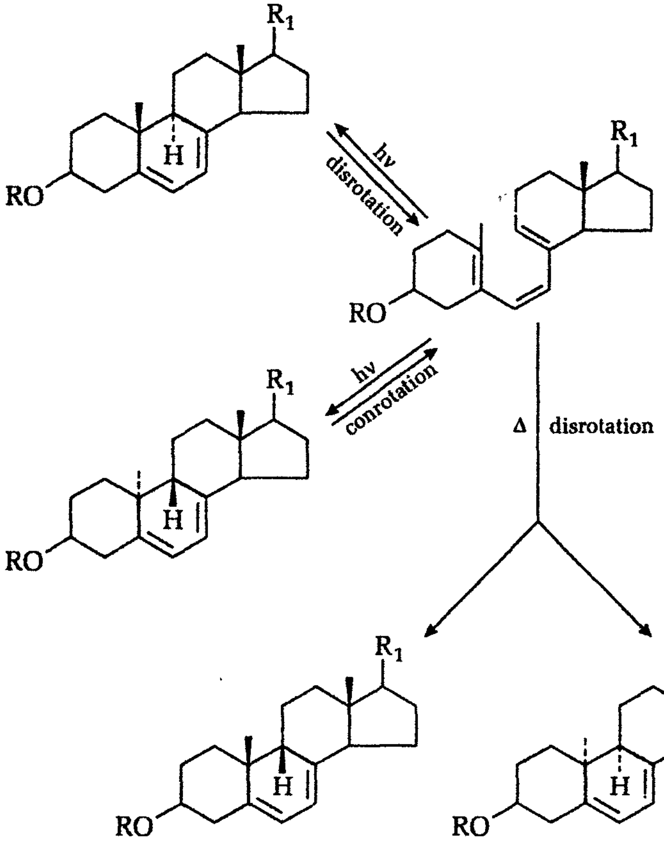


Fig. 4.6. Ring openings in *cis* and *trans*-cyclohexadienes.

(b) Thermal and photochemical transformations in Vitamin D series are also stereospecific* as given below :



(c) When two substituents of cyclohexadiene form part of a ring as an bicyclic systems like **norcaradiene**(III) thermal ring-opening occurs through disrotation as both the substituents move inwards to give all *cis*-cycloalkatriene(V), because in this case steric repulsion is absent. Two double bonds here can be accomodated only in large-sized rings; not in smaller ones.

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* E. Havinga, R.J. De Kock and M.P. Rappold, Tetrahedron, 11, 278 (1960).

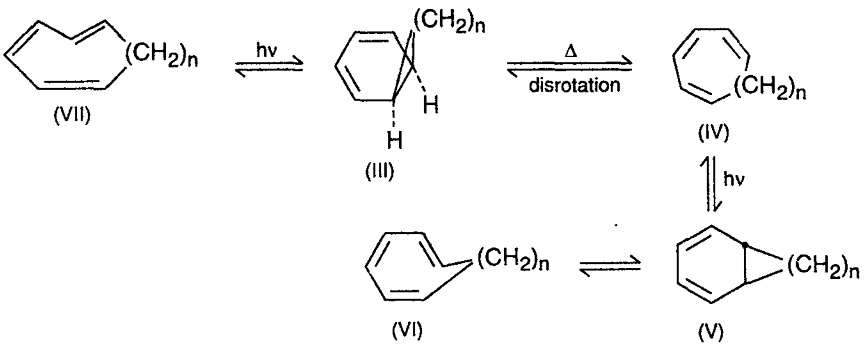

Fig. 4.7. Electrocyclic reaction of bicyclic cyclohexadiene.

4.1.4 Perturbational Molecular Orbital (PMO)* Method :

(has been discussed in Unit (III)

* * *

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*M.I.S. Dewar, "The Molecular Orbital Theory of Organic Chemistry". McGraw-Hill (1969).

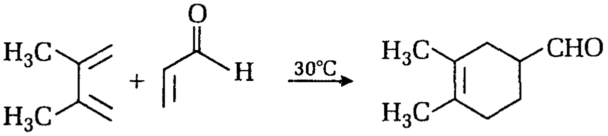
UNIT

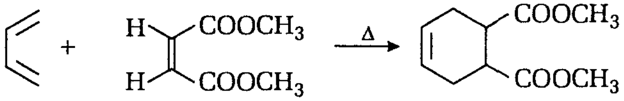
5

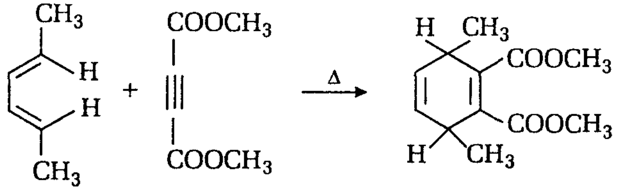
CYCLOADDITION REACTIONS

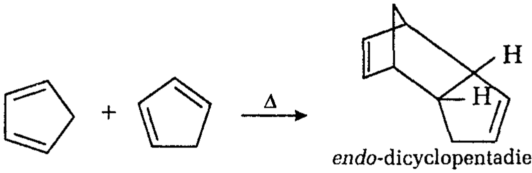
In cycloaddition reactions an olefinic system with $m\pi$ electrons adds up to a system with $n\pi$-electrons to give a cyclic partner with $(m-2)+(n-2)\pi$-electrons. In the process two σ-bonds are formed at the cost of four π-electrons. These addition reactions are called $(m+n)$ cycloadditions. They occur with high degree of stereoselectivity under thermal as well as photochemical conditions. They are referred to as $(m+n)$ or $(m+n+...)$ reactions keeping in view number of π-electrons involved in the process. Some examples are cited below :

1.  4 + 2 cycloaddition (Diels-Alder reaction)

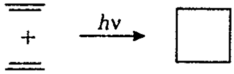
2.  4 + 2 cycloaddition

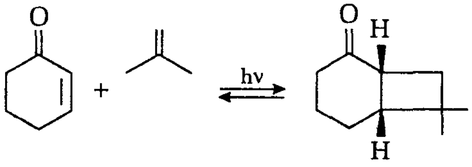
3.  4 + 2 cycloaddition

4.  4 + 2 cycloaddition

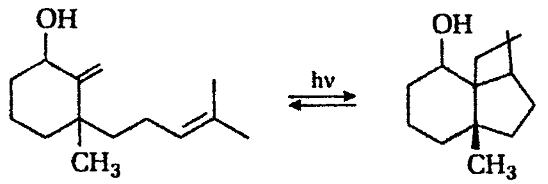
5.  4 + 2 cycloaddition

endo-dicyclopentadiene

6.  2 + 2 cycloaddition

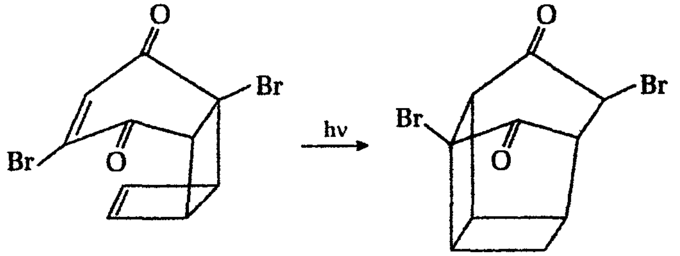
7.  2 + 2 cycloaddition

8.



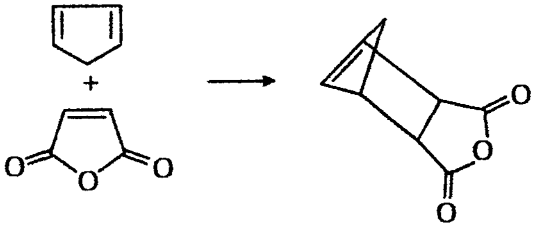
2 + 2
cycloaddition

9.



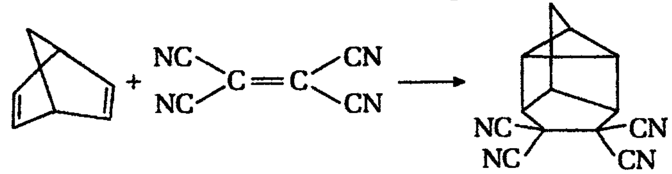
2 + 2
cycloaddition

10.



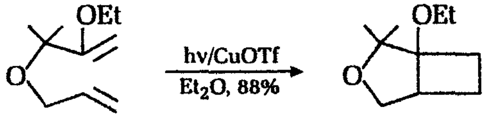
2 + 4
cycloaddition

11.



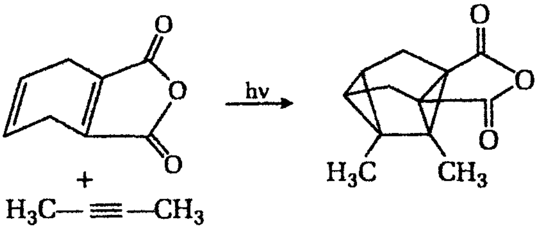
2 + 2 + 2
cycloaddition

12.*



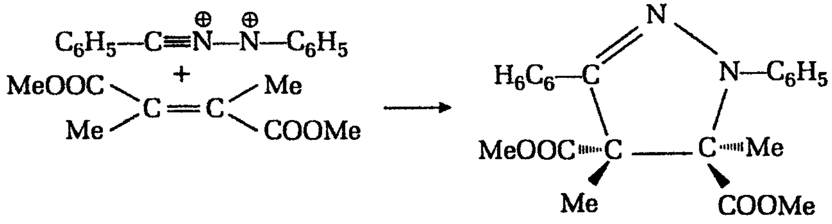
2 + 2
cycloaddition

13.



2 + 2 + 2
cycloaddition

14.



1, 3-dipolar cycloaddition

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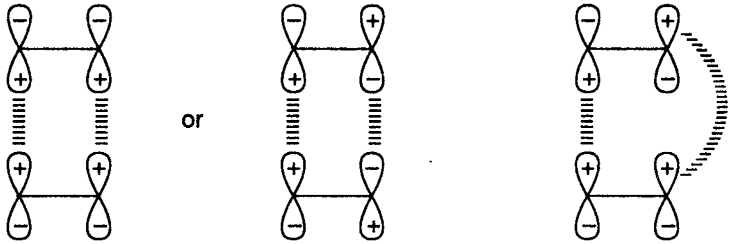
* S. Samajdar, A. Ghatak, S. Banerjee and S.Ghosh, **Tetrahedron**, 57, 2011 (2001).

5.1 SUPRAFACIAL AND ANTARAFACIAL PROCESS

Because during cycloaddition, there is addition of two olefinic systems, therefore, two feasibilities are there : (a) addition may take place in such a way that lobes of same phases of one component with the lobes of same phases of other component may overlap (b) lobes of same phase of one component may overlap with the lobes of opposite faces of other component. (a) is known as **suprafacial cycloaddition** and (b) as **antarafacial cycloaddition.***



(a) Suprafacial cycloaddition (b) Antarafacial cycloaddition

Fig. 5.1.

Antarafacial processes are difficult because in them twisting of *p*-orbitals is required; though both the process are feasible on symmetry ground.

As both the π-systems are involved in the cyclo addition, it is essential to specify the modes with respect to each of them. Specification is made by placing subscript *S* or **a** after the number refering to π-component. For instance, suprafacial addition with respect to each component of Diels-Alder reaction is specified as $\pi_s^2 + \pi_s^4$ cycloaddition. Another way is simply writting it as $2s+4s$ cycloaddition.

"PREDICTION OF FEASIBILITY"

5.2 (A) CORRELATION DIAGRAM METHOD

Control of orbital symmetry on cycloaddition can be well expressed by the simple example of suprafacial-suprafacial addition of the two ethylene molecules ($2s+2s$) to give cyclobutane. During the course of this reaction both mirror-plane (*m*), *i.e.*, vertical symmetry as well as c_2-axis of symmetry (c_2) *i.e.*, horizontal symmetry are conserved. (Fig. 5.2).

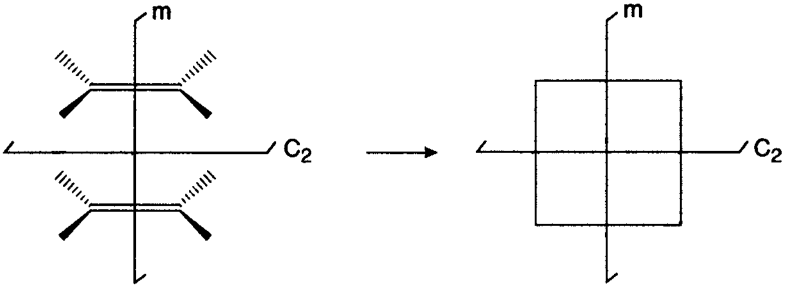


Fig. 5.2. Symmetry conservation during cycloaddition.

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* R.B. Woodward and R. Hoffmann, J. Amer. Chem. Soc; 87, 2511 (1965).

In this transformation four π-orbitals of two ethylene molecules and four σ-orbitals of cyclobutane are involved. As symmetry properties of other orbitals do not undergo change, they are not taken into acount. Shape and symmetries of involved orbitals, *i.e.*, π and π* orbitals of both the ethylene molecules and σ and σ* orbitals of cyclobutane are shown in the fig. 5.3 and 5.4 given below :

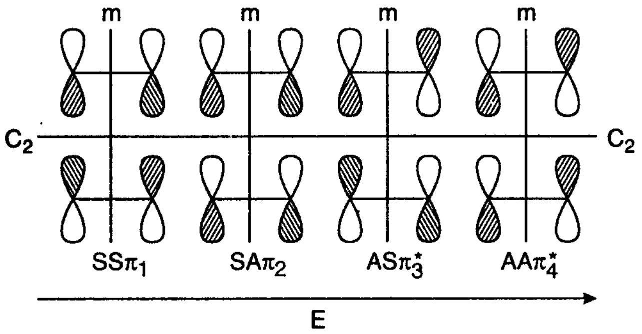

Fig. 5.3. **Symmetry properties of two ethylene molecules involved in the formation of cyclobutane.**

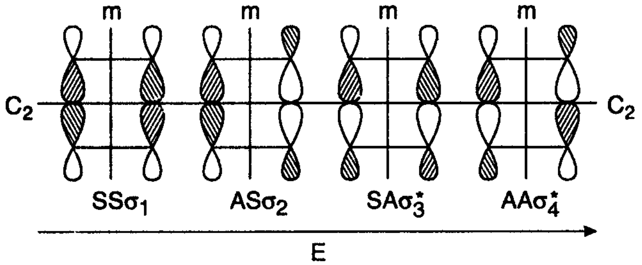

Fig. 5.4. **Symmetry properties of σ-orbitals of cyclobutane.**

A correlation diagram may be prepared on the basis of symmetry properties of ethylene molecules and cyclobutane that predicts feasibility of this cycloaddition (Fig. 5.5).

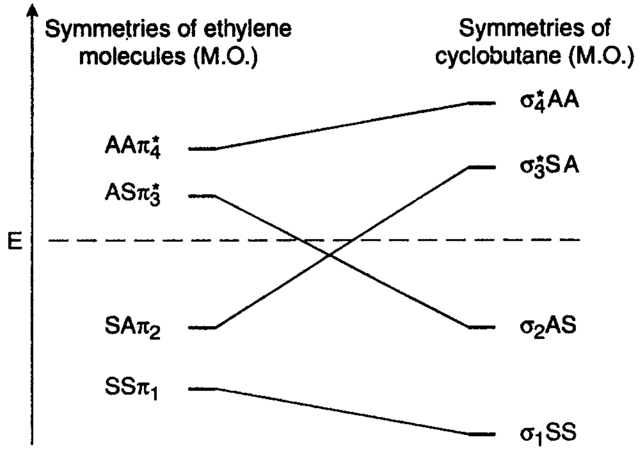

Fig. 5.5. **Correlation diagram for ethylene-cyclobutane interconversion.**

From the above correlation diagram it is clear that reaction is photochemically feasible because first E.S. of ethylene correlates with G.S. of cyclobutane making it symmetry allowed. On the other hand this reaction is thermally forbidden on account of the fact that G.S. of one ethylene molecule does not give G.S. of cyclobutane, therefore, ground state of two ethylene molecules can not combine to give cyclobutane while conserving symmetry of orbitals.

5.2.1 Diels-Alder Reaction

Correlation diagram may also be constructed to predict feasibility of Diels-Alder reaction which is $\pi^4 s + \pi^2 s$ cycloaddition. Results have been found in conformity with observed fact that reaction is thermally feasible. In Diels-Alder reaction only *m*-plane of symmetry is conserved. Symmetry properties and correlation diagram for Diels-Alder reaction is given below (Fig. 5.6).

Diels-Alder reaction involves ψ_1, ψ_2, ψ_3 and ψ_4 orbitals of 1, 3-butadiene and π and π^* orbitals of ethylene as reactants m.os and $\sigma_1, \sigma_2, \pi, \pi^*, \sigma_3^*, \sigma_4^*$ orbitals of cyclohexene which are product molecular orbitals. When these molecular orbitals are arranged in the increasing order of their energies alongwith their symmetries, ground state molecular orbitals of reactants correlate with the ground state molecular orbitals of their product, therefore, reaction is thermally allowed; but photochemically forbidden on account of the fact that first excited state of reactant does not correlates with first excited state of product (Fig. 5.6).

$$\psi_1^2 \pi^2 \psi_2 \psi_3 \not\leftrightarrow \sigma_1^2 \sigma_2^2 \pi \pi^*$$

5.2.2 Cycloadditions of Benzene and its Derivatives

There are large number of cycloaddition reactions of benzene and its derivatives. Correlation diagram can be constructed to predict them which can be represented by examples of **ortho-**, **meta-** and **para**-cycloadditions of benzene and ethylene or benzene and butadiene. **Ortho-**, **meta-** and **para**-additions give different products.

5.2.2.1 Reactions between Benzene and Alkenes

These are all stereospecific with respect to alkenes. Though reaction requires excitation of benzene chromophore, but involves initial excitation of alkene. Sometimes charge transfer complex between alkene and benzene also undergoes excitation. All the three cycloadditions involve singlet excited states of benzene ring.

π-molecular orbitals of benzene and their *m*-plane symmetry is depicted in Fig. 5.8.

(a) Ortho-addition : Correlation diagram for **ortho**-addition is depicted below (Fig. 5.9).

Since, symmetry properties of reactants, *i.e.*, benzene and ethylene match with that of product in ground state reaction is thermally feasible; but photochemical *ortho* cycloaddition between benzene and ethene is unfavourable.

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* J.M. Coxon and B. Halton, "Organic Photochemistry," Cambridge University Press (1986).

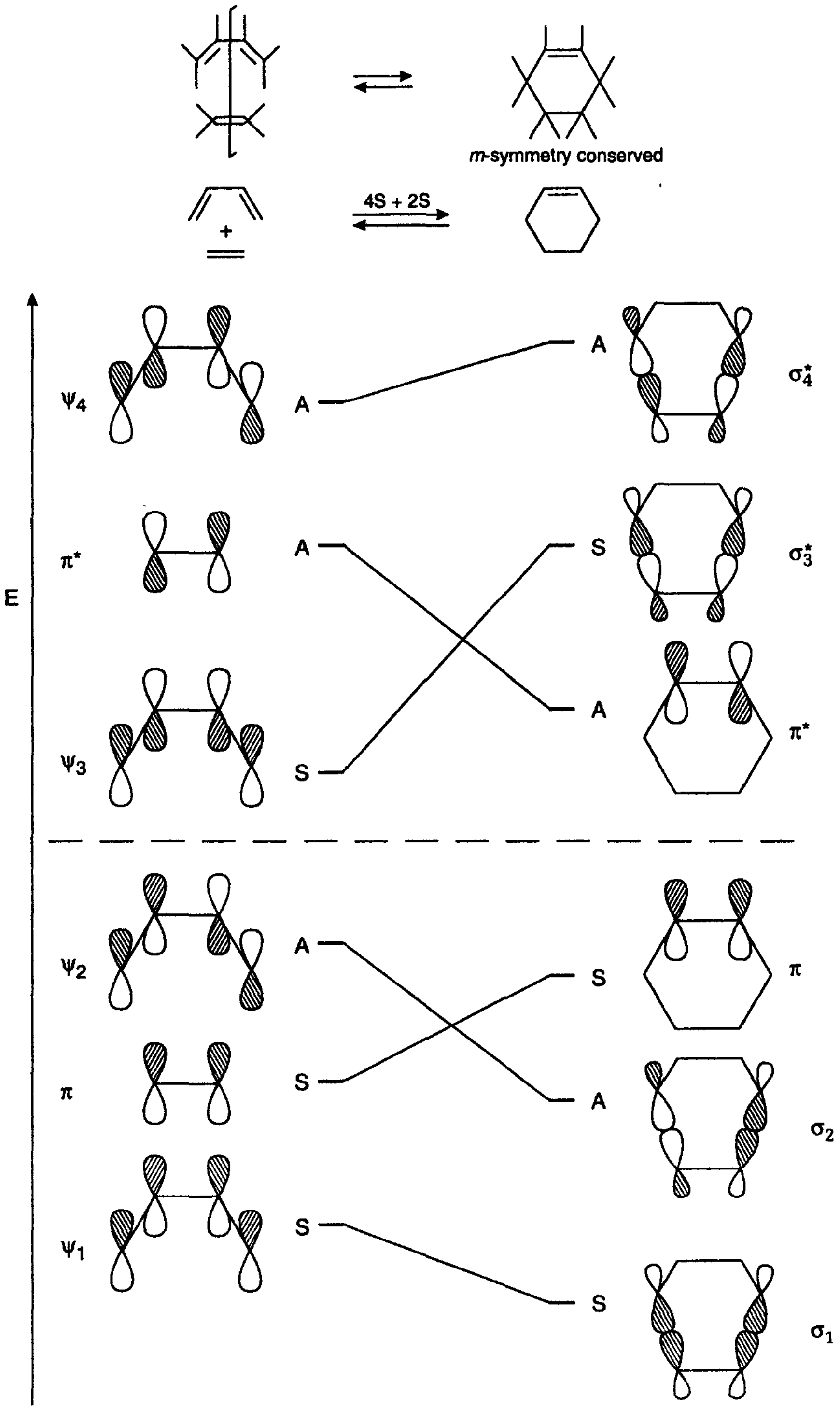


Fig. 5.6. Correlation diagram for Diels-Alder reaction.

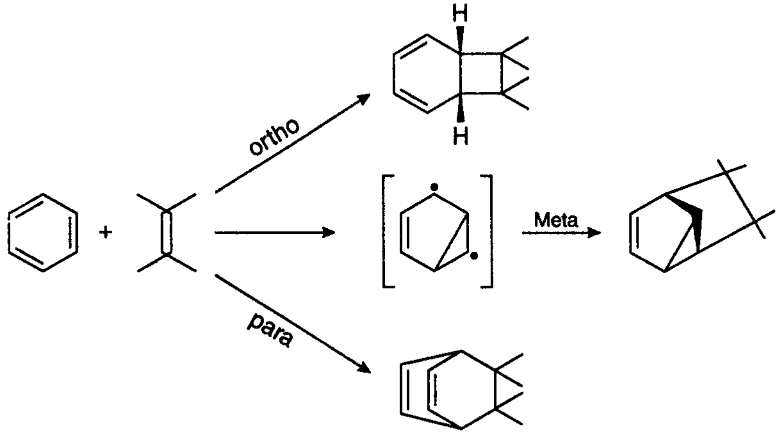


Fig. 5.7. *Ortho*, *meta* and *para* addition of ethene to benzene.

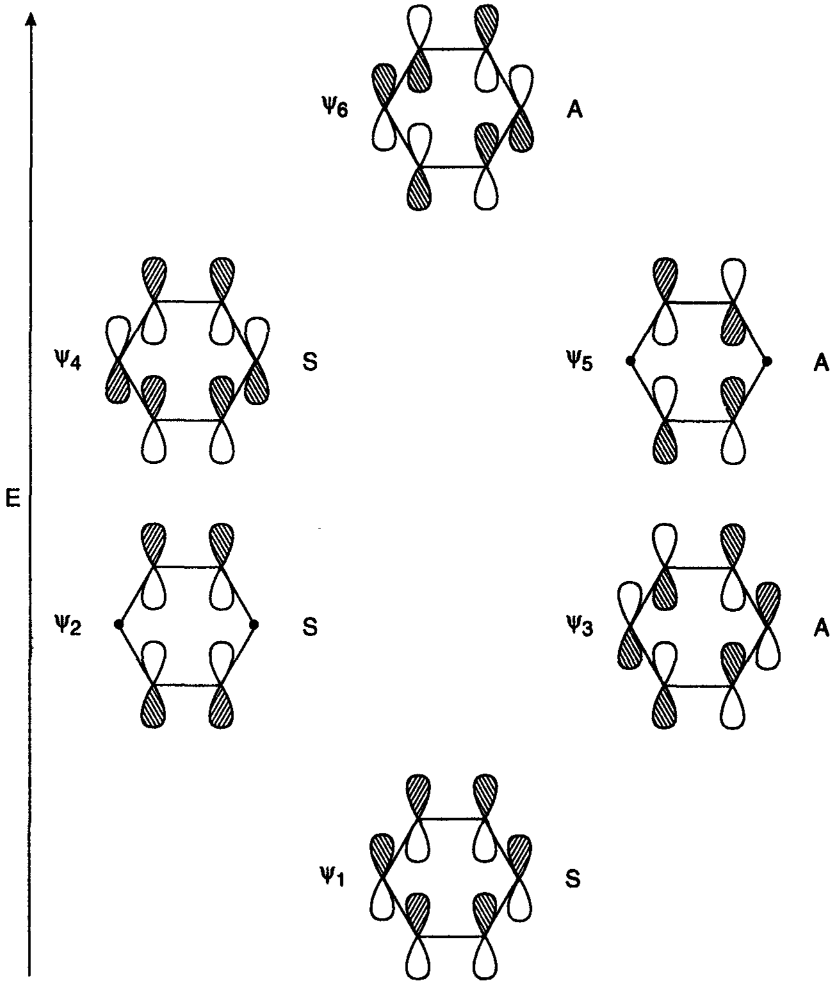


Fig. 5.8. Molecular orbital of benzene.

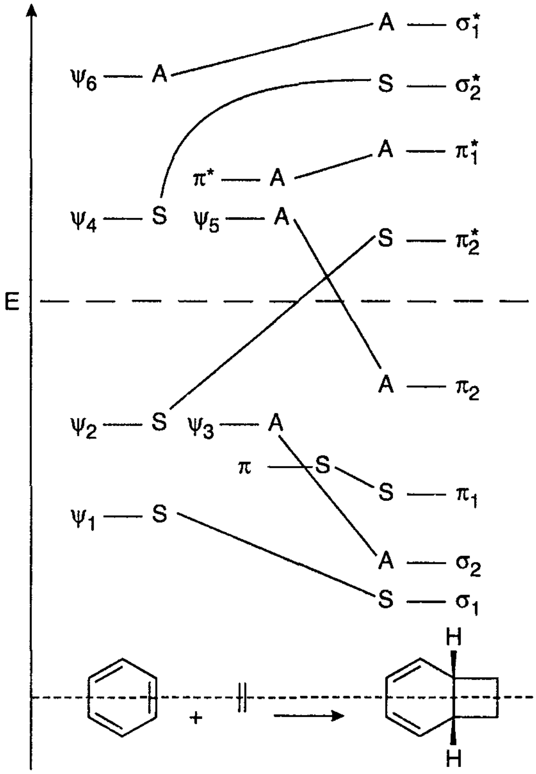
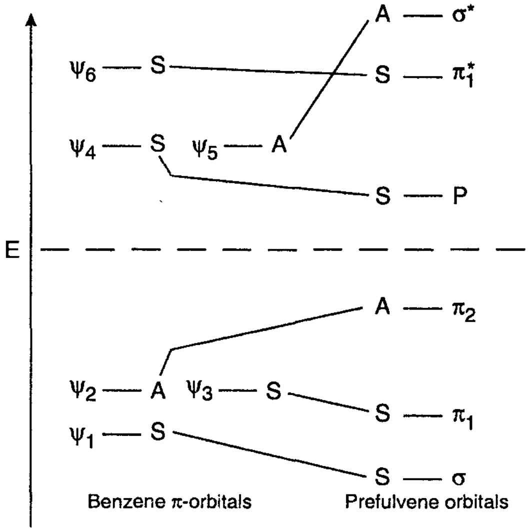


Fig. 5.9. Correlation diagram for *ortho*-addition of benzene to ethene.

(b) Meta-addition : Similar to **ortho**-addition correlation diagram can also be prepared for **meta**-addition between benzene and ethylene (Fig. 5.10). **Meta** addition is photochemically allowed.



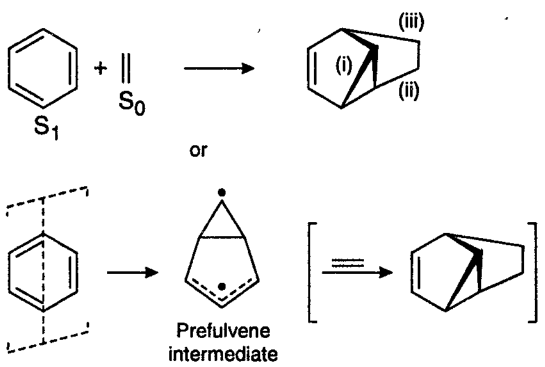


Fig. 5.10 (a). Correlation diagram for benzene-ethene meta-cycloaddition through prefulvene intermediate (initial formation of (i) bond)

In **meta**-addition either direct concerted cycloaddition or initial **meta**-bonding in excited singlet state to give prefulvene type intermediate takes place. Formation of bond (i) can be before (ii) and (iii) or vice versa or subsequent to (ii) and (iii). This reaction is stereospecific and insensitive to proton donor and solvent which suggests that (ii) and (iii) may be formed is concerted step.

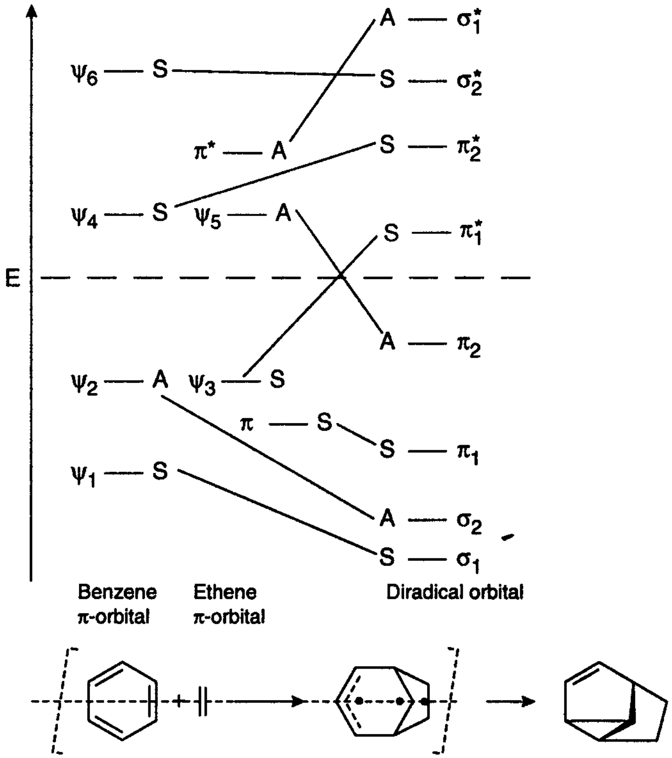


Fig. 5.10 (b). Correlation diagram for benzene-ethene *meta*-cycloaddition (initial formation of (ii) and (iii) bond).

(c) Para-addition : Correlation diagram for *p*-addition to predict the feasibility by thermal mode of cycloaddition is shown in Fig. 5.11.

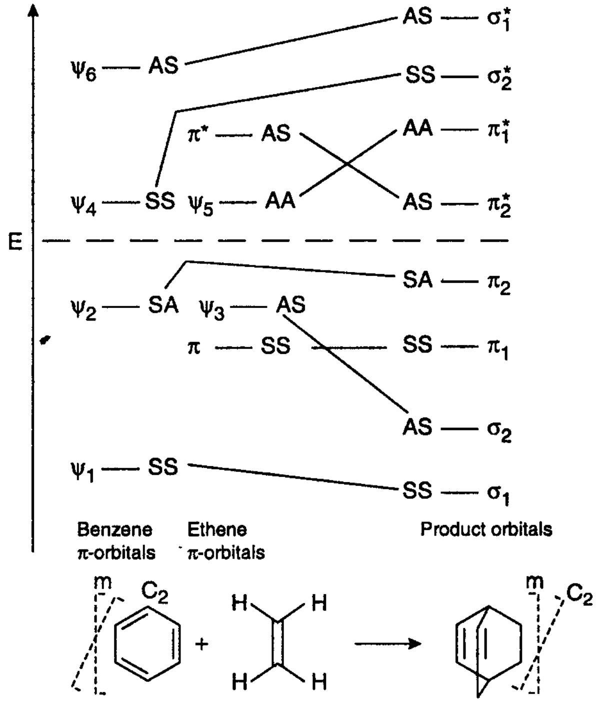


Fig. 5.11. Correlation diagram for *para*-cycloaddition of benzene and ethene.

Ortho-cycloaddition takes place with a olefin which has **low ionization potential** in comparison to benzene where polar nature of reaction overpowers the symmetry imposed barrier to this reaction. Polar nature of **ortho**-cycloaddition is supported by the fact that in case of doner substituted ethylenes, reaction is promoted by polar solvent, but in *meta*-addition no solvent effect is there. *o*-and *p*-photocycloadditions are disallowed to occur as concerted addition between S_1 of benzene and S_0 of alkene until mixing of **charge-transfer states** occurs.

Cycloadditions are also favoured through singlet exciplexes*. Exciplexes mediated cycloadditions are **concerted** and **stereoselective** processes. Since, **ortho**-additions are symmetry forbidden these reactions occur in the system with prominent doner-acceptor character, otherwise *meta*-additions occur.

In a large number of cases initial products of cycloaddition are unstable and they decompose through electrocyclic ring opening. For instance, reaction of benzene with 1, 1-dimethoxyethene gives *ortho*-addition product which under

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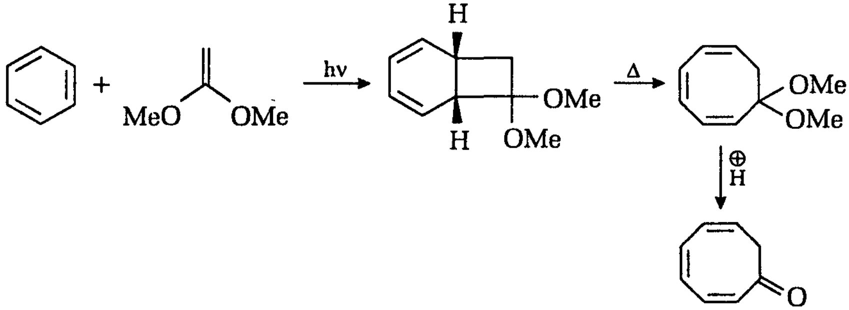
* **Exciplexes** : Frequently formed complexes between excited fluorescent molecules and added foreign molecules are called exiplexes.

$$^1A^* + Q \longrightarrow [^1AQ]^* \text{ exciplex}$$

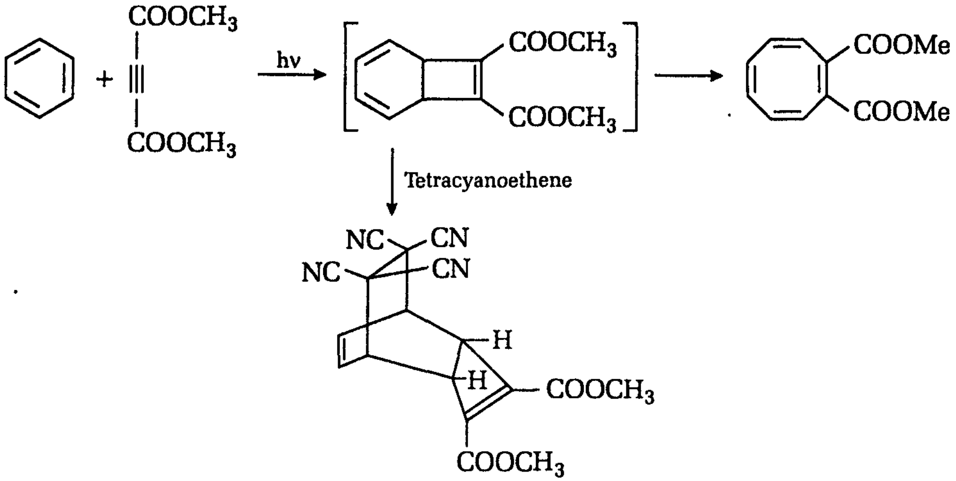
1 = singlet level

thermal conditions provides cyclooctatrieneone according to scheme-1. This scheme constitutes important synthetic route for the synthesis of cyclooctatrieneone.



Scheme 1.

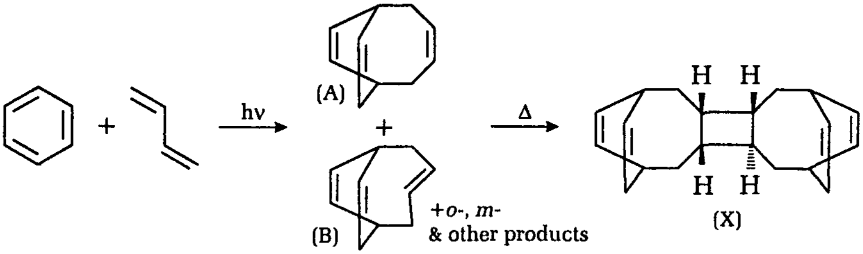
Initial addition products can be trapped before ring opening too. For example, Adduct of benzene with dimethylethynedicarboxylate can be trapped with tetracyanoethene according to scheme-2.

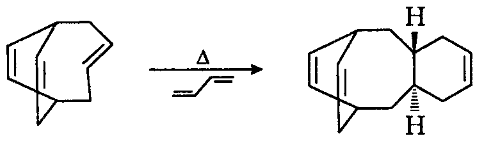


Scheme 2.

5.2.2.2 Reactions between Benzene and 1, 3-butadiene :

1, 4-additions occur between benzene and butadienes. $\pi^4 + \pi^4$ cycloadditions occur : 1, 3-Butadiene adds to benzene and *p*-addition product containg *cis*- and *trans*-double bonds along with **ortho-**, **meta-** and other products are formed. Addition product of benzene and *trans*-alkene undergoes thermal addition with butadiene to give dimeric product (*X*) and monomeric product (*Y*).





(Y)

Dimeric product is supposed to be formed by thermally allowed $\pi_s^2+\pi_a^2$ cycloaddition of initial products (*A*) and (*B*). Correlation diagram for $\pi^4+\pi^4$ cycloaddition of benzene and *trans*-1, 3-butadiene and benzene with *cis*-1, 3-buta- diene are shown in Fig. 5.12 and 5.13, respectively.

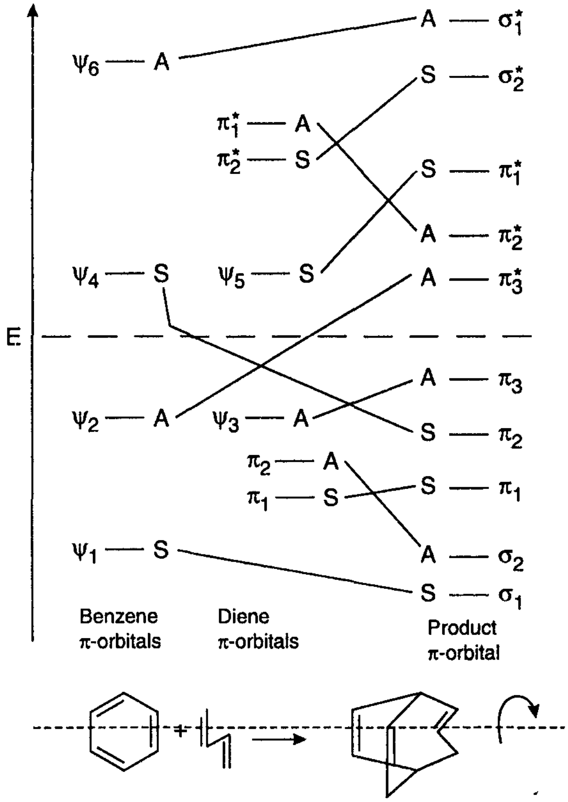


Fig. 5.12. Correlation diagram for cycloaddition between benzene of *trans*-butadiene.

Product from cycloaddition of benzene and *trans*-butadiene is predominates. To benzene *trans*-butadiene adds more readily. $\pi^4+\pi^4$ cycloaddition is photochemically allowed. Formation of charge transfer complex between two ground state molecules or an exciplex between excited state of one molecule and ground state of other may lower the energy barrier to this pericyclic reaction. $\pi^4+\pi^4$ cycloaddition may occur is case of two aromatic substrates also. For examples, dimerization of naphthalene and anthracene is very common (shown on next page).

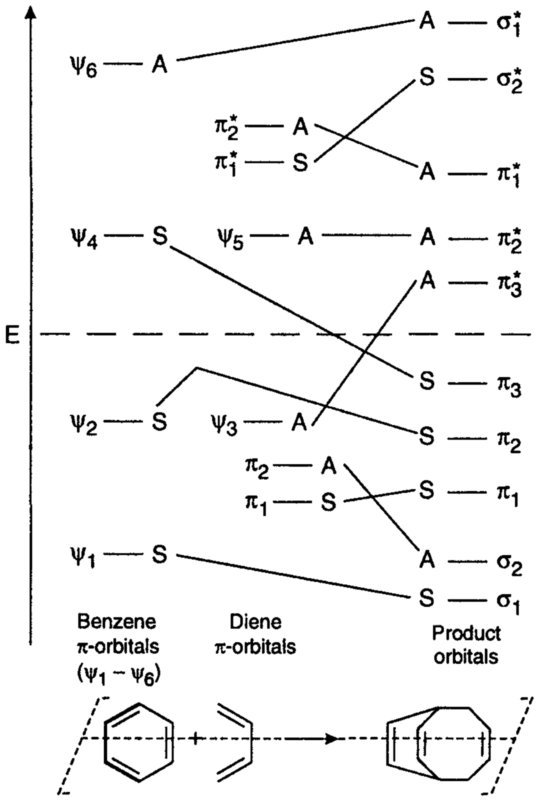
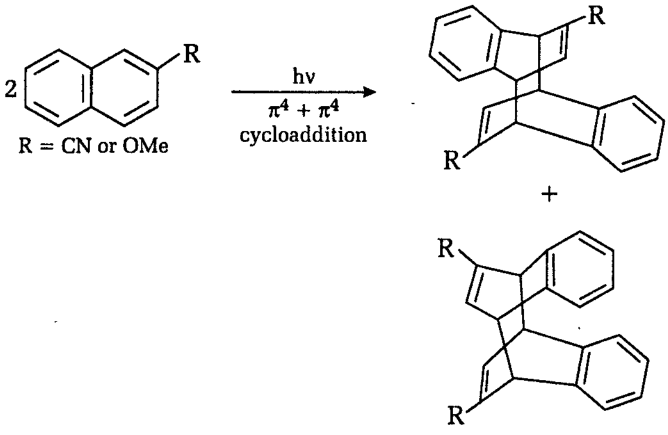


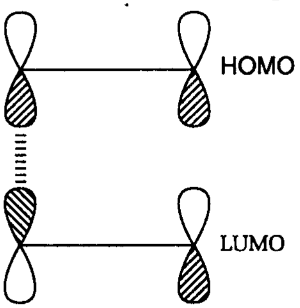
Fig. 5.13. Correlation diagram for cycloaddition between benzene and *cis*-butadiene.



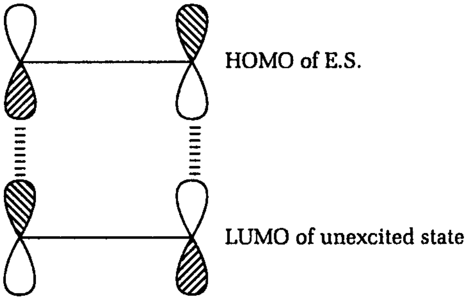
5.3 FRONTIER MOLECULAR ORBITAL (FMO) METHOD

Frontier molecular orbital (FMO) approach to predict course of cycloaddition reaction takes into account the symmetry properties of HOMO of one reactant and LVMO of other reactant. Reaction is favourable when signs of cofficient of HOMO and LVMO are same. Cycloaddition of ethylene is

$2s + 2s$ reaction which involves interaction of HOMO of one molecule of ethylene and LVMO of other molecule of reactant (ethylene) to yield the product cyclobutane. Because, in ground state signs of HOMO and LVMO of two ethylene molecules are not same, therefore, reaction is thermally forbidden. Upon irradiation one electron from the HOMO of one ethylene molecule is promoted from bonding to antibonding orbital which now becomes HOMO and sings lobes of HOMO of one molecule of ethylene and LUMO of another molecule become same reaction becomes photochemically feasible.

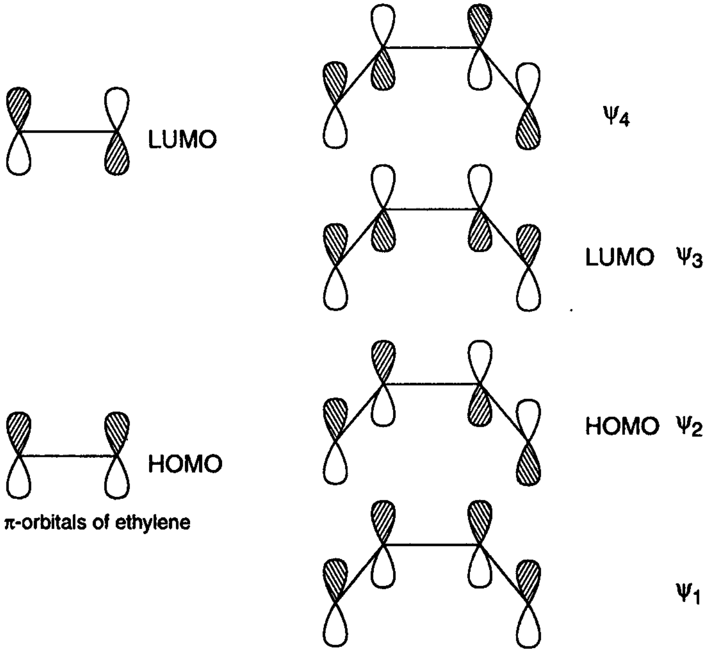


G.S.
(Δ forbidden)



E.S.
(hv-allowed)

Diels-Alder Reaction : In the manner similar to cycloaddition of ethylene Diels-Alder reaction can be analysed which involves π-molecular orbitals of butadiene and ethylene.

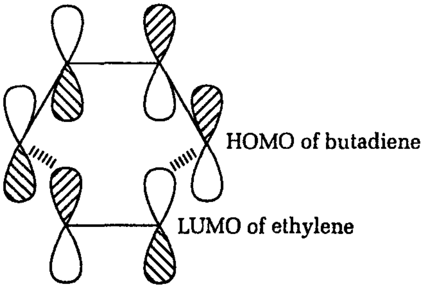


π-orbitals of ethylene

π-orbitals of butadiene

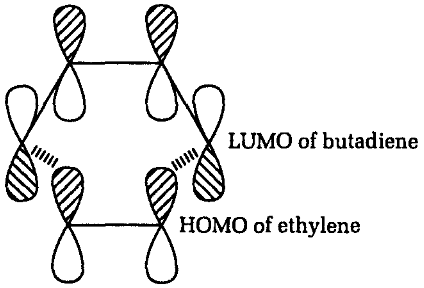
Fig. 5.14. π-molecular orbitals of ethylene and butadiene.

Signs of 1, 4-lobes of butadiene HOMO and ethylene LUMO are same, therefore, they interact and make the reaction thermally feasible.



Reaction thermally feasible

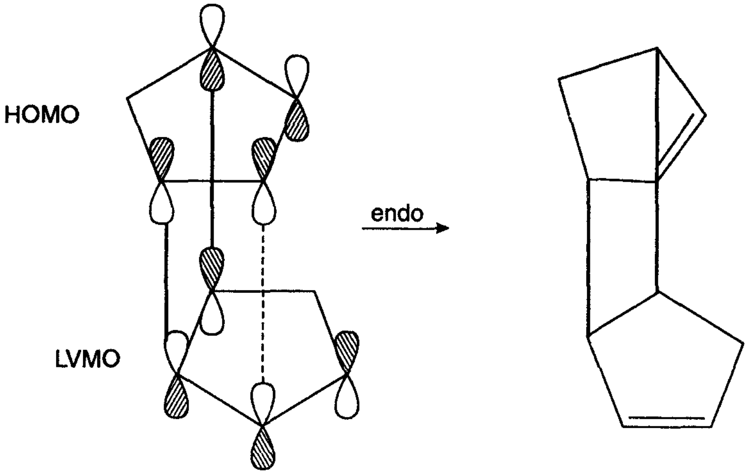
Same conclusion is drawn if we consider HOMO of ethylene and LUMO of butadiene.



Reaction thermally feasible

Upon imadation with U.V. light such interaction is not feasible, therefore, reaction is photochemically forbidden.

Another important example of application of FMO method on Diels-Alder reaction is dimerization of cyclopentadiene to yield dicyclopentadiene. In this case **endo** isomer is formed rather than **exo** although **exo** isomer is thermodynamically more stable. Reason behind this is that in case of **endo** isomer favourable secondary interactions are there between diene and dienophile*



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* S.M. Mukherji and S.P. Singh "Reaction Mechanism in Organic Chemistry" MacMillan India Limited (2000).

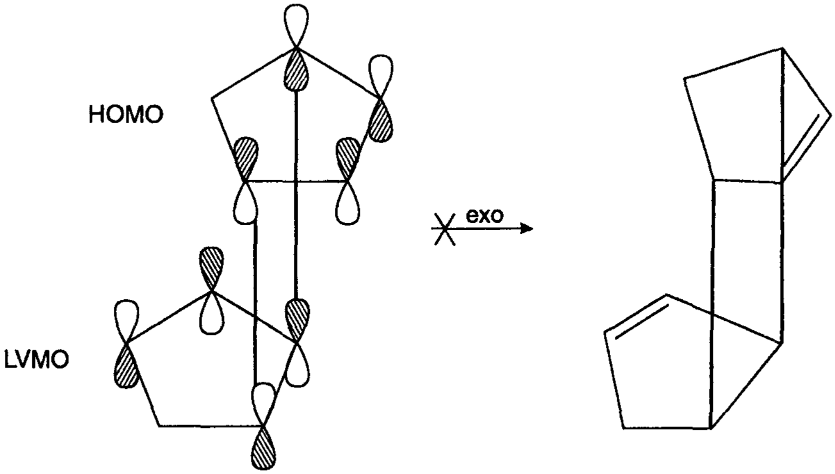
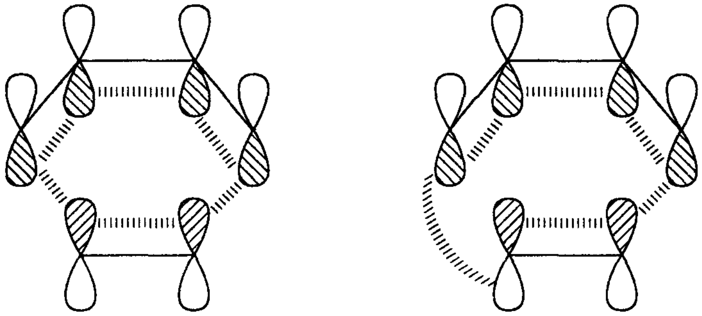


Fig. 5.15. Orbital interactions in dimerization of cyclopentadiene.

[shown by broken lines; whereas actual bonding interactions are shown by thick lines (Fig. 5.15)]. **Endo**-transition state is stablized Vs **exo**, therefore **endo**-attack is favoured. In some cases steric effect overpowers this effect and favours the formation of **exo**-transition state. Salem* has pointed out the possibility of symmetrical transition state, for example during the dimerization of cyclopentadiene.

5.4 PERTURBATIONAL MOLECULAR ORBITAL (PMO) METHOD

Cycloaddition reactions can also be predicted through PMO-method. If a given process is allowed can be determined through transition state. $\pi^4s+\pi^2s$ cycloaddition, *i.e.*, Diels-Alder reaction is allowed because the transition state is Hückel's type and is isoconjugate with benzene (a Hückel type system).



4s + 2s cycloaddition; 0 node,
6 electrons, aromatic, Δ allowed

4s + 2a cycloaddition; 1 node,
6 electrons, antiaromatic, hν allowed

The transition state for $2s+2s$ cycloaddition has 4-electrons with zero node and is therefore antiaromatic, hence, this reaction is thermally forbidden.

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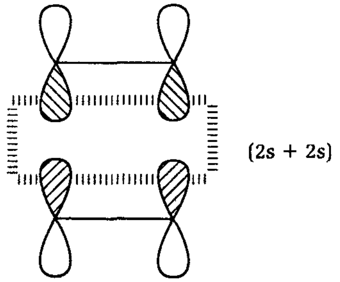
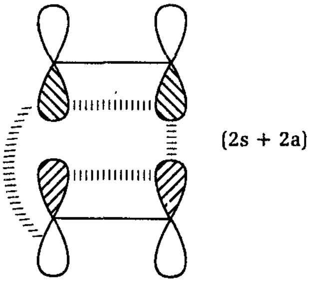
* L. Salem, J. Amer. Chem. Soc; **90**, 543, 553 (1968).

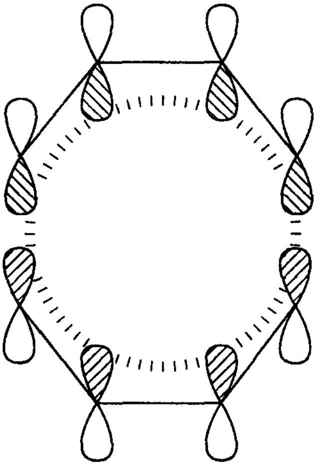


0 node, 4 electrons,
antiaromatic, hv-allowed

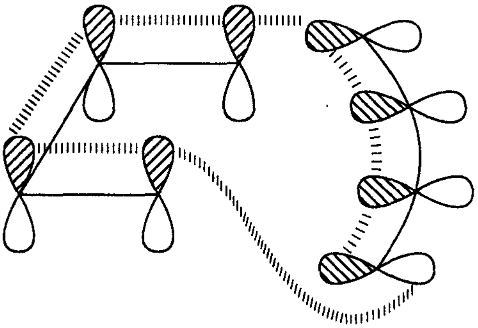


1-node, 4 electrons,
aromatic, Δ-allowed

In the similar manner $\pi^4s+\pi^4s$ cycloaddition is expected to be thermally forbidden as transition state is isoconjugate with cyclooctatetraene (Hückel antiaromatic system). On the other hand $\pi^4s+\pi^4a$ cycloaddition takes place under thermal conditions through aromatic transtion state.



$\pi^4s+\pi^4s$ cycloaddition; 0 node, 8 electrons, antiaromatic T.S., thermally disallowed



$\pi^4s+\pi^4a$ cycloaddition; 1 node, 8 electrons, aromatic T.S., Δ-allowed

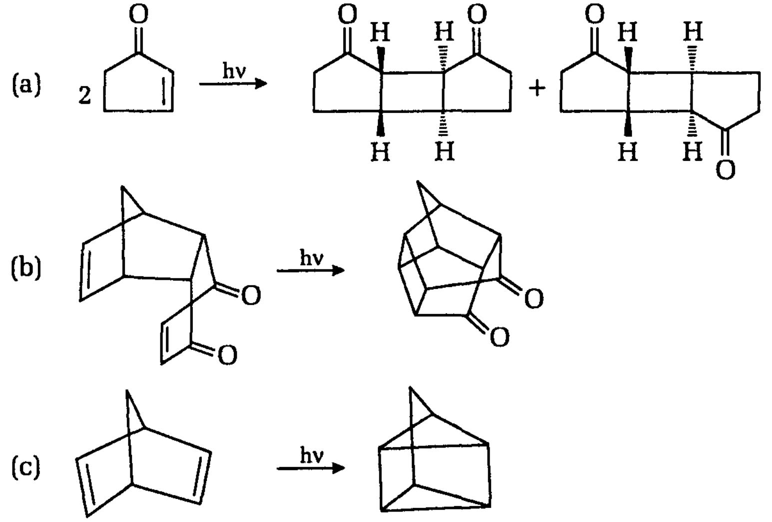
Conclusions drawn from all the three methods are same. Selection rules (for PMO-method) arrived at can be summarized as follows :

m + *n* electrons	Number of nodes	Aromaticity	Δ allowed	*h*ν allowed
4*q*	o or even	antiaromatic	—	supra-supra antara-antara
4*q*	odd	aromatic	supra-supra antara-antara	—
4*q* + 2	o or even	aromatic	supra-supra antara-antara	—
4*q* + 2	odd	antiaromatic	—	supra-supra antara-antara
q is an integer.				

5.5 MECHANISM OF CYCLOADDITION REACTIONS

5.5.1 2 + 2 Cycloadditions

$\pi^2 s+\pi^2 s$ are photochemical processes is supported by experiment and are highly useful in the synthesis of natural products which are highly strained molecules. Examples are :



Several questions are to be answered while considering mechanistic aspects of cycloaddition reactions. For example :

(i) What is the impact of multiplicity of excited state on the reaction?

(ii) If triplet excited state undergoes concerted cycloaddition?

(iii) If triplet excited state leads to triplet biradicals.

Let us consider photocycloaddition of *trans*-stilbene to the olefins. During this cycloaddition S_1 state of *trans*-stilbene attacks olefin, whereas, T_1 state results in *cis-trans*-isomerization without involving addition to olefines. Stereochemical identity of *trans*-stilbene is maintained during the course of this reactions.

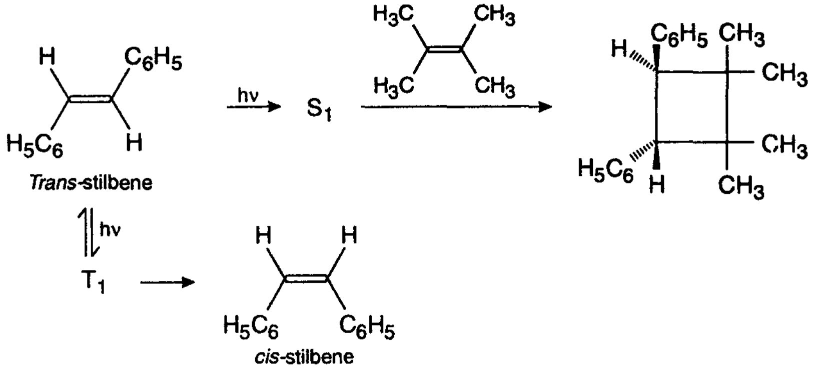
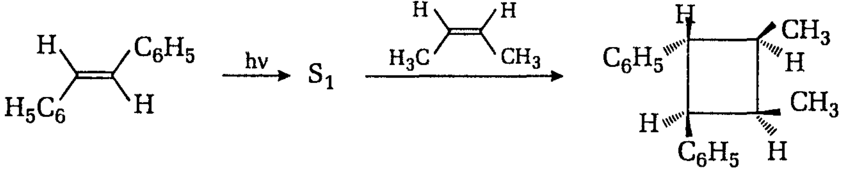
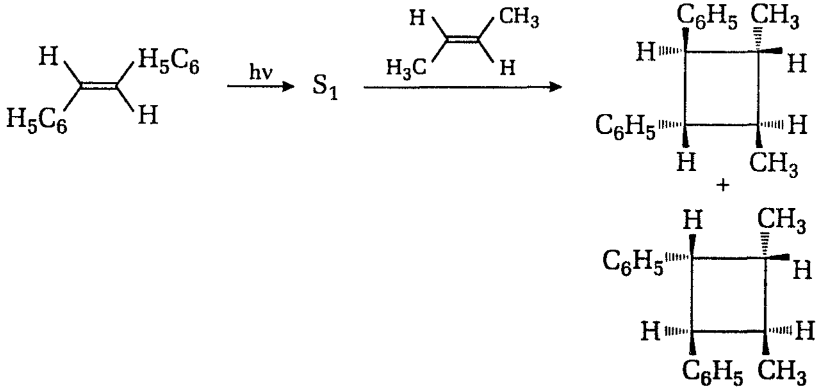


Fig. 5.16. Cycloaddition of stilbene to olefin.

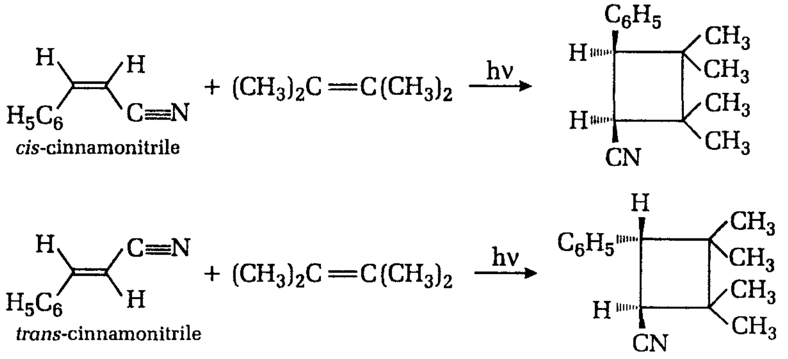
On the other hand, photocycloaddition of *trans*-stilbene to *cis* and *trans* 2-butene result in conservation of stereochemistry of both stilbene as well as olefin. Thus, it may be concluded that addition of S_1 of *trans*-stilbene to olefin is concerted process :





Quenching of emission of light from an excited state is helpful in the study of mechanism, specially in the identification of reactive singlet state. Irradiation of *trans*-stilbene alongwith tetramethyl ethylene results in 1 : 1 adduct with the quantum efficiency (ϕ) of ·54 at room temperature. Photocycloaddition of *trans*-stilbene to tetramethylethylene when sensitized with thioxanthone, only *trans* to *cis* isomerization is observed which indicates but does not prove low-lying singlet excited state of *trans*-stilbene adds to tetramethylethylene. *trans*-Stilbene emits light from singlet state, *i.e.*, it fluoresces. Addition of tetramethylethylene to S_1 state of *trans*-stilbene should quench the fluorescence. Quenching follows the **Stern-Volmer equation.**

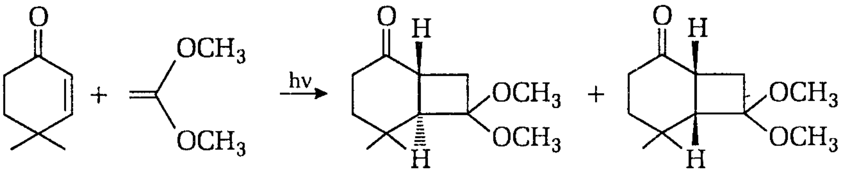
It is important to note that much higher concentrations of quencher are required to quench the excited state (singlet) than for quenching the triplet



Scheme-3

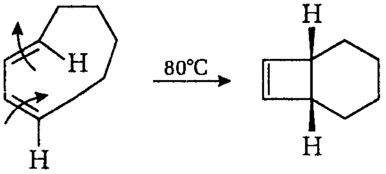
excited state in 4, 4-dimethyl-2-cyclohexenone. Quenching of *trans*-stilbene fluorescence by tetramethylethylene is a consequence of exciplex formation. *cis* and *trans*-cinnamonitrile adds to tetramethylethylene with retention of stereochemistry. Addition of *cis* and *trans*-cinnamonitrile to olefin also involves singlet excited state (Scheme-3).

The addition of 4, 4-dimethyl-2-cyclohexenone to 1, 1-dimethoxyethylene also involves triplet excited state. In this cycloaddition less stable, highly strained *trans*-addition product is predominantly formed in comparison to more stable *cis*-adduct :

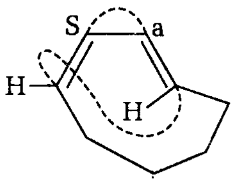


Trans-adduct *Cis*-adduct

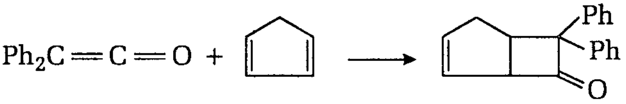
$\pi^2 a+\pi^2 s$ **Cycloaddition** : This type of thermal cycloadditions are rare. *trans*, *cis*-Cycloocta-1, 3-diene isomerizes to *cis*-bicyclo [4.2.0] oct-7-ene. This is an example of $\pi^2 s+\pi^2 a$ cycloaddition.



This addition is **antarafacial** on *trans*-double bond and **suprafacial** on *cis*-double bond.



Thermal addition of ketene to olefin is **antara** on ketene and **supra** on olefin. Here $\pi^2 a+\pi^2 s$ cycloaddition is preferred over $\pi^2 s+\pi^2 s$ cycloaddition.*

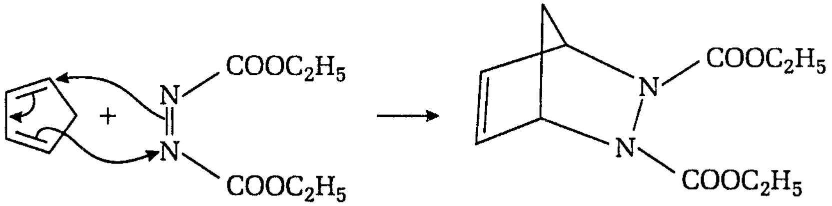


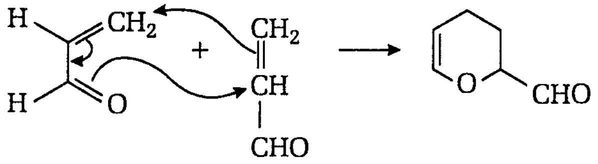
5.5.2 (4 + 2) Cycloadditions

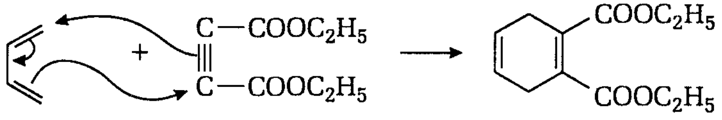
As already stated, (4+2) cycloadditions are thermally allowed and are known as **Diels-Alder reactions.** They involve addition not only to carbon-carbon double bond or carbon-carbon triple bond but also to nitrogen-nitrogen double bond or carbon oxygen double bond as shown below :

---

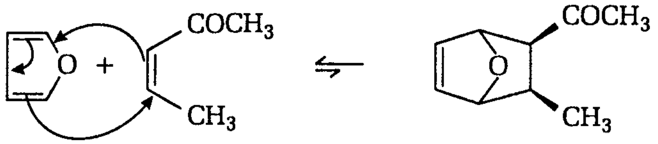
* (a) R. Huisgen and P. otto, Tetrahedron Lett., 4491 (1968).
(b) J.E. Baldwin and J.A. Kapecki, J. Amer. Chem. Soc; **91**, 3106 (1969).

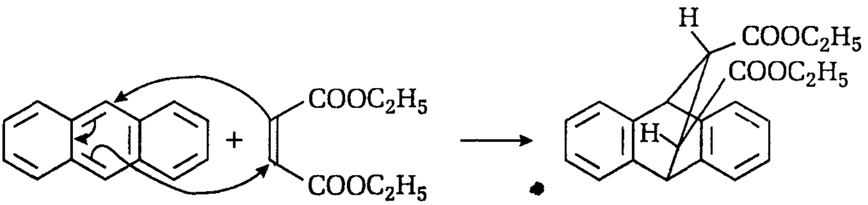






Few aromatic systems like furan and anthracene etc also undergo Diels-Alder reaction as illustrated below :

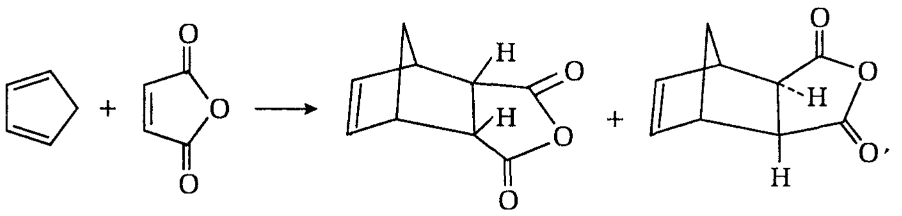




Benzene and naphthalene do not give this reaction. These reactions are highly stereospecific and geometries are maintained through out the course of reaction. As a result of these reactions six-membered ring is formed.

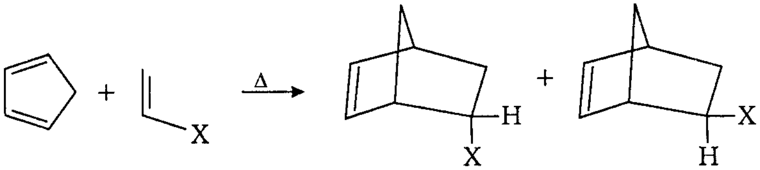
***Endo-Exo* Stereochemistry** : Sometimes Diels-Alder reactions give two types of products, viz, *endo* and *exo* isomers. The product in which substituent on dienophile are *cis* to double bond formed in diene after Diels-Alder reaction is known as *endo*-isomer and the other product in which substituent on dienophile are *trans*-to double bond is known as *exo*-isomer. Alteranatively, the product in which substituent is on the side away from bridge is known as *endo*-isomer and the product having substituent on the same side of the bridge is known as *exo*-isomer.

(i)



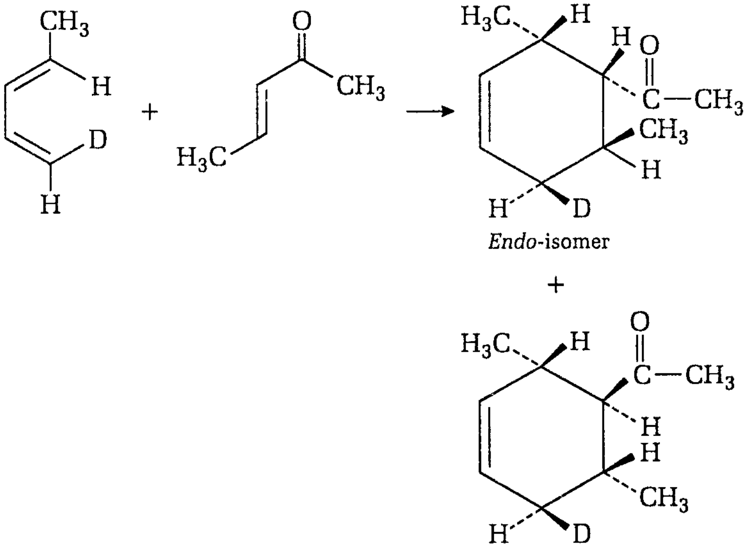
Endo-product *Exo*-product

(ii)



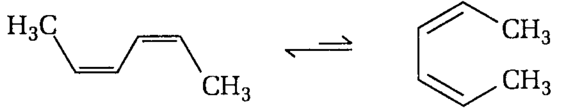
Endo-isomer *Exo*-isomer

Endo-exo products can be formed in **Diels-Alder** reactions of acyclic dienes also. For example :



According to Alder's ***Endo* rule** (1930) ***Endo*** isomers are major products in Diels-Alder reactions. These results look surprising on the grounds that *Endo*-isomers are less stable for steric reasons. But, *Endo-rule* can be rationalized on the basis of **frontier orbital theory**. *Endo*-transition state is stablized by **secondary interactions** in comparison to *exo*-isomers in which secondary interactions are absent. This facts makes *endo*-isomers more stable, *i.e.*, why they are major-products in Diels-Alder reactions.

Reactivities in Diels-Alder Reactions : Rates of Diels-Alder reactions are affected by steric as well as electronic factors. For Diels-Alder reaction to proceed dienes must have double bonds on the same side of central-single bond, *i.e.* there must be *cis*-conformation; because this is high energy conformation.



trans (low energy conformation) *cis* (high energy conformation)

Dienes with one or both substituents at $C-1$ anc $C-4$ *cis*-to other double bond either react very slowly or do not react at all in Diels-Alder reaction, because formation of *S-cis* conformation in this case becomes even more difficult than in absence of substituents. Presence of substituent at $C-2$ of diene increase its reactivity towards Diels-Alder reaction as energy difference in favour of *S-trans* conformation is reduced in this manner. Most reactive dienes are those in which both the double-bonds are in a ring. For example, cyclopentadiene undergoes dimerization at room temperature. Diels-Alder reactions between two hydrocarbons are extremely slow. For high yields, dienophile must be substituted with powerful electron withdrawing group like carbonyl group or carboxyl group which is rationalized by the fact that reactions occur easily if one is substituted good electron acceptor and other is good electron donor.

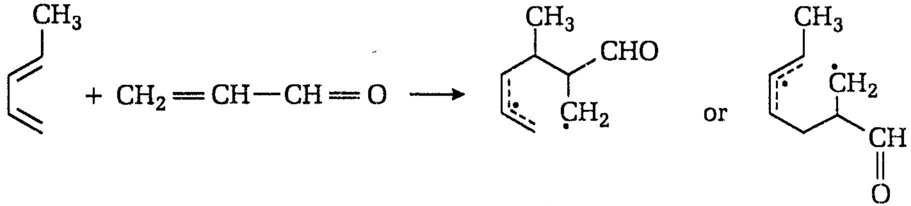
Effect of substituent on reactivity of Diels-Alder reactions may also be visualized in terms of frontier molecular orbital theory. Interaction of these two orbitals result in the formation of two new orbitals one of lower energy than either of interacting orbitals and other of higher energy. Extent of energy difference between two depends upon energies of interacting orbitals. If HOMO of one component is much lower than LUMO of other component; newly formed HOMO will be much lower in energy than original HOMO. On the other hand, if energy difference between two interacting orbitals is low, the energy difference between original orbitals and transition states will increase; the reaction in that condition will proceed at faster rate. In this case electrons of original HOMO will go to transition state of lower energy.

If electron-donating group on one component of Diels-Alder reaction is there, energy of HOMO will be increased in that case; on the other side if electron withdrawing group is present on the other component energy of its LUMO will be lowered. Therefore, under these conditions reaction will proceed at faster rate when one component has electron donating group and other component bears electron withdrawing group. However, reaction between diene bearing electron donating group and dienophile with electron withdrawing group is relatively easier.

Lewis acids (strong) act as catalyst for Diels-Alder reactions. Lewis acid usually forms complex with **dieneophile** which lowers energy of its LUMO. This way activation energy of reaction is decreased, hence, reaction proceeds at faster rate.

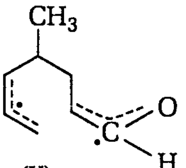
Regioselectivity in Diels-Alder Reaction : Regioselectivity during Diels-Alder reaction is based upon the rule that **major product from Diels-Alder reaction will arise from transition state that resemble the most stable of the possible diradical intermediates that might be formed in the reaction.** An example is discussed below :

In the Diels-Alder reaction between 1, 3-pentadiene and acrolein following four diradicals [(*W*), (*X*), (*Y*) and (*Z*)] are possible :



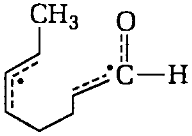
(W) (X)

or



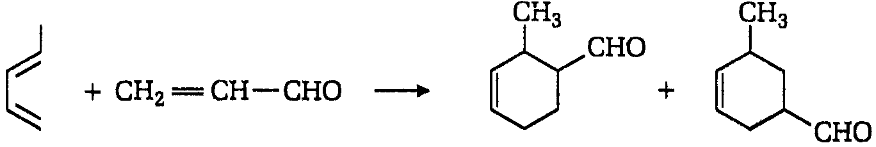
(Y)

or



(Z)

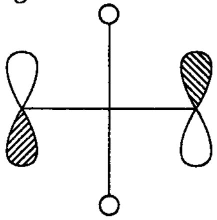
In (*W*), (*X*), (*Y*) and (*Z*), (*Z*) is most stable diradical which can be written as hybrid of two secondary radical resonance forms. (*Y*) contains pentadiene as a hybrid of one secondary radical resonance form and one primary radical form. In (*W*) and (*X*) there is only resonance stablization. Thus, in this reaction major product will be from (*Z*) and minor product from (*Y*). Major regioisomer in Diels-Alder reaction can be predicted on the basis of **diradical like transition state rule.**



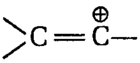
Major product Minor product

5.6 2 + 2 THERMAL CYCLOADDITION OF KETENES

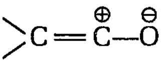
2*s*+2*a* thermal cycloadditions are symmetry allowed. But this stereochemical mode of cycloaddition can be expected only when two double bonds are disposed **orthogonally** to each other (*i.e.*, they are perpendicular to each other) as given in figure *A* below :



(A)

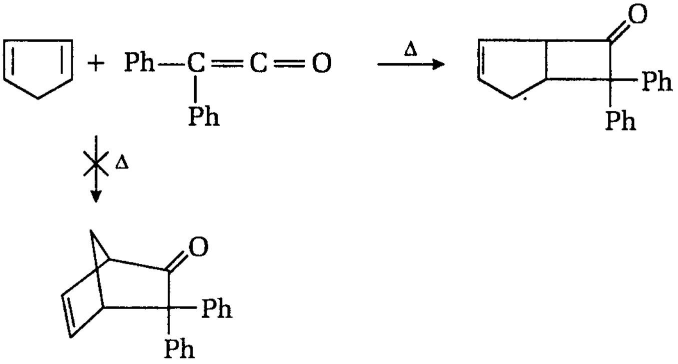


(B)



(C)

This type of orientation is rarely feasible. Vinyl cation (*B*) or Ketene (*C*) add to ethylene readily under thermal conditions to give cyclobutanes; even cyclopentadiene in which 1, 4-addition is expected add this way.



Frontier molecular orbital (FMO) treatment of these reactions indicates that bond formation between $C-1$ and $C-1$ of ketene and olefin is due to interaction of HOMO of alkene and LUMO of Ketene. At the same time bond formation between $C-2$ of olefin and $C-2$ of ketene is by the coupling of HOMO of ketene and LUMO of alkene as shown below :

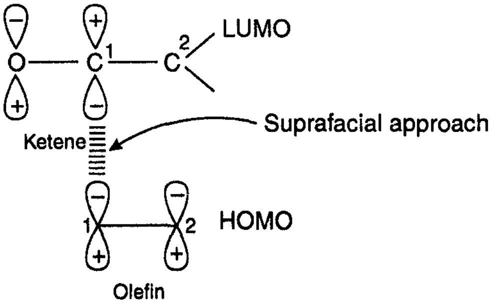


Fig. 5.17. Bond formation between C_1 of olefin and C_1 of ketene.

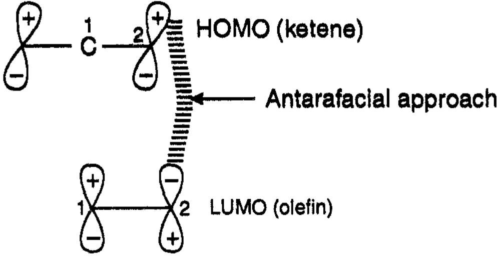
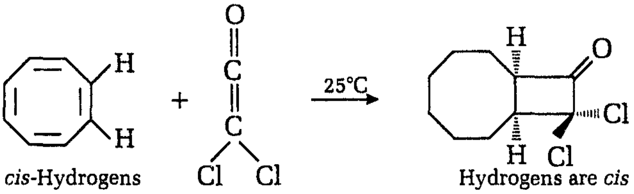


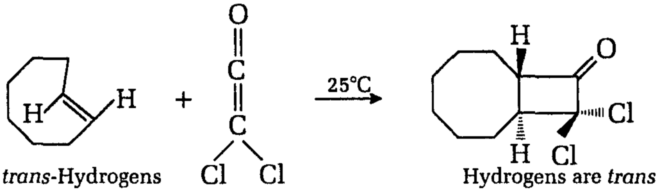
Fig. 5.18. Bond formation between C_2 of ketene and C_2 of olefin.

This addition is *syn*. Geometry of reactants is conserved in the products. For example :

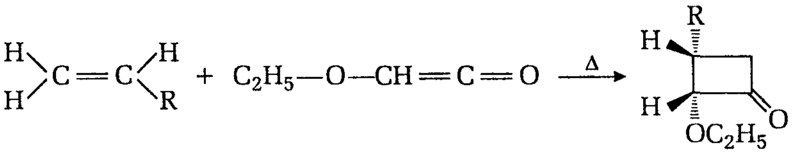
(a)



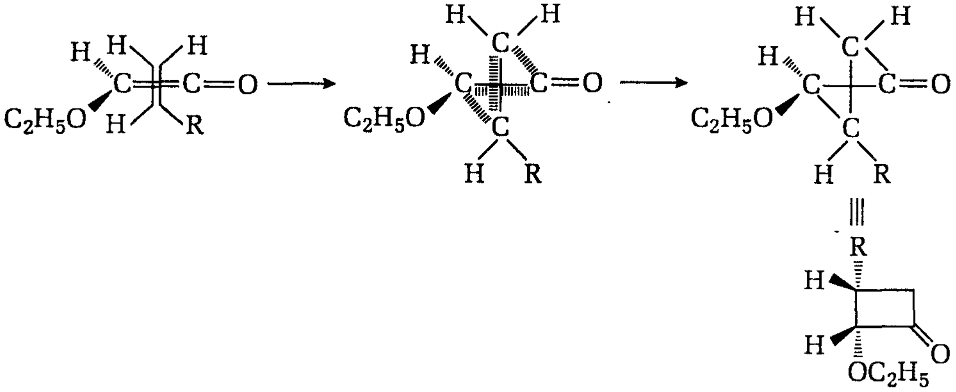
(b)



(c)



Mechanism of last reaction is :



5.7 1, 3-DIPOLAR CYCLOADDITIONS

1, 3-Dipolar cycloaddition reactions were investigated by Huisgen and his co-workers. 1, 3-Dipolar cycloadditions provide a versatile method for stereospecific synthesis of five membered heterocyclic compounds by the addition of 1 3-dipolar compounds to ethylenic and acetylenic double bonds (dipolarfiles). 1, 3-dipolar systems are four π-electron species which undergo $\pi_s^4 + \pi_s^2$ concerted cycloadditions across π-bonds of olefins and acetylenes.

1, 3-Dipoles are classified into three categories :

Type (a) : 1, 3-Dipoles with a double bond and non-bonding pair of electrons on central atom. Examples are : azides, diazoalkanes, nitrile ylides etc.

$$\overset{\oplus}{X}{=}Y{-}\overset{\ominus}{\underline{Z}} \longleftrightarrow X{\equiv}\overset{\oplus}{Y}{-}\overset{\ominus}{\bar{Z}}$$ /(a 1, 3-dipolar species)

(i) $|\overset{\oplus}{\underline{N}}{=}\overline{N}{-}\overset{\ominus}{\underline{\overline{N}}}{-} \longleftrightarrow \overline{N}{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{\underline{\overline{N}}}{-}$
Azides

(ii) $|\overset{\oplus}{\overline{N}}{=}\overline{N}{-}\overset{\ominus}{\underline{C}}< \longleftrightarrow \overline{N}{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{\underline{\overline{C}}}<$
Diazoalkanes

(iii) $-\overset{\oplus}{C}{=}\underline{N}{-}\overset{\ominus}{C}< \longleftrightarrow -C{\equiv}\overset{\oplus}{N}{-}\overset{\ominus}{C}<$
Nitrile ylides

Type (b) : 1, 3-dipoles with non-bonding pair of electrons on central atoms. For examples : nitrones, ozone, azoxy compounds, azomethine ylides etc.

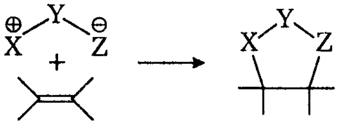
$$\overset{\oplus}{X}{-}\overline{Y}{-}\overset{\ominus}{\underline{Z}}| \longleftrightarrow X{=}\overset{\oplus}{Y}{-}\overset{\ominus}{\underline{Z}}|$$

(i) $|\overset{\oplus}{\underline{O}}{-}\overline{O}{-}\overset{\ominus}{\underline{\overline{O}}}| \longleftrightarrow |\overline{O}{=}\overset{\oplus}{O}{-}\overset{\ominus}{\underline{\overline{O}}}|$
Ozone

(ii) $>\overset{\oplus}{C}{-}\overset{|}{\underline{N}}{-}\overset{\ominus}{\underline{C}}< \longleftrightarrow\ >C{=}\underset{|}{\overset{\oplus}{N}}{-}\overset{\ominus}{\underline{C}}<$
Azomethine

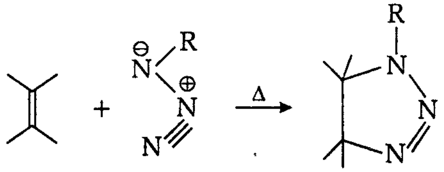
Type (c) : 1, 3-Dipoles with a double bond. For example : ketonitrenes, methylenes, ketomethylenes etc.

Some examples of 1, 3-dipolar cycloadditions are :

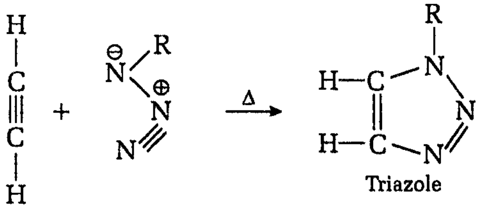


General example

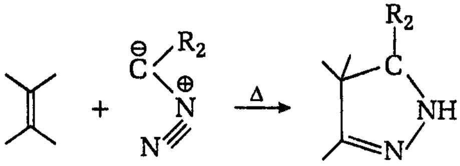
Few specified examples are :

(1)


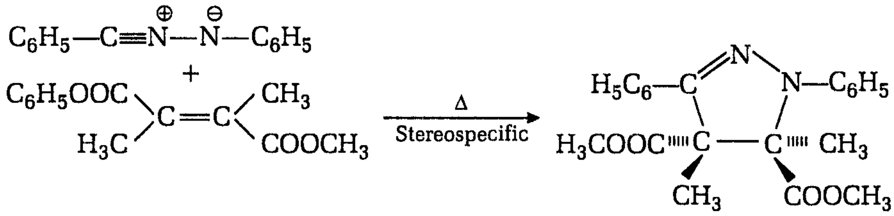
Triazoline

(2)


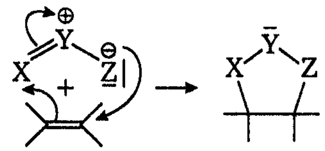
Triazole

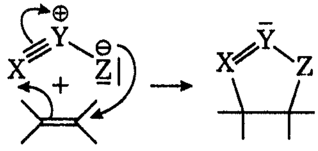
(3)


Pyrazoline

(4)


Mechanisms of reactions can be illustrated as given below :

(a)


(b)


Feasibility of reaction can be depicted as follows :

This cycloaddition involves 6π-electrons, one pair present as non-bonding pair of electron on central atom (let *y*) and other two pairs involved in σ-bonds C—X and C—Z. During this cycloaddition *m*-plane symmetry is conserved.

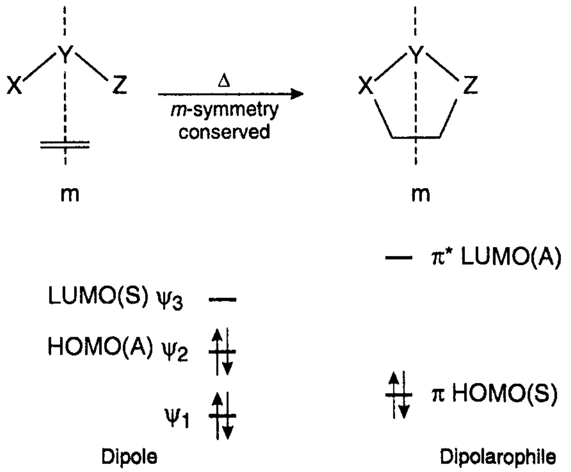


Fig. 5.19. Electronic occupancy of M.Os of 1,3-dipole and alkene (dipolarophile) and symmetry w.r.t. *m*-plane .

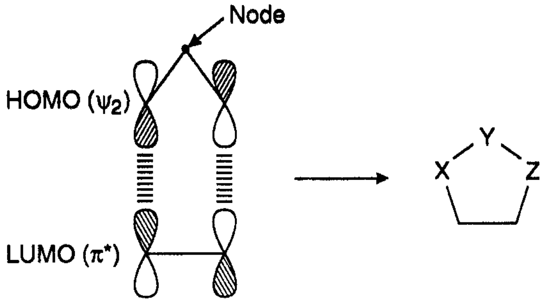


Fig. 5.20. FMO treatment of 1,3-dipolar cycloaddition.

FMO method can be employed to understand 1 ,3-dipolar cycloadditions. HOMO (ψ_2) of 1, 3-dipole and LUMO (π^*) of dipolarophile both are antisymmetric with respect to *m*-plane; hence signs of atomic orbitals are favourable for the overlapping in 1, 3-dipolar cycloaddition. This reaction is allowed under thermal conditions.

Besides, reactions of 1, 3-dipole, nitrons, too are widely studied 1 3-dipolar cycloadditions*. Nitrons are N-alkylated oximes. Nitrons too undergo $\pi^4 s + \pi^2 s$ cycloadditions to olefins and acetylenes to yield isoxazolidines and isoxazolines respectively. These two isoxazoles can be used as templetes for the synthesis of 1, 3-difunctionalised compounds which can act as key synthetic intermediates. This regioselective cycloaddition generates 4 or 5-substituted isoxazolines/ oxazolidines from monosubstituted acetylene and olefins depending upon nature of substituent. With most substituents 5-substituted heterocycles are formed preferentially. Strongly electron withdrawing groups on dipolarophile change the selectivity in the favour of 4-substituted heterocycle. Beside this selectivity is also affected by electronic and steric demands which are very delicately balanced as is clear by **Table 1.**

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* A. Banerji, J. Indian Chem. Soc; 77, 637 (2000).

Table 1 : Regioselectivity in Nitrone Cycloadditions

Olefins	Nitrones	Ratio of 5 : 4 substitution
Ph—CH=CH$_2$	C, N-Diphenyl	~100 : 0
CH$_3$O$_2$C—CH=CH$_2$	C, N-Diphenyl	100 : 0
AcO—CH=CH$_2$	C, N-Diphenyl	~100 : 0
PhSO$_2$—CH=CH$_2$	C-phenyl, N-methyl	32 : 68
CH$_3$O$_2$C—C≡CH	C-phenyl, N-methyl	42 : 58
(E) CH$_3$—CH=CH—CO$_2$Me	C, N-Diphenyl	~0 : 100
(E) Ph—CH=CH—NO$_2$	C-Benzoyl, N-phenyl	~0 : 100

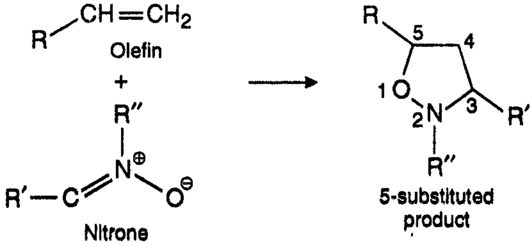
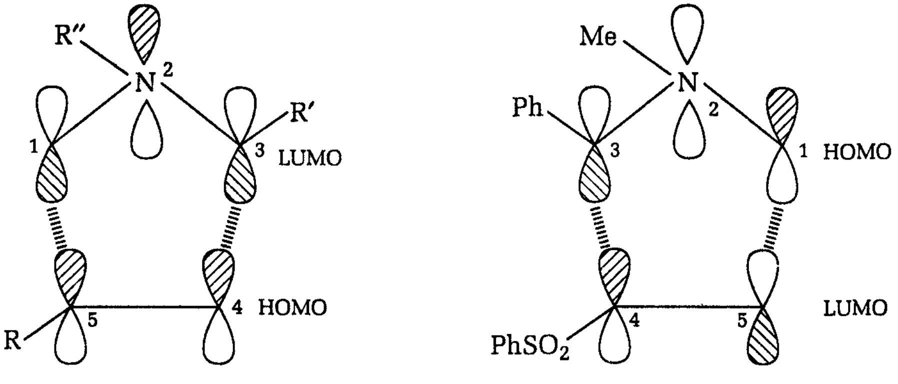


Fig. 5.21. Formation of isoxazolidine form 1,3-dipolar cycloaddition.

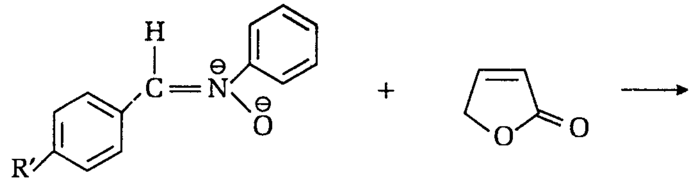
Interactions leading to 5-substituted and 4-substituted products can be represented as follows :



5-substituted product | 4-substituted product

Some cycloadditions involving nitrones are given below :

(i)*



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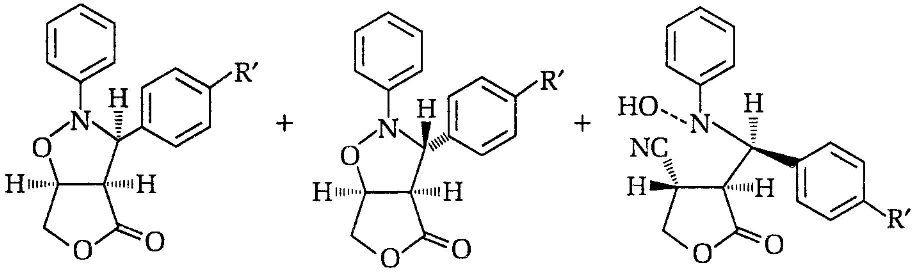
* A. Banerji and S. Basu (nee Sinha),Tetrahedron, **48**, 3335 (1992).



(A) (B) (C)

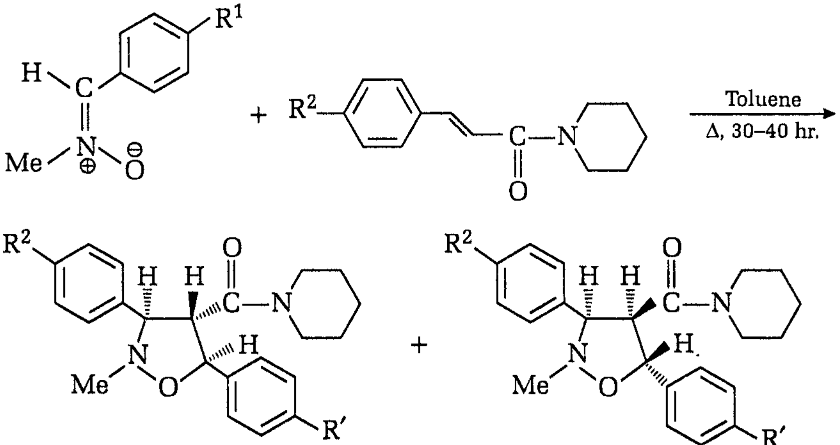
(i) Cycloaddition of nitrone to Lactone-2-butenolide (figure above)

(*A*) and (*B*) = Diasteroisomeric Tetrahydrofuro [3, 4-*d*] isoxazoles derived bicyclic cycloadducts

(*C*) = Ring opened product

Ring opened product is derived from *cis*-isomer which is obtained by refluxing reactants is moist toluene. Under these conditions *trans*-isomer remains unchanged. Lability of *cis*-cycloadduct can be explained on the basis of greater non-bonded steric interaction. This reaction involves $S_{N}2$ -displacement at C-6a. Here FMO interaction involves dipole HOMO and dipolarophile LUMO. The total yield of *cis*-isomer (including ring opened product) is derived from the exo-approach and in ~ 2 : 1 ratio is comparison to cycloadduct derived from endo approach.

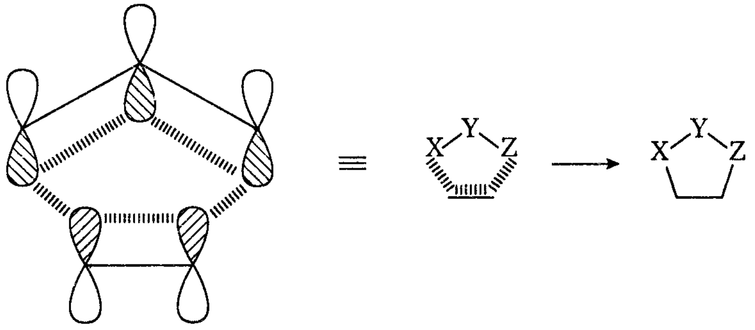
(ii) **Cycloaddition of C-aryl-N-methyl nitrone with differently substituted cinnamic acid piperidines :**



3, 4-*trans* (D) 3, 4-*cis* (E)

In (II) all *trans*-2-methyl-3, 5-diaryl-4- piperidinoyloxoisozolidine cyclo addition (*D*) is the major product in comparison to diastereomeric cycloadduct (*E*).

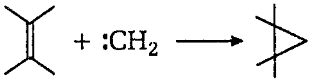
PMO-treatment of 1, 3-dipolar cycloaddition : The transition state for concerted 1, 3-dipolar cycloaddition has six electrons without any node; it is aromatic. Hence, reaction is thermally allowed.



T.S. : 0 node, 6 electrons, aromatic, thermally allowed

5.8 CHELETROPIC REACTIONS

Cheletropic reactions are special type of concerted cycloadditions or cycloreversions in which two bonds are formed on or fissioned from same atom. For example, reaction of a singlet carbene with olefin.



These reactions can be considered in terms of HOMO-LUMO interactions of reactants. Carbenes can approach alkenes in two ways :

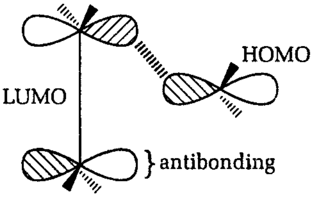
(i) linearly (ii) Non-linearly.

There are two π-molecular orbitals in carbene :

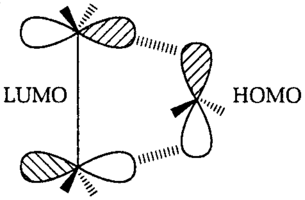
(i) HOMO containing both the electrons

(ii) LUMO which is vacant.

(i) Linear approach : In linear approach of carbene, plane of two substituents is perpendicular to C—C bond of olefin.



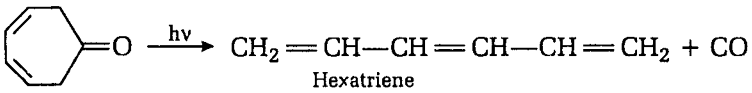
(ii) Non-linear approach : In non-linear approach, plane of bonds of two substituents on carbene is parallel to C—C bond of olefin.



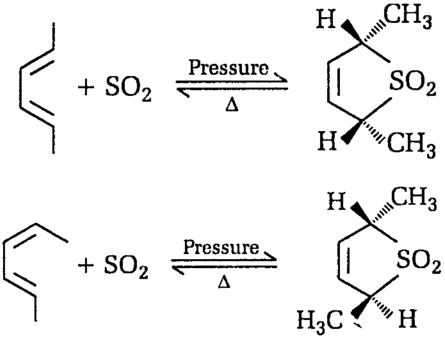
It is clear that is non-linear approach HOMO-LUMO interaction approach is suprafacial and bonding. In this approach electrons reorganise themself into a new bond. However, whether approach is linear or non-linear is not proved.

Few examples of cheletropic rearrangement are discussed below :

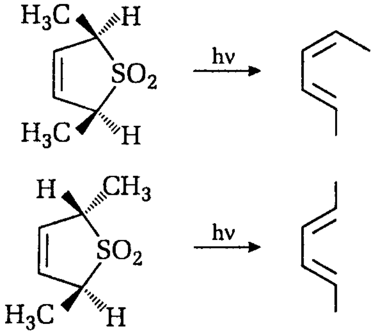
(1) Elimination of carbon monoxide from cyclic ketones.



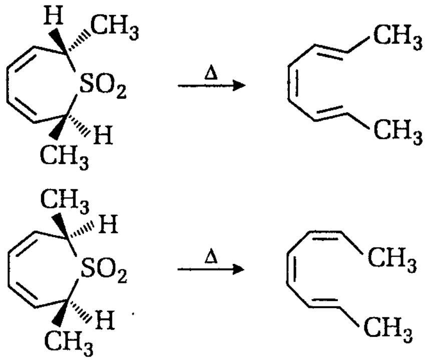
(2) Addition of SO_2 to hexadienes : This reaction carried out under pressure gives dihydrothiophene dioxides or thermal explusion of SO_2.*



Under photochemical conditions, structures of products are opposite to that under thermal conditions.



2. Thermal expulsion of SO_2**



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* W.L. Mock, J.A.CS **88**, 2857 (1966).

** W.L. Mock, J-A-C.S., **91**, 5682 (1969); **92**, 3807 (1970).

Interaction of HOMO and LUMO applied to $4q\pi$ and $(4q+2)\pi$ systems during addition and expulsions of SO_2 are discussed below :

(i) $4q\pi$-system : Linear approach of SO_2 to $4q\pi$ system is suprafacial to olefinic system and is bonding. This reaction is thermally allowed through disrotation.

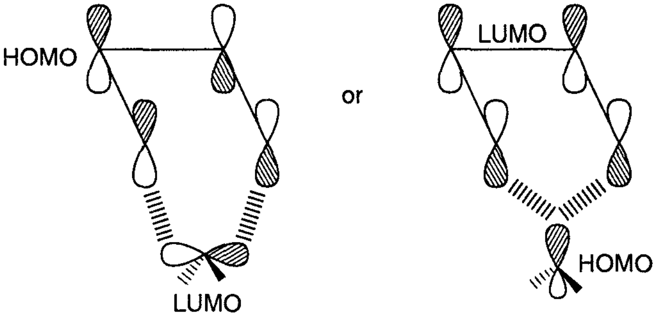


Fig. 5.22. Linear approach of SO_2 suprafacial to $4q\pi$-system.

On the other hand non-linear approach of SO_2 antarafacial to $4q\pi$ system is too symmetry allowed. Reaction involving ring closure as well as expulsion of SO_2 proceeds through conrotation.

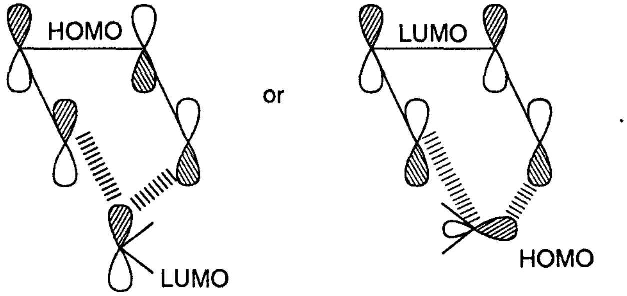


Fig. 5.23. Non-linear approach of SO_2 antarafacial to $4q\pi$-system.

Because suprafacial approach is bond-forming, hence reagent approaches $4q\pi$-system linearly.

(ii) $(4q+2)\pi$-system : Approach of SO_2 antarafacially to $(4q+2)\pi$-system in linear manner can be explained by considering HOMO-LUMO of these two systems. However, ring closure in this manner is not experimentally proved. HOMO-LUMO interactions in this manner take place under thermal condition and are bonding interactions. Besides, conrotatory mode of ring-closure is followed.

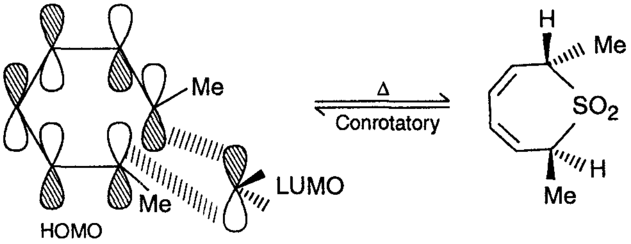


Fig. 5.24. Linear approach of SO_2 to $(4q + 2)\pi$-system antarafacially.

However, non-linear approach of SO_2 to $(4q+2)\pi$-system takes place suprafacially. This is also symmetry allowed and follows disrotatory mode of ring-closure.

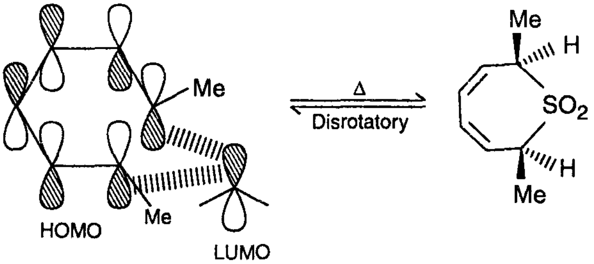


Fig. 5.25. Non-linear approach of SO_2 to $(4q + 2)$ π-system suprafacially.

From the above discussion it is clear that linear approach of SO_2 to $(4q+2)\pi$-system antarafacially is favoured is conrotatory fashion, whereas non-linear approach antaraficially is symmetry-forbidden.

Table : Selection Rules for thermal cheletropic Reactions

m	Linear Approch	Non-linear Approach
$4q$	Disrotatory	Conrotatory
$4q+2$	Conrotatory	Disrotatory
m = Number of electrons, q = an integer including zero.		

PMO-treatment of Cheletropic Reactions : Cheletropic reactions can be easily explained on the basis of aromatic and antiaromatic transition states by PMO-method. Transition states in each mode of linear and non-linear approach of carbene both suprafacially and antarafacially to π-system are drawn below :

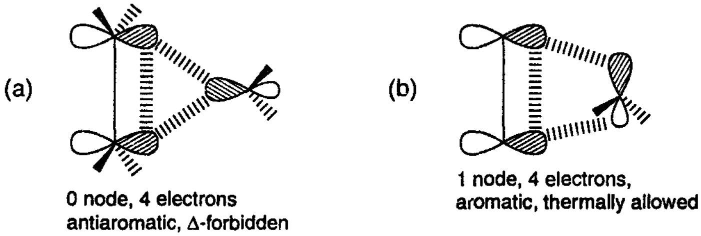


Fig. 5.26. Transition states (a) For linear suprafacial approach (b) Non-linear suprafacial approach of carbene to a $(4q + 2)$ π-olefinic system.

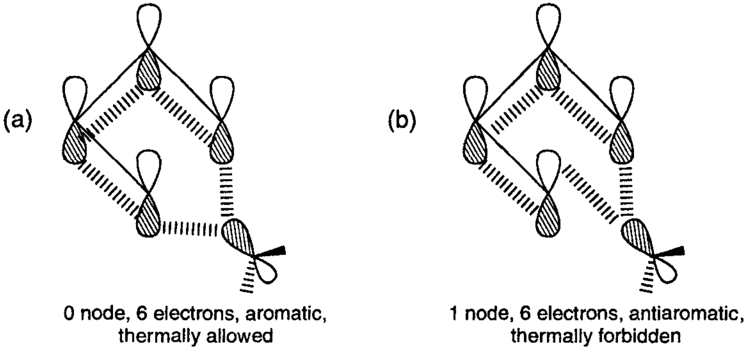
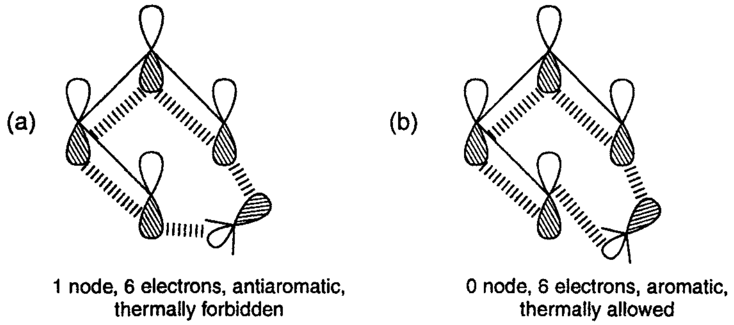


Fig. 5.27. Transition states (a) For linear suprafacial approach (b) For linear antarafacial approach of carbene to $4q$ π-system.



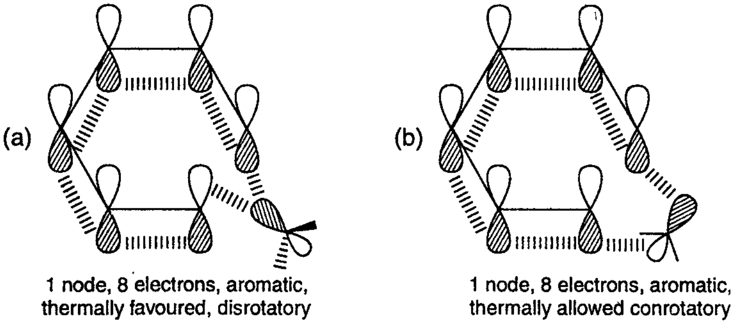
1 node, 6 electrons, antiaromatic, thermally forbidden

0 node, 6 electrons, aromatic, thermally allowed

Fig. 5.28. Transition states (a) For non-linear suprafacial approach (b) For non-linear antarafacial approach of carbene to $4q$ π-system.

Aromaticity of transition state decides if the reaction is thermally allowed or forbidden on the basis of Evan's rule.

Linear-antarafacial approach (*a*) as well as non-linear-suprafacial approach (*b*) in figure given below for the addition of SO_2 to triene, $[4q+2]\pi$ system, both are thermally favourable.



1 node, 8 electrons, aromatic, thermally favoured, disrotatory

1 node, 8 electrons, aromatic, thermally allowed conrotatory

Fig. 5.29. (a) T.S. for linear approach (antarafacial) of SO_2 to $(4q + 2)$ π-system. (b) T.S. for non-linear (suprafacial) approach of SO_2 to $(4q + 2)$ π-system.

Conversly linear-suprafacial as well as non-linear-antarafacial approaches both involve antiaromatic transition states with eight electrons and 0 nodes. Hence, both reactions are thermally disallowed. However, there is no way to prove if approach of SO_2 is linear or non-linear.

❑❑❑

UNIT

6

SIGMATROPIC REARRANGEMENT

Sigmatropic shift has already been defined as [*i*, *j*]-order migration of a *sigma*-bond which is flanked by one or more p_i-electron systems from its original position *i* to new position *j*. Well known examples of sigmatropic rearrangement are Claisen and cope-rearrangements etc. Analysis as well as examples of sigmatropic rearrangement are discussed in this unit.

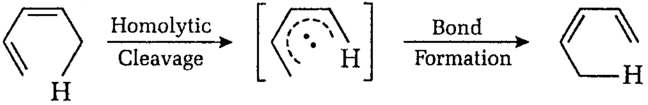
6.1 CORRELATION DIAGRAM METHOD

Correlation diagram method is not suitable for the analysis of sigmatropic-rearrangements because only transition state but not reactants or products possess molecular symmetry elements. Methods for the analysis of this type of reactions are discussed in forthcomming discussion.

6.2 FRONTIER MOLECULAR ORBITAL METHOD

For the analysis of sigmatropic rearrangement it may be assumed that migrating bond undergoes homolytic cleavage to yield a pair of radicals. But bonding character is maintained throughout the rearrangement. Most important bonding interactions are those in which HOMO of two species are produced by cleavage which contain unpaired electrons.

Sigmatropic 1, 5-shift : This method of analysis can be illustrated by the example of suprafacial [1, 5] sigmatropic rearrangement of hydrogen in which homolytic cleavage produces H-atom and pentadienyl radical :



Ground state electronic configuration of pentadienyl radical is $\psi_1^2\psi_2^2\psi_3^1$. HOMO among these M. Os is ψ_3 which has same signs on terminal lobes (hence possesses mirror plane symmetry). For this reason 1, 5-sigmatropic shift is thermally allowed in suprafacial manner.

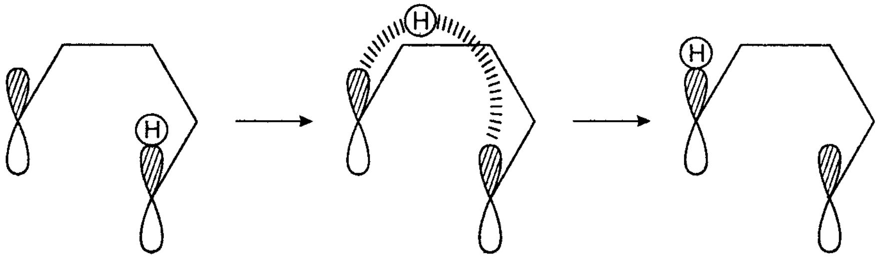


Fig. 6.1. 1,5-sigmatropic shift (suprafacial).

The first excited state of pentadienyl radical has configuration $\psi_1^2\psi_2^2\psi_4^1$, therefore, symmetry properties are reversed. Now, HOMO (ψ_4) has C_2-axis of symmetry. [1, 5]-suprafacial sigmatropic shift is no longer possible. Therefore, photochemical [1, 5]-sigmatropic shift proceeds antarafacially.

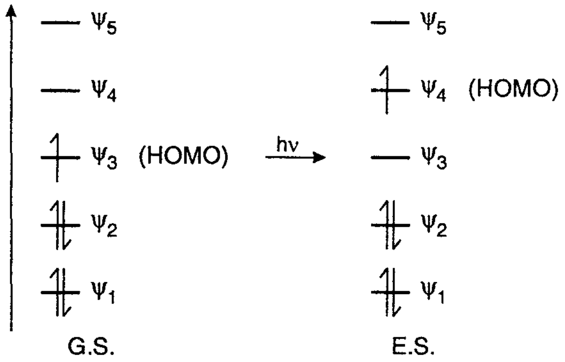


Fig. 6.2. HOMO of pentadienyl radical in G.S. and E.S.

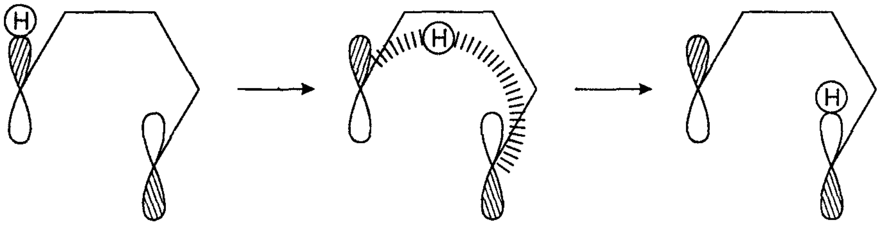


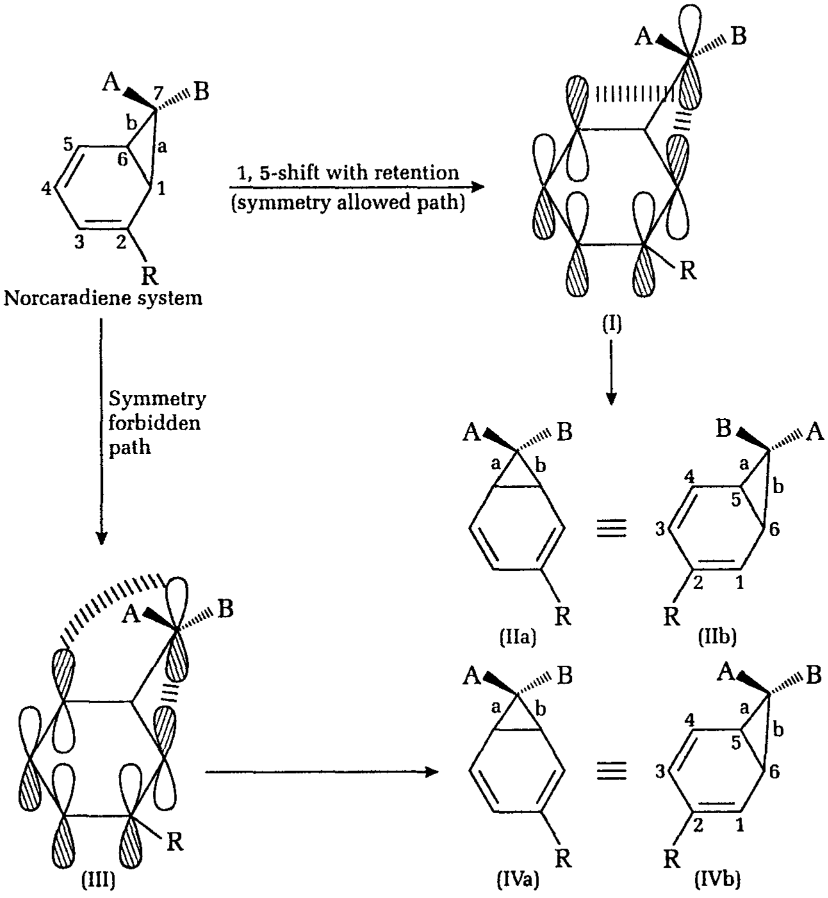
Fig. 6.3. [1, 5] sigmatropic shift (antarafacial).

6.3 PERIPATETIC CYCLOPROPANE BRIDGE

Stereochemical outcomes of 1, 5-sigmatropic shifts with retention in cyclic systems can be analysed in a thermally allowed suprafacial sigmatropic process by the application of FMO method. Let us illustrate this by the example of thermolysis of hypothetical norcaradiene system.

HOMO of π-skeleton of 5 electrons of biradical transition state (I) is ψ_3 with mirror plane symmetry. In(I) same signs are on extreme lobes of supraface. Front lobes of opening σ-bond *a* at the migrating centre C_7 may overlap with suprafacial lobe at C_5 to form new σ-bond in IIa. Bonds of C_7—*A* and C_7—*B* at migrating centre of norcaradiene system and plane of σ-bonds '*a*' and '*b*' turn to same extent (180°) as given in (IIb) as a result of which configuration at C_7 is retained. If we consider symmetry-disallowed path, the *tail* lobe of bond *a* at migratory centre C_7, will overlap with suprafacial lobe at C_5; then inversion will be at C_7. During thermolysis of this system *A* and *B* alternately become *endo* and *exo* during suprafacial 1,5-shifts with retention at migratory centre. Conversly, in 1, 5-shift with inversion groups *A* and *B* remain *endo* and *exo*, respectively through out the shift (Scheme 6.1).

1, 3, 5-cycloheptatrienes undergo 1, 5-sigmatropic rearrangement through norcaradiene intermediates. This is another example of peripatetic cyclopropare bridge (Fig. 6.4 and 6.5). Thermally allowed suprafacial 1, 5-shifts proceed



Scheme 6.1

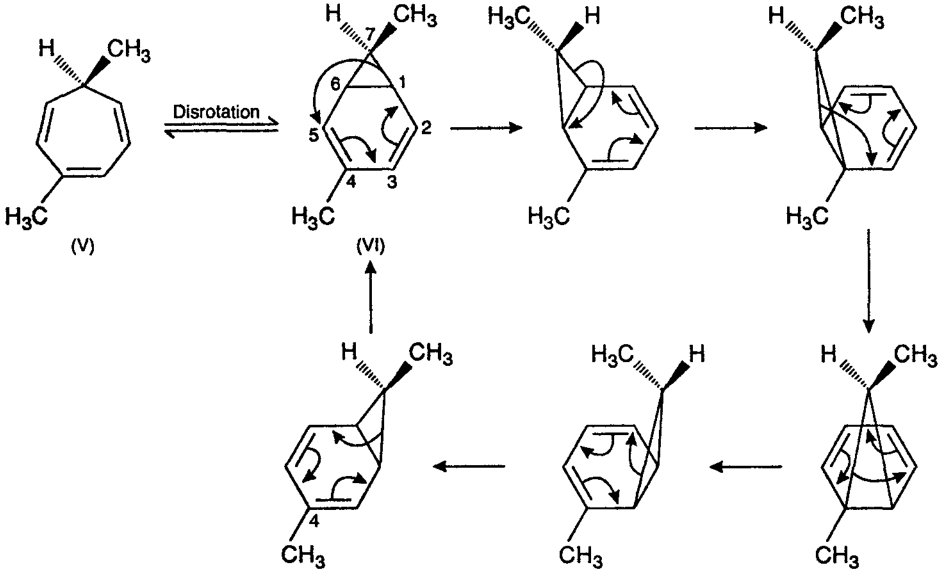


Fig. 6.4. 1,5-σ-bond shift in 1,3,5-cycloheptatriene through thermally allowed path.

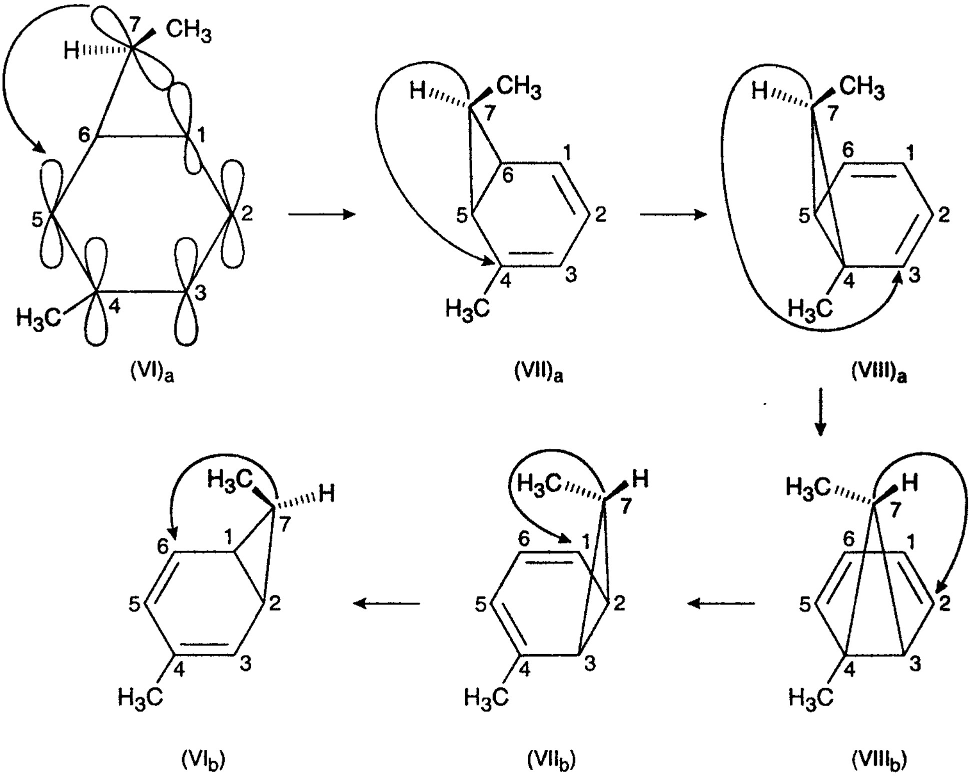


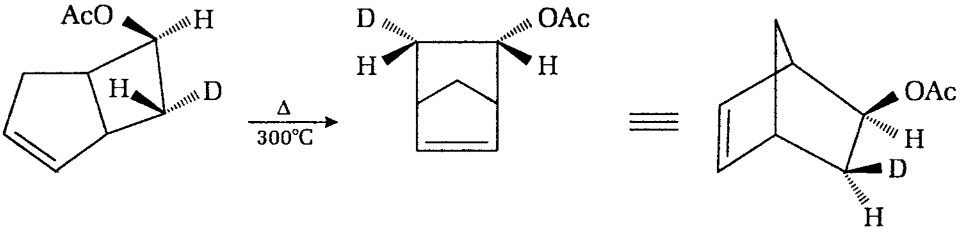
Fig. 6.5. 1,5-σ-bond shift in 1,3,5-cycloheptatriene through thermally disallowed path.

through retention of configuration at C_7 in norcaradienes is proved by the fact that thermal rearrangement of an optically active tropilidene, *e.g.* (V) involves no change in optical activity of enantiomer. 1, 5-sigmatropic shift through thermally forbidden path, that is suprafacial shift, through inversion at C_7 produces three enantiomers (VIa) and (VIb); (VIIa) and (VIIb); (VIIIa) and (VIIIb); thus racimization takes place.

Thus, groups *A* and *B* at C_7 become *endo* and *exo* in therolysis in 1, 3, 5-cycloheptatriene like systems in a series of suprafacial, 1, 5-shift with retention of configuration at C_7.

6.4 1, 3-SIGMATROPIC SHIFT

An example of thermal 1, 3-sigmatropic rearrangement (isomerization) is depicted in the following figure :



This rearrangement, although forbidden, but proceeds with inversion at carbon atom that moves. Here transition state has strong non-bonded interactions and migration is with retention of configuration at migrating carbon. This 1, 3-sigmatropic rearrangement is **suprafacial** at migratory centre and is equivalent to [1, 3]-**antarafacial** shift which is a thermally allowed process. Orbital picture of this process is illustrated below :

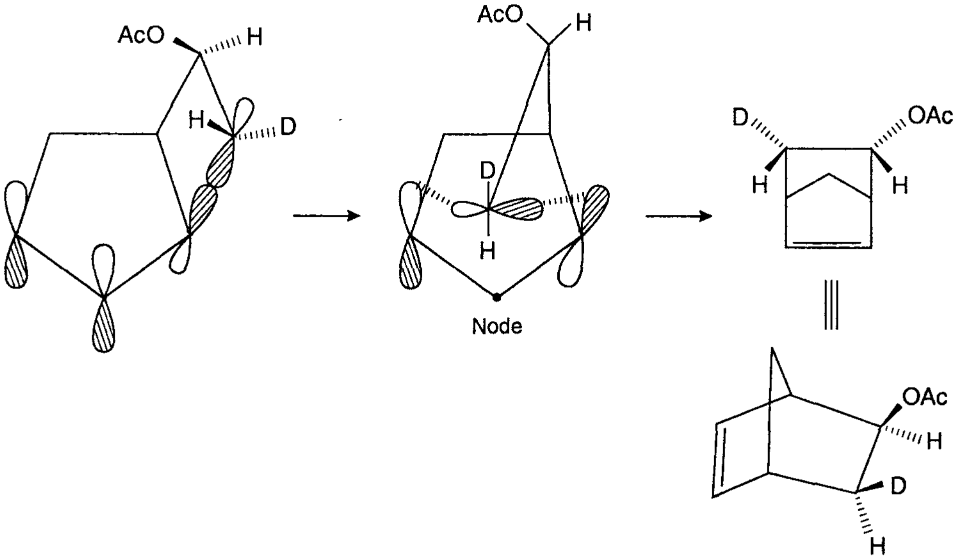


Fig. 6.6. Thermal [1, 3]-sigmatropic shift with inversion at migratory centre.*

Selection Rule for Sigmatropic Rearrangement (FMO Method) :

$i + j$	**Ground state, *i. e.*, thermally allowed**	**Excited state, *i. e.*, photochemically allowed**
$4n$	antara-supra supra-antara	supra-supra antara-antara
$4n + 2$	supra-supra antara-antara	antara-supra supra-antara
i and j are > 1, n = an integer.		

6.5 PERTURBATIONAL MOLECULAR ORBITAL METHOD

Analysis of sigmatropic rearrangement is also possible by PMO method and conclusion about their feasibility are same as by other methods. For instance, 1, 3-sigmatropic suprafacial shift occurs via transition state with 0 nodes and 4 electrons (antiaromatic) and hence it is thermally forbidden. But [1, 3]-antarafacial sigma migration occurs through a transition state with 1 node and four electrons (aromatic T.S.) and is therefore thermally allowed.

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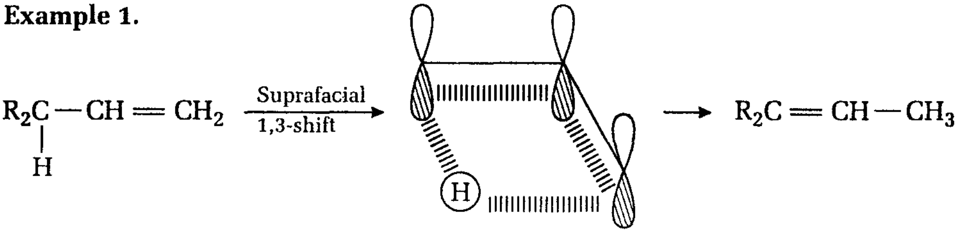
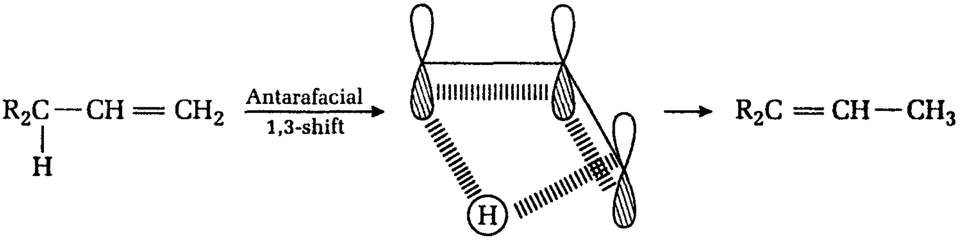
* J. A. Berson and G.L. Nelson, J. Amer. Chem. Soc; **89**, 5503 (1967); **92**,109 (1970)

Example 1.



$$R_2\underset{\underset{\displaystyle H}{|}}{C}-CH=CH_2 \xrightarrow[\text{1,3-shift}]{\text{Suprafacial}} \longrightarrow R_2C=CH-CH_3$$

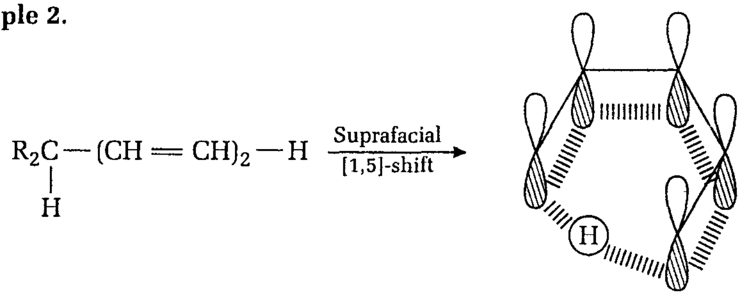
T.S. with 0 node, 4 electrons,
antiaromatic, hν allowed



$$R_2\underset{\underset{\displaystyle H}{|}}{C}-CH=CH_2 \xrightarrow[\text{1,3-shift}]{\text{Antarafacial}} \longrightarrow R_2C=CH-CH_3$$

T.S. with 1 node, 4 electrons,
aromatic, Δ-allowed

Example 2.



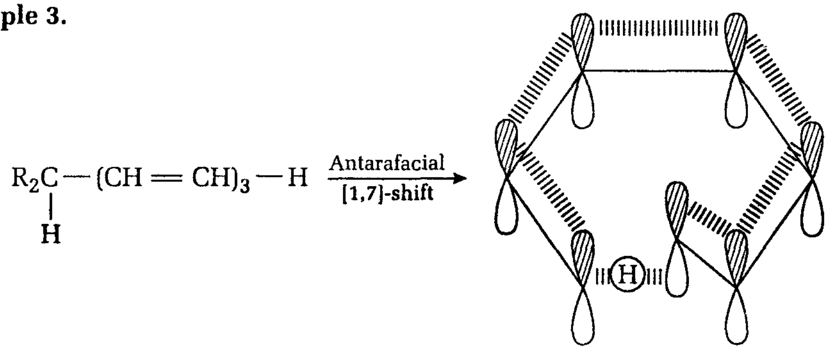
$$R_2\underset{\underset{\displaystyle H}{|}}{C}-(CH=CH)_2-H \xrightarrow[\text{[1,5]-shift}]{\text{Suprafacial}}$$

T.S. with 0 node, 6 electrons,
aromatic, Δ-allowed

$$\downarrow$$

$$R_2C=CH-CH=CH-CH_3$$

Example 3.



$$R_2\underset{\underset{\displaystyle H}{|}}{C}-(CH=CH)_3-H \xrightarrow[\text{[1,7]-shift}]{\text{Antarafacial}}$$

T.S. with 1 node, 8 electrons,
aromatic, Δ-allowed

$$\downarrow$$

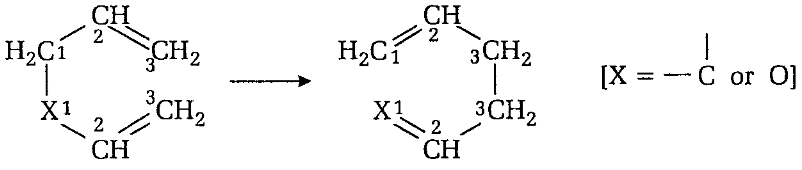
$$R_2C=CH-(CH=CH)_2-CH_3$$

Selection rule for sigmatropic rearrangement of the order [1, *j*] (PMO-method)

Number of electrons involved (*i* + *j*)	Number of nodes	Aromaticity of T.S.	Mode of migration
$4n$	0 or even	antiaromatic	supra ($h\nu$)
$4n$	odd	aromatic	antara (Δ)
$4n+2$	0 or even	aromatic	supra (Δ)
$4n+2$	odd	antiaromatic	antara ($h\nu$)
n= an integer			

3, 3-; 3, 5- and 5, 5-Sigmatropic Rearrangements

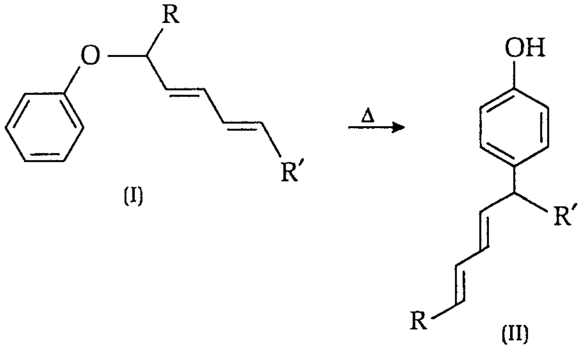
(a) **3, 3-Sigmatropic Rearrangement :** Very often the migrating σ-bond is situated between two conjugated π-bonds as in Cope and Claisen rearrangements :



[3,3]-shift

(b) **[3, 5]-Sigmatropic rearrangement*** : A symmetry allowed [3, 5]-sigmatropic reaction must be an excited state reaction if constrained to be suprafacial on both components. So far, only few examples of it are known.

(c) **[5, 5]-sigmatropic rearrangements) :** First [5, 5]-sigmatropic shift has been found in facile stereospecific rearrangement of (I) to (II).



6.6 IMPORTANT FACTS ABOUT SIGMATROPIC REARRANGEMENTS

1. Antarafacial processes are very-very rare which occur through small or medium sized ring.
2. Distortion of carbon framework impairs coupling with π-bonds, which renders symmetry allowed processes difficult. Because of it,

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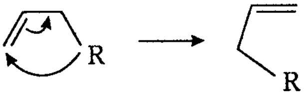
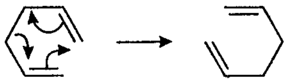
*K. Schmid and H. Schmid, Helv. chim. Acta, **36**, 687 (1953).

antarafacial processes are difficult in case of [1, 3]-shifts but not in [1, 7]-shifts.

3. Cyclopropane ring can replace π-bond for sigmatropic shift.
4. Orbital symmetry rules apply to sigmatropic reactions within ionic species also. For this reason, [1, 2]-shift in a carbonium ion is symmetry allowed; [1, 4]-shift occurs with inversion of configuration, *e.g.*, in but-2-en-1-yl cation; [1, 6]-shift in hexa-2, 4-diene-1-yl cation is expected through **suprafacial** transition state.
5. Sigmatropic shift may be regarded as special case of cycloaddition. Hence, [1, 3]-sigmatropic shift in following example of allylic system is $[\sigma^2 + \pi^2]$ reaction :



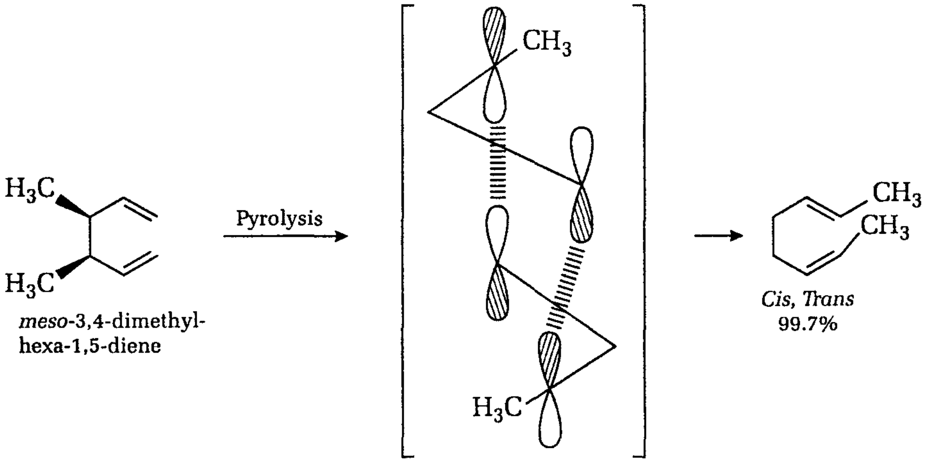
In the similar manner [3, 3]-sigmatropic shift of 1, 5-hexadiene is $[\pi^2 + \sigma^2 + \pi^2]$ concerted cycloaddition.



6.7 SOME IMPORTANT EXAMPLES OF SIGMATROPIC REARRANGEMENT

6.7.1 The Cope Rearrangement

1, 5-Dienes under thermal conditions undergo [3, 3]-sigmatropic shift known as Cope-rearrangement. Stereochemical outcome of this reaction can be rationalized through chair-shaped transition state as given below :

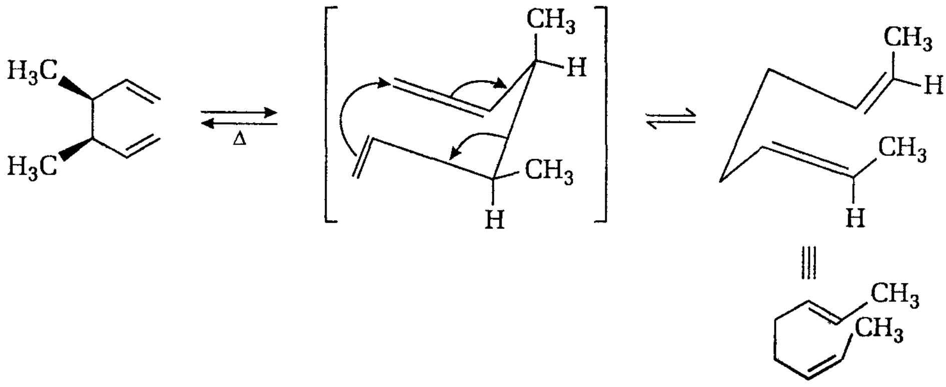


meso-3,4-dimethyl-hexa-1,5-diene

Cis, Trans 99.7%

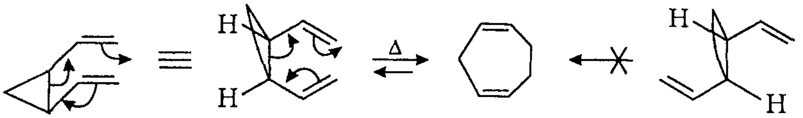
Chair-shaped transition state

meso-3, 4-Dimethyl-1, 5-hexadiene gives *cis, trans*-2, 6-octadiene (in the starting compound two methyl groups are *cis* to each other. In chair form of cyclohexane only 1 ,2-axial, equatorial relationship is *cis*.) If transition state is boat form then product will be either *cis, cis* or *trans, trans*. Alternatively this reaction is represented as :



ZE-2,6-Octadiene
(*cis, trans*-isomer)

cis-Divinylcyclopropane rapidly undergoes Cope-rearrangement to 1, 4-cycloheptadiene. Because of unfavourable molecular geometry, corresponding rearrangement of *trans*-isomer to cycloheptadiene is not concerted, because terminal ends of molecule between which bond is formed are at large distance. In contrary in *cis*-isomer besides favourable geometry for bonding between two ends bond to be broken is strained also which reduces enthalphy of activation.

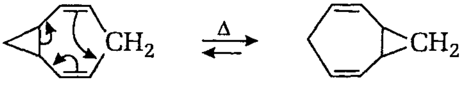


cis-1,2-divinylcyclopropane

1,4-cyclo-heptadiene

Trans-1,2-divinylcyclopropane

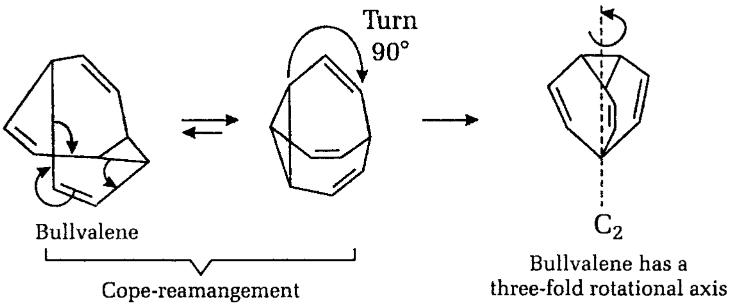
Sigmatropic rearrangement of divinylcyclopropane can occur more easily if entropy of activation is made more negative by the incorporation of both vinyl groups into a ring. By the incorporation of both vinyl groups in the ring, system becomes homotropilidiene (scheme 6.2) which undergoes a degenerate cope-rearrangement. Product formed from degenerate cope rearrangement cannot be distinguished from reactant. By the bridging of two methylene groups of homotropilidiene one molecule of bullvalene is formed (Scheme 6.3). At 100°C PMR-spectrum of bullvalene shows a peak at 4.22 ppm. Bullvalene has a three-fold rotational axis, thus all the three bonds are equivalent. The cope-rearrangement is degenerate in all the three faces. All the three double bonds in it are equivalent. Bullvalene is fluxional molecule : a molecule that undergoes rapid degenerate rearrangement.



Homotropilidiene

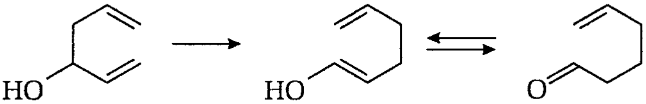
Still homotropilidiene

Scheme 6.2

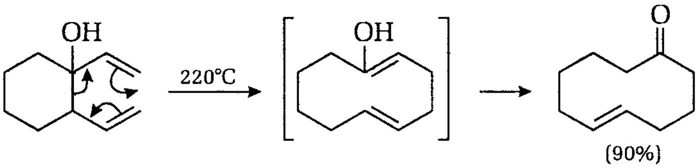


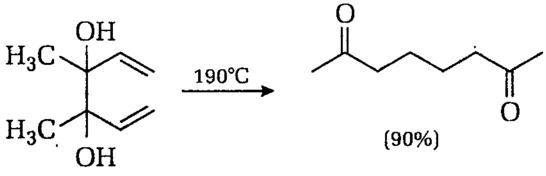
Scheme 6.3

Oxy-Cope rearrangement : Cope-rearrangement reaction is reversible and gives equilibrium mixture of two 1, 5-dienes which are richer in thermodynamically more stable isomer. But, reaction of 3-hydroxy-1, 5-diene can not be reversed, because 3-hydroxy-1, 5-diene tautomerises to carbonyl compound as given below. This rearrangement is known as **Oxy-cope rearrangement.**



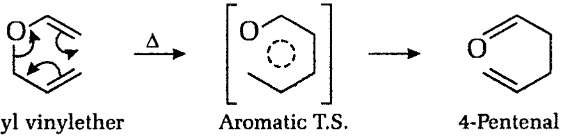
This rearrangement provides a useful route for the synthesis of δ, ε-unsaturated aldehydes and ketones; with —OH substituent at $C-3$ and $C-4$ of the diene 1, 6-dicarbonyl compounds are produced.





6.7.2 The Claisen Rearrangement

This rearrangement also involves [3, 3]-sigmatropic pathway like cope-rearrangement. However, in Claisen rearrangement the substrate incorporates one or more heteroatoms in place of carbon in 1, 5-hexadiene system.* Simplest example of Claisen-rearrangement is thermal conversion of allyl-vinylether to 4-pentenal :



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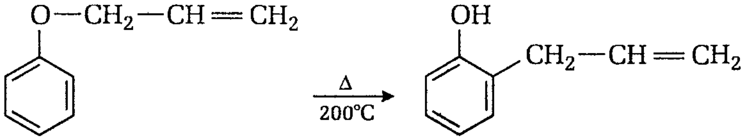
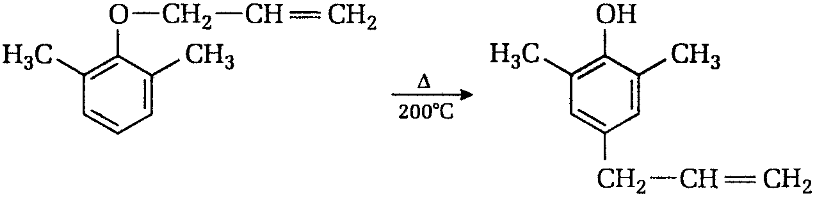
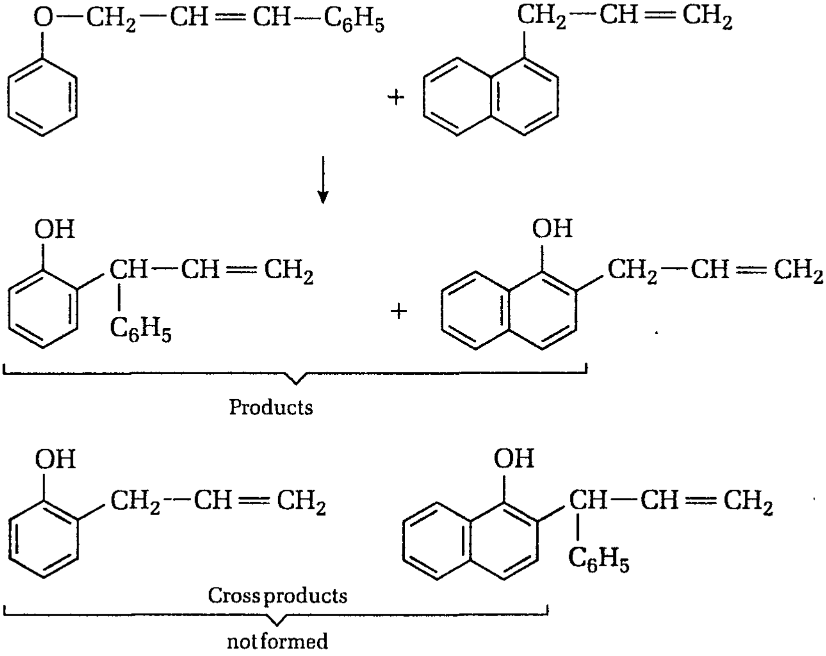
* S.J. Rhoads and N.R. Raulins, Organic Reactions 22, 1 (1975)

This reaction proceeds through a transition state of six-orbitals and 6-electrons, *i.e.*, aromatic T.S. Similarly, allyl ethers of phenol when heated to 200°C, allyl group moves to *ortho*-position, if both the *ortho*-positions are occupied, then migration is to *para*-position. This migration is known as Claisen rearrangement.

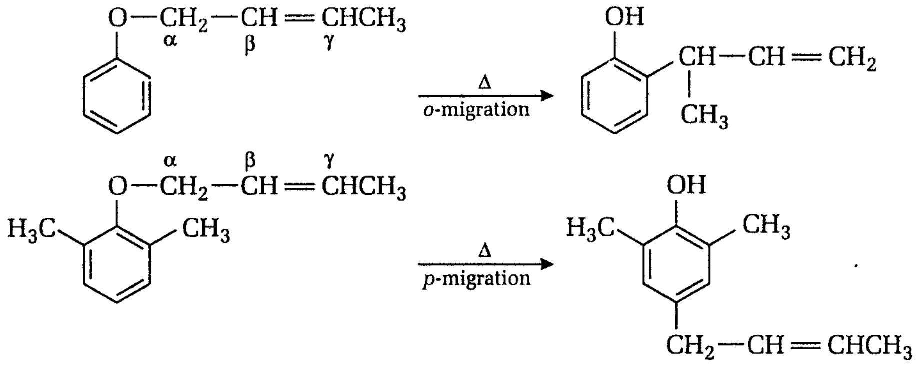




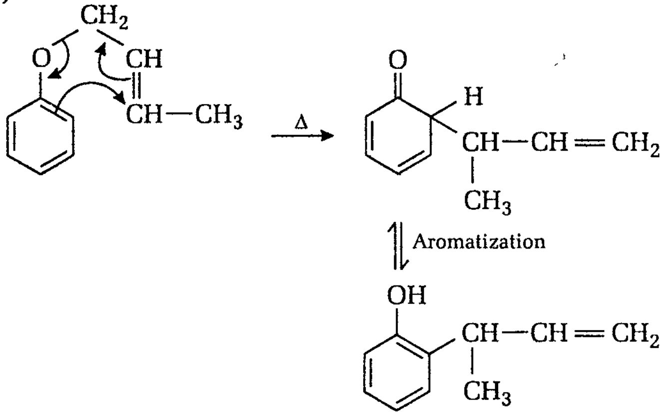
Migration at *meta*-position does not occur. When a mixture of two different ethers is heated, no cross-product formed. Hence, this is intramolecular rearrangement in which allyl group does not separates from the molecule.



One important feature of this rearrangement is that during *ortho*-migration carbon atom through which migrating group attaches to ring is γ-to oxygen atom as was present in the original ether. But in *para*-migration no inversion in the positions of allyl group is seen.

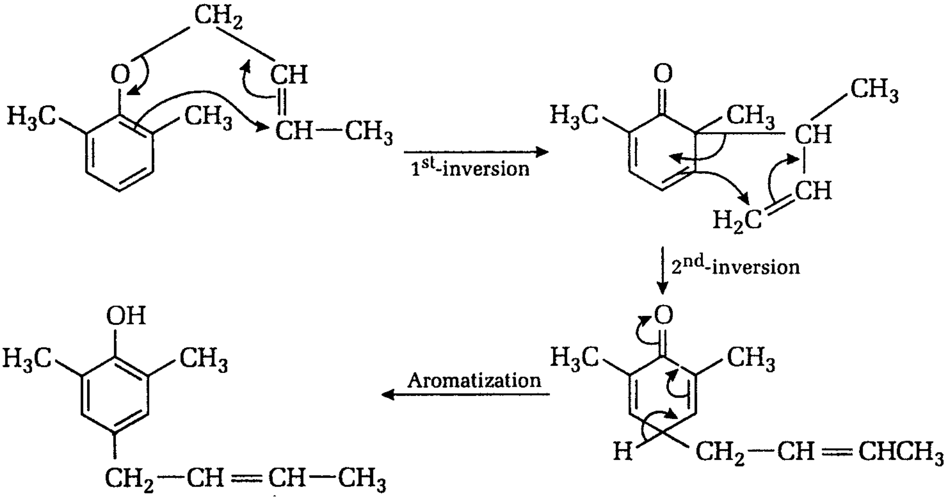


Above reaction results can be explained only if reaction occurs in concerted manner and through a six-membered cyclic transition state. In *ortho*-migration there is only one inversion therefore ends of allyl group exchange their position (Scheme 6.4).



Scheme 6.4

In *para*-migration there are two simultaneous inversions, therefore, there is no net inversion and hence ends of allylic group do not interchange their positions (Scheme 6.5).

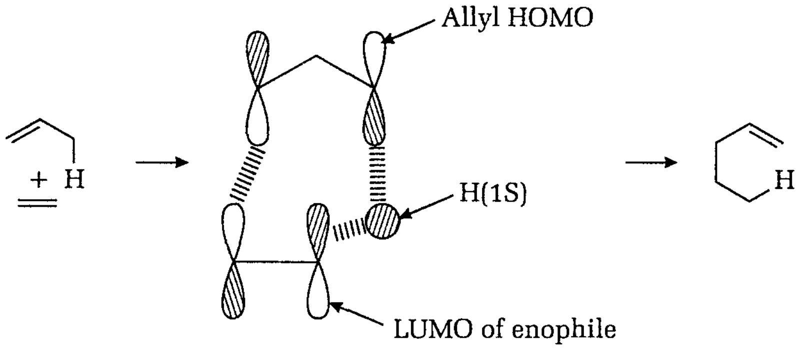


Scheme 6.5

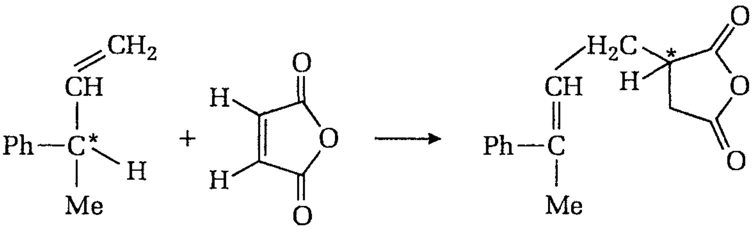
In a [3, 2]-sigmatropic rearrangement, the reactants have a two-atom migrating unit where one atom has a negative charge; this is equivalent to two π-electrons of an unsaturated bond in a three-atom moiety. The rearrangements of allylic sulphoxides, selenoxide and amide oxide are examples of Claisen rearrangements. But is **Sommlet** rearrangements two atom unit is nitrogen ylide $-\overset{\oplus}{N}R_2-\overset{\ominus}{C}H_2$.

6.7.3 The Ene Reaction

The reaction in which allylic hydrogen adds to dieneophile (*e.g.*, C═C, C═O, N═N etc.) under thermal conditions to form a new σ-bond to the terminal carbon of allylic double bond is called Ene reaction. Ene-reaction is followed by 1, 5-migration of allylic hydrogen and position of allylic double bond is also changed. Thus reaction is a combination of cycloaddition and [1, 5]-sigmatropic rearrangement. This reaction proceeds in a concerted manner and there is little charge development in transition state. During the reaction there is primary kinetic isotopic effect and C—H bond breaks up during rate determing step. Allylic oxidation of alkenes with selenium dioxide is an example of Ene reaction. Interaction of H-atom with HOMO of allyl radical and LUMO of enophile is symmetry allowed process under thermal conditions.



The reaction between maleic anhydride and optically active PhCHMeCH═CH$_2$ gives an optically active product, which is an strong evidence for concerted nature of the reaction.



6.7.4 Fluxional Tautomerism

Doering revealed that degenerate Cope-rearrangement (isomerization of identical structures) occurs in homotropilidiene :

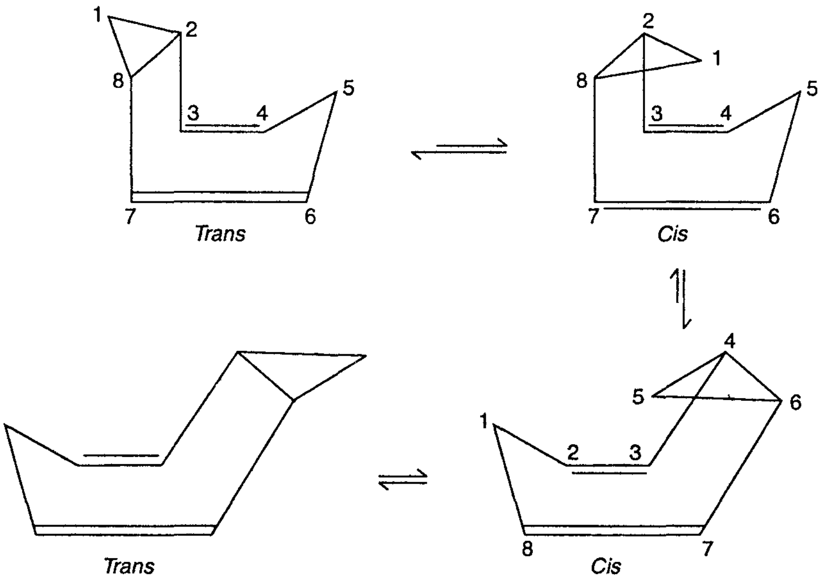
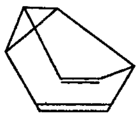
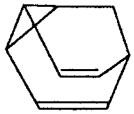


Fig. 6.7. Fluxional tautomerism (degenerate cope rearrangement).

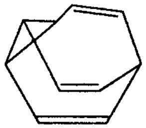
Two *cis*-structures of homotropilidine are interconvertable 1000 times per second at 180°C. This interconvertabity can be enhanced by eliminating possibility of formation of *trans*-isomer which can be achieved by connecting 1 and 5-positions either directly or through a methylene group. Ethylene bridge solves the same problem. As a result of these operations we get semibullvalene, barbaralene and bullvalene, respectively.



Semibullvalene



Barbaralene

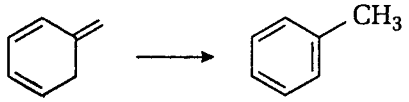


Bullvalene

Bullvalene is an example of fluxional molecule. In bullvalene there is three-fold axis of symmetry, therefore, three equivalent cope-rearrangements are possible in it with each isomer. Out of total ten C—H groups each group can occupy ten positions in the molecule. Because of presence of ten *C*-atoms and three-fold axis of symmetry 10!/3 (= 1,209,600) identical isomers are possible for bullvalene which are degenerate. Bullvalene, has been synthesised and its NMR-spectrum has shown that it fluctates about 4000 times per second at room temperature. There is only one signal located at δ4.22 in NMR spectrum at 100°C.* Degenerate cope-rearrangement should not be confused with resonance which is hypothetical; whereas former is actual equilibrium.

6.7.5 Conversion of Triene (A) to Toluene

(A)



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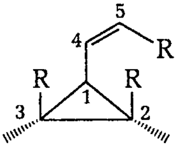
*M. Saunders, Tetrahedron letters, 1699 (1963).

This reaction is symmetry forbidden [1, 3]-shift and proceeds in uncatalysed manner.

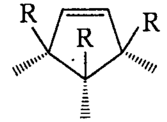
6.7.6 Vinylcyclopropane → Cyclopentene Conversion

For vinylcyclopropane(I) symmetry-allowed reactions are :

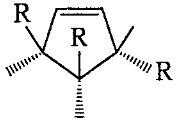
(i) Suprafacial [1, 3]-shift of 1, 2-bond to C_5 with inversion at $C-2$, to give (II).



(I)



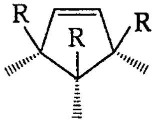
(II)



(III)

(ii) Antarafacial [1, 3]-shift of 1, 2-bond to C_5 with retention at $C-2$ to yield (III).

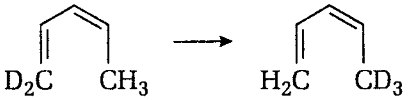
(iii) (IV) can not be produced in a symmetry-allowed process.



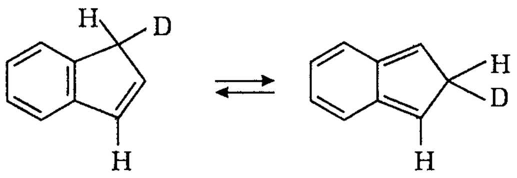
(IV)

6.7.7 1, 5-Shift in 1, 3-pentadiene

Rearrangement of (v) to (VI) exhibits large kinetic isotope effect of 12.2 at 25°C which is consistent with highly symmetrical transition state in a concerted process. [1, 5]-shift is preferred over [1, 3]-shift has been shown by Roth. The [1, 5]-shift takes of deuterium label in (VII) over all aromatic positions at high temperature, inspite of necessity to proceed through unstable isoindene. But base catalysed reaction involve [1, 3]-shift.



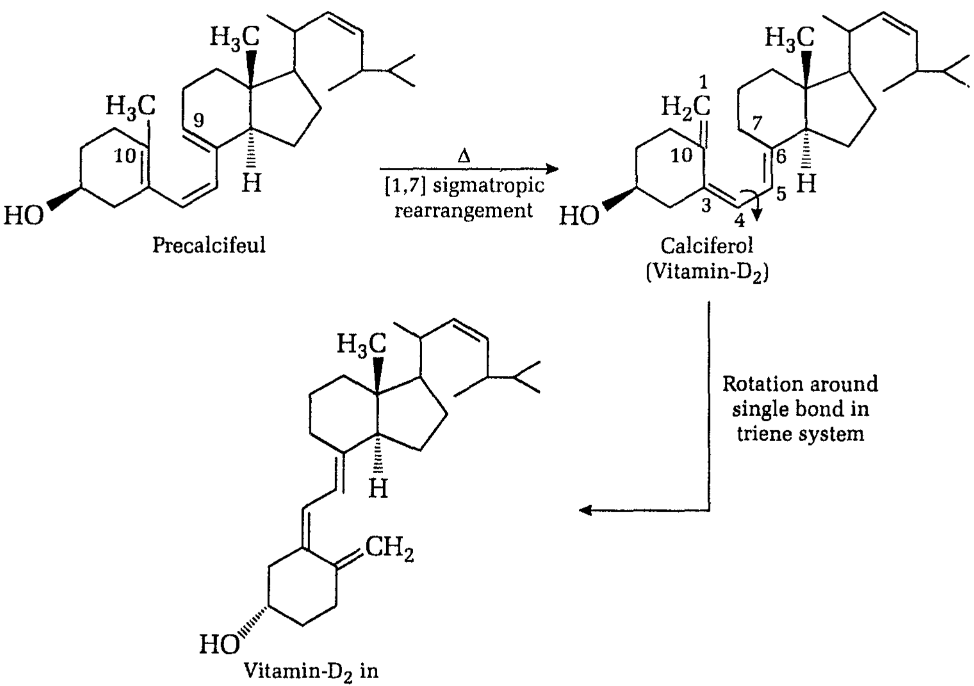
(V) (VI)



(VII) (VIII)

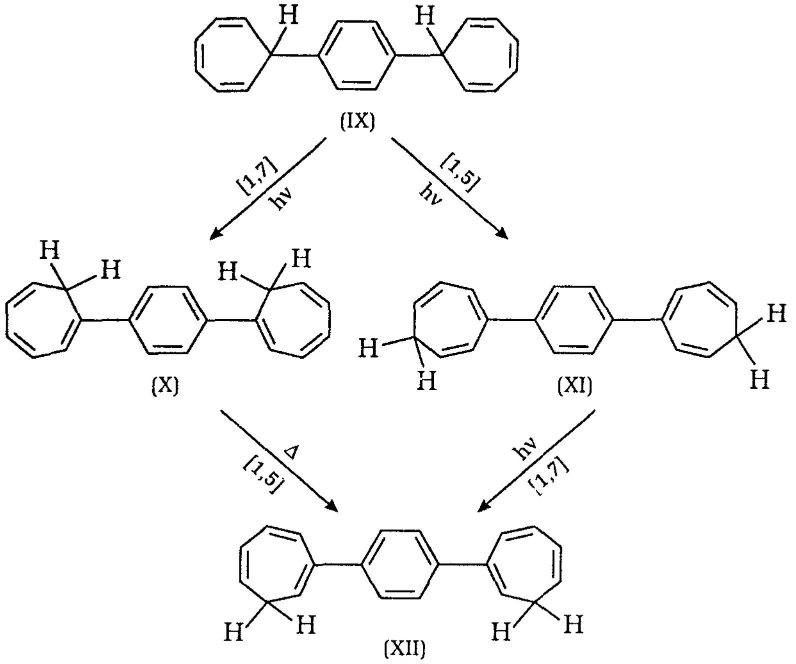
6.7.8 Precalciferol → Calciferol Conversion

Antarafacial sigmatropic rearrangement of the order [1, 7] has been observed in this case. This is very important reaction from biological point of view.



Vitamin-D$_2$ in most stable form

6.7.9 [1, 5]-Thermal and [1, 7]-photochemical Sigmatropic Hydrogen Shifts in the Isomers of 1, 4-di (cycloheptatrienyl) Benzene*



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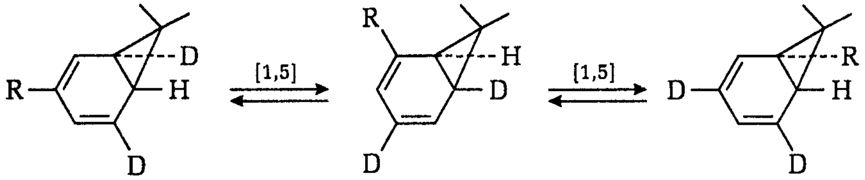
* R.W. Murray and M.L. Kaplan, J. Amer. Chem. Soc; **88**, 3527 (1966).

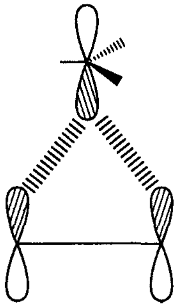
6.8 SEQUENTIAL SIGMATROPIC SHIFTS

Berson and Willcott observed a sequence of [1, 5]-sigmatropic shifts in norcaradienes which must proceed with retention of configuration at migratory carbon.* This is given below :

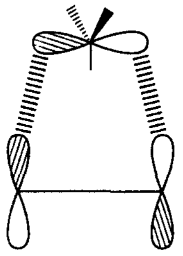


6.9 SIGMATROPIC MIGRATION OF CARBON

Contrary to H-atom which has only one electron and one lobe (1S-orbital), a carbon free radical has odd electrons in *p*-orbital which has two lobes in opposite phases. In cyclic transition state during migration of carbon in thermal [1, 5]-suprafacial migration symmetry is conservable only if carbon moves in such a manner that lobe which was attached originally remains attached, that is it proceeds with retention of configuration at migratory carbon. But, in 1, 3-migration in suprafacial manner the lobe of carbon which was attached becomes free as a result of which there is inversion of configuration at migratory carbon.



Thermal [1,5] suprafacial migration (with retention)



Thermal [1,3]-suprafacial migration (with inversion)

❑❑❑

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* J.A. Berson and M.R. Willcott, J-Amer. Chem. Soc; **87**, 2751, 2752 (1965), **88**, 2494 (1966).

UNIT

7

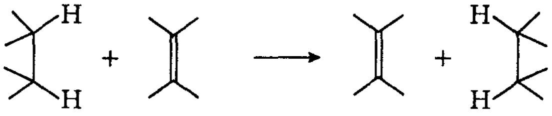
MISCELLANEOUS

7.1 GROUP TRANSFERS AND ELIMINATIONS

7.1.1 Group Transfer*

These reactions are characterized by transfer of group or groups from one molecule to another. Some examples are discussed below :

(1) Transfer of two hydrogen atoms from ethane to ethylene.



A correlation diagram can be drawn for this reaction using the symmetry plane bisecting two molecules (given below) :

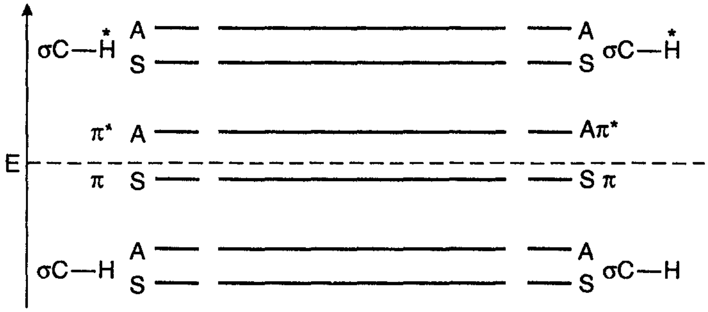
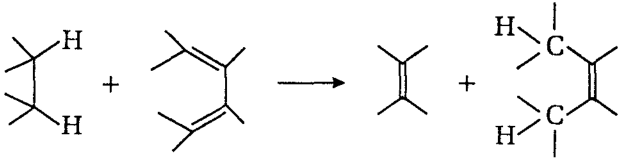


Fig. 7.1. Correlation diagram for group transfer (1).

This process is clearly symmetry allowed in ground state under thermal conditions is concerted manner.

(2) Transfer of two hydrogens from ethane to both terminal ends of butadiene : This transfer is also concerted and correlation diagram for this can be drawn as given below :



This reaction is thermally-forbidden as symmetries of HOMO match under excited state.

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* R.B. Woodward and R. Hofmann.

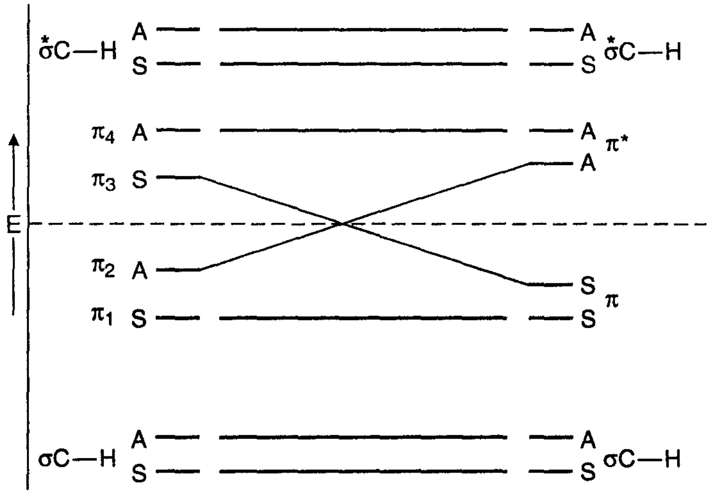
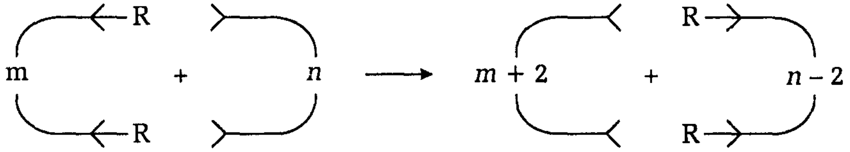


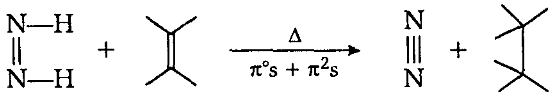
Fig. 7.2. Correlation diagram for group transfer (2).

(3) Double-group transfer : This is symmetry allowed in ground state when $m+n=4q+2$ and is symmetry allowed in excited state if $m+n=4q$; m and n are number of π-electrons in two reactants and q is an integer (0, 1, 2...). This rule also applies to antarafacial process on both components and is reversed when process is antarafacial on one component only.

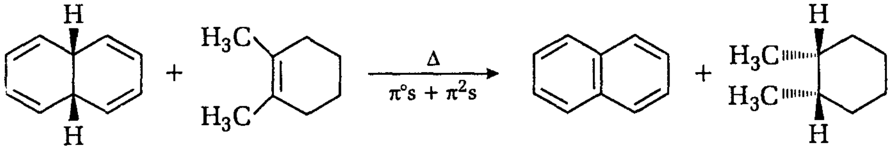


Following are some important examples of double group transfer.

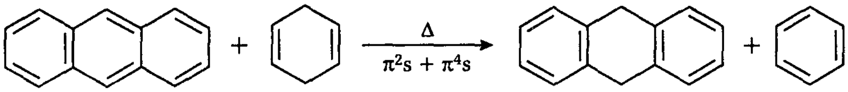
(a)



(b)

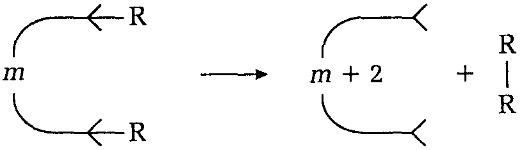


(c)



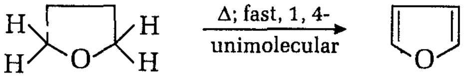
7.1.2 Group-Elimination

When $n=0$ in the above rule concerted eliminations occur. According to selection rules non-catalytic dehydrogenation should involve 1, 4-elimination rather that 1, 2-elimination :

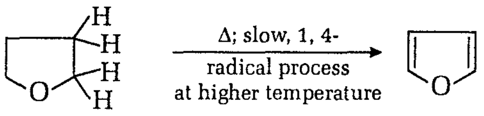


Some examples of group elimination are cited below :

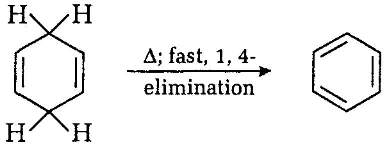
(a)



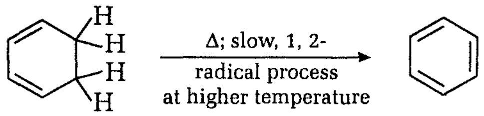
(b)



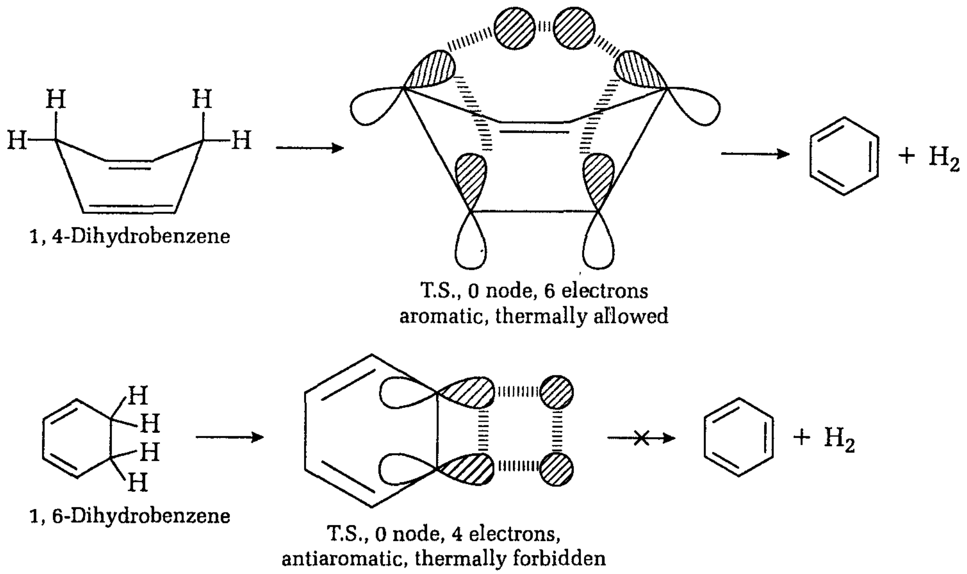
(c)



(d)

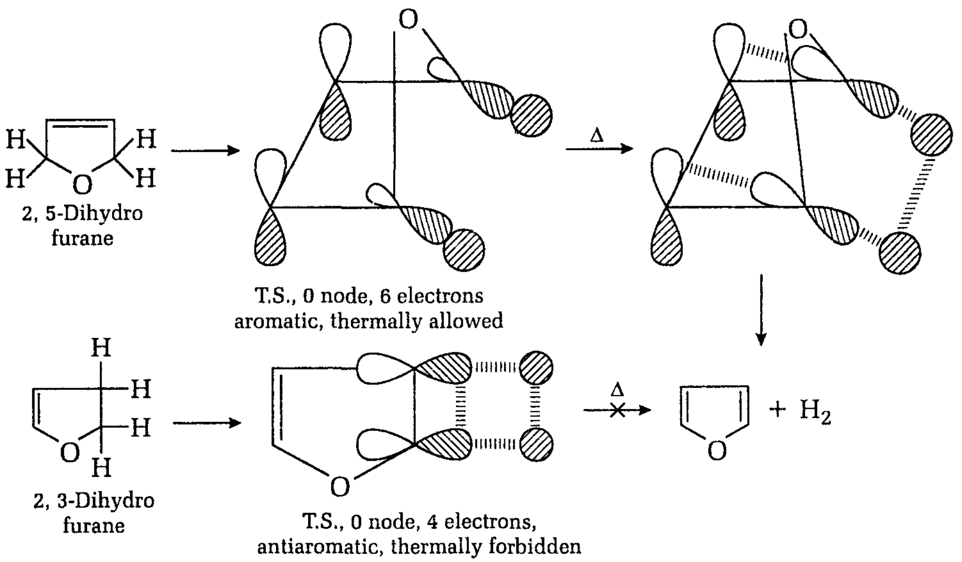


Double group elimination can be easily explained by PMO method. Eliminations in 1, 4-and 1, 6-dihydrobenzenes are illustrated below (scheme 7.1).



Scheme 7.1

Likewise 1, 4-and 1, 2-eliminations in 2, 5-dihydrofurane and 2, 3-dihydrofurane can be analysed by PMO method (scheme 7.2).



Scheme 7.2

The concerted loss of two geminal groups also fall under this cateogy (scheme 7.3). This reaction is also symmetry-allowed.

Scheme 7.3

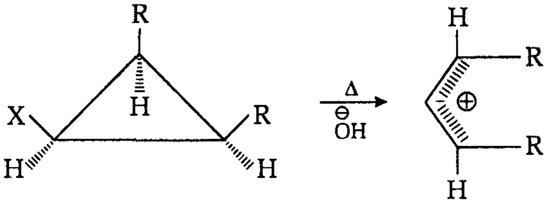
7.2 PERICYCLIC REACTIONS INVOLVING IONIC TRANSITION STATES

Rules for these reactions are same as for normal pericyclic reactions; because they are based on number of electrons in transition state and not on the number of orbitals.

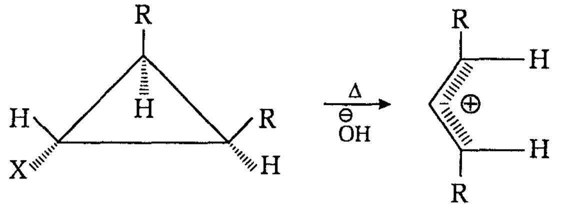
7.2.1 Electrocyclic Reactions

7.2.1.1 FMO Method

(1) When an organic compound with polar bond is dissolved in polar solvent a carboniumion and an anion are produced. If cyclopropanes with C—X bond, (I) and (II), are dissolved in polar solvents they undergo solvolysis and carbonium ions (III) and (IV) are produced, respectively.

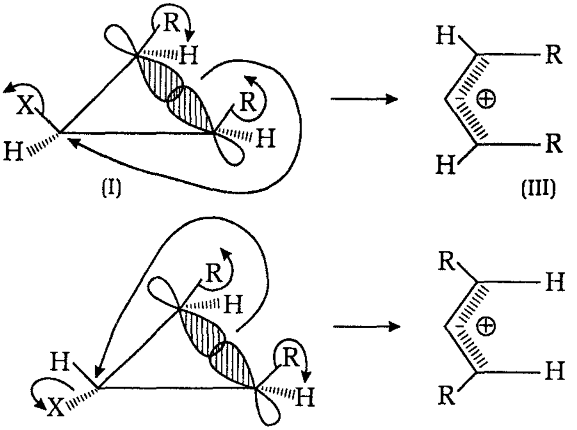


(I) (III)



(II) (IV)

Cyclopropane ring opening is concerted and follow disrotatory mode. When groups *R* are on the same side of ring as C—X bond, they rotate towards each other and give(III). But,when C—X bond and *R* are on opposite side of the ring they rotate away from each other of give(IV). Both the modes of ring opening are symmetry allowed. As this transition state involves 2π electrons, therefore, it is $(4q + 2)\pi$ system. Conrotatory mode of ring opening will be symmetry forbidden here. Disrotatory opening of cyclopropane ring in (I) and (II) can be visualized by considering attack on C—X bond from the back side as in S_N2 -reactions.

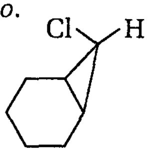


(I) (III)

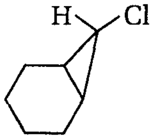
(II) (IV)

As attack is similar to in S_N2 reactions, therefore, if R and R groups are bulky solvolysis will be easier in (II) than in (I) for steric reasons. But, if *R* and *R* are part of small ring, ring opening will be facile in cyclopropane ring of the type (I), other wise *trans* type compound formation will be there, formation of which is sterically hindered in transition state. We may conclude that leaving group with *endo* confirmation undergo facile solvolysis.

(2) Compound (V) undergoes solvolysis readily in comparison to (VI). (V) is *endo* isomer and (VI) is *exo*.



(V)



(VI)

(3) On the basis of properties of *endo* and *exo*-leaving groups two isomers can be differentiated; *e.g.*, (VII) and (VIII) which are formed is equal amount by cheletropic addition of chlorobromocarbene to cyclopentene.* (Scheme 7.4 and 7.5).

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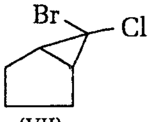
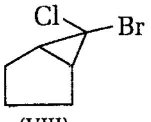
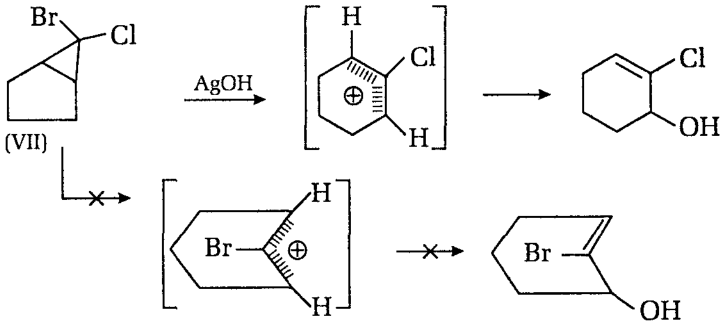
* P.S. Skell and R.L. Sandler, J. Amer. Chem, Soc; **80**, 2024 (1958).



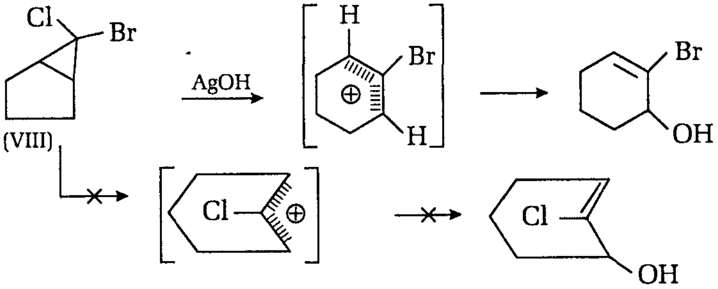
(VII)



(VIII)



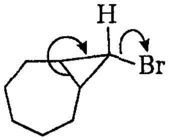
Scheme 7.4



Scheme 7.5

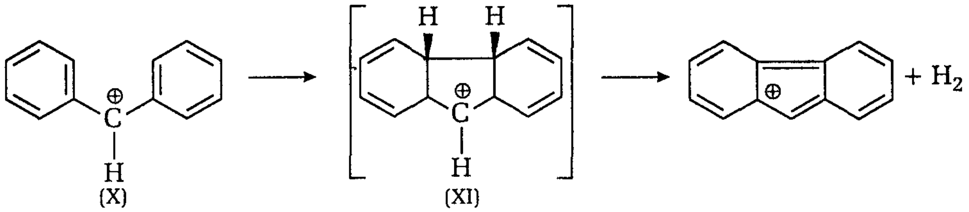
If compound is (VII) with -Br substituent at *endo*-position 2-chlorocyclohexenol will be formed; whereas for compound (VIII), 2-Bromocyclohexenol will be the product upon solvolysis.

Endo-group is preferentially expelled because it gives more stable *cis*-isomer. *exo*-substituent is expelled only if *trans*-isomer is more stable than *cis*-isomer, for instance in case of compound (IX).



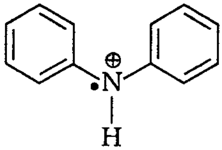
(IX)

(4) Diphenyl methyl cation (X) cyclizes to hydrofluorene which loses two H-atoms in a single step indicating probably transition state *cis* (XI) ion which is

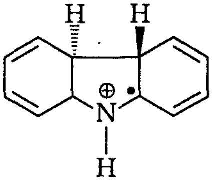


probably product of symmetry-allowed electrocyclization of first excited state of cation (X).

In contrast radical cation (XII) undergoes cyclization to hydrocarbazol radical cation which loses one H-atom at a time, therefore, it is probably *trans-ion* (XIII). This process is also symmetry allowed under excited state.

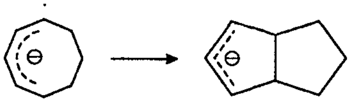


(XII)



(XIII)

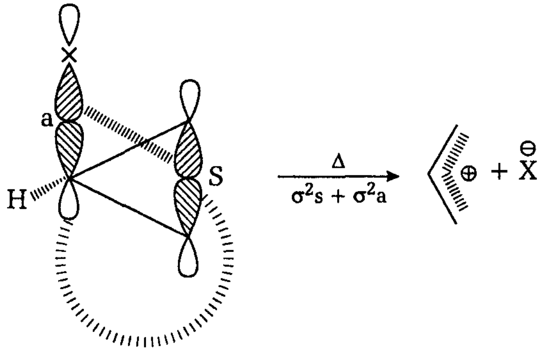
Anions also undergo electrocyclic ring-closure. For example anion (XIV) gives bicyclic anion (XV).



(XIV) (XV)

7.2.1.2 PMO Method

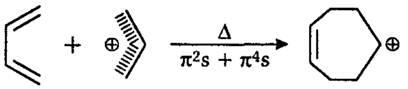
Solvolysis of cyclopropyl halide to give acyclic carbocation can also be explained by PMO-method. Here backside attack of opening σ-bond electrons on C—X bond takes place in transition state which is aromatic, therefore, reaction is thermally allowed. This process is illustrated below :

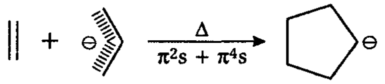


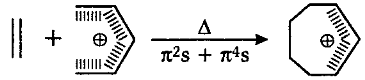
Transition state : 1 node,
4 electrons, aromatic,
thermally allowed reaction

7.2.2 Cycloadditions

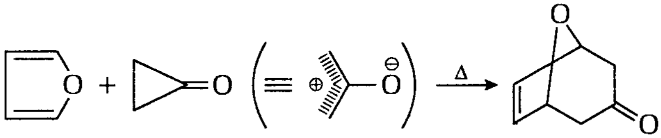
Following supra-supra cycloadditions are thermally allowed according to selection rules :

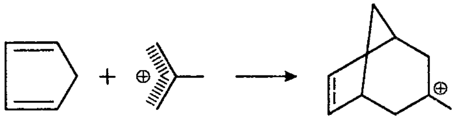
(a) 

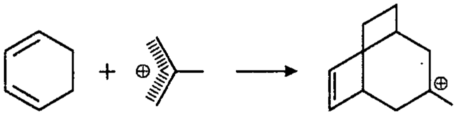
(b) 

(c)


Few 4*s* + 2*s* cycloadditions are given below :

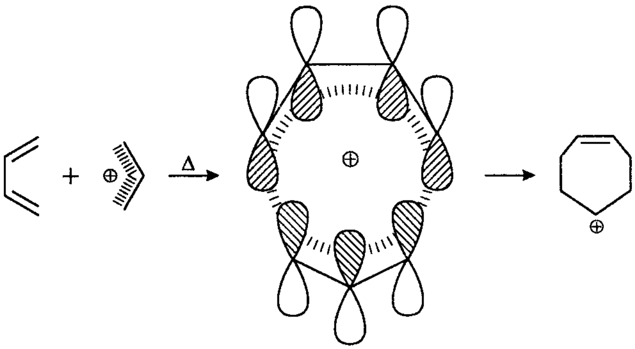
(a)


(b)


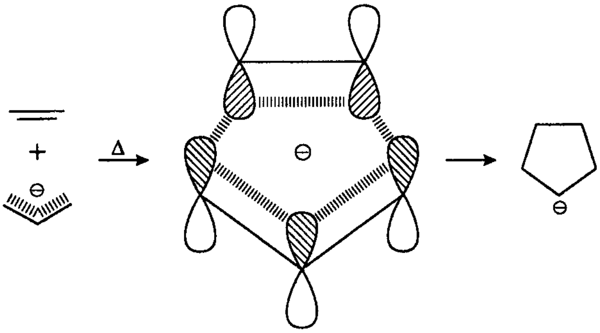
(c)


7.2.2.1 PMO Method

PMO method representation of some cycloaddition reactions involving ionic transition states are figured below :

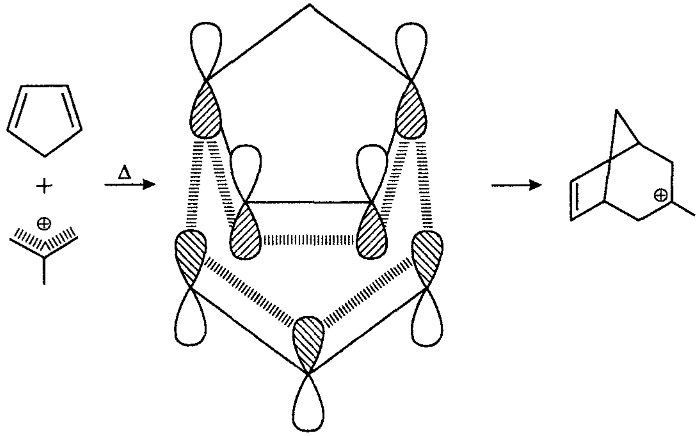
(a)


Transition state, 0 node, 6 electrons, aromatic, thermally allowed

(b)


Transition state, 0 node, 6 electrons, aromatic, thermally allowed

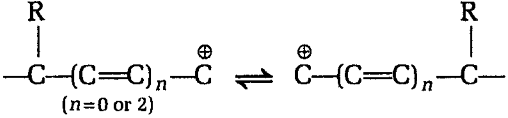
(c)



Transition state, 0 node, 6 electrons, aromatic, thermally allowed

7.2.3 Sigmatropic Reactions

(i) [1, 2] and [1, 6]-sigmatropic shifts : [1, 2] and [1, 6]-sigmatropic rearrangements involving ionic transition states are discussed below. Most important examples of these shifts (suprafacial) are in carbonium ions and benzenonium ions, respectively.



$$-\overset{\overset{\displaystyle R}{|}}{C}-(C{=}C)_n-\overset{\oplus}{C} \rightleftharpoons \overset{\oplus}{C}-(C{=}C)_n-\overset{\overset{\displaystyle R}{|}}{C}-$$

$(n=0 \text{ or } 2)$

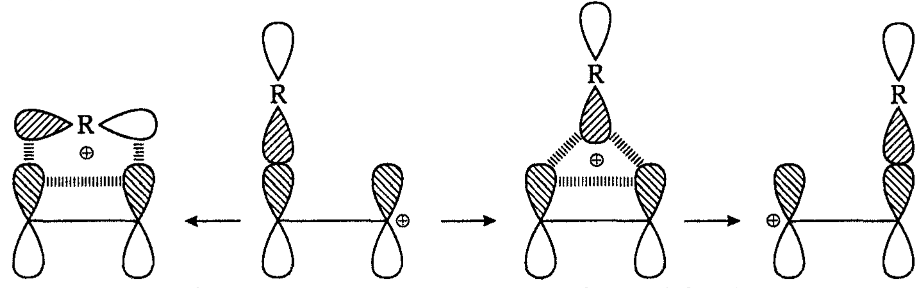
7.2.3.1 FMO Method

The π-framework during the transition state of [1, 2]-shift is vinyl radical cation $(C{=}C{-})^+$; and during [1, 6]-shift is hexatriene radical cation, $(C{=}C{-}C{=}C{-}C{=}C)^+$. During [1, 2]-shift HOMO of π-framework of transition state is π and during [1, 6]-shift it is ψ_3. In both cases HOMO has *m*-symmetry; therefore, suprafacial shift without inversion at the migrating centre is thermally allowed.

7.2.3.2 PMO Method

We reach to the same conclusion by PMO-method as reached by FMO-method; rearrangement with aromatic transition state is thermally allowed in case of [1, 2] as well as [1, 6]-sigmatropic shift. An example of each is given below :

(a) [1, 2]-shift with carbocation :

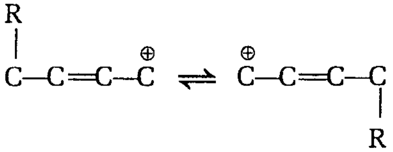


T.S. for 1, 2-shift with inversion at R; 1 node, 2 electrons, antiaromatic, Δ-forbidden

T.S. for 1, 2-shift with retention at R; 0 node, 2 electrons, aromatic, Δ-allowed

(b) [1, 6]-shift may be illustrated in the similar manner as [1, 2]-shift.

(ii) [1, 4]- and [1,5]-Sigmatropic-shifts : In contrary to [1, 2]-and [1, 6]-shift [1, 4]-sigmatropic shifts are thermally allowed through antarafacial mode, without any inversion at migratory group, because, HOMO of π-skeleton of transition state here is ψ_2 with C_2-axis of symmetry. For example : in case of butadiene radical cation, *e.g.*, $(C{=}C{-}C{=}C)^+$:



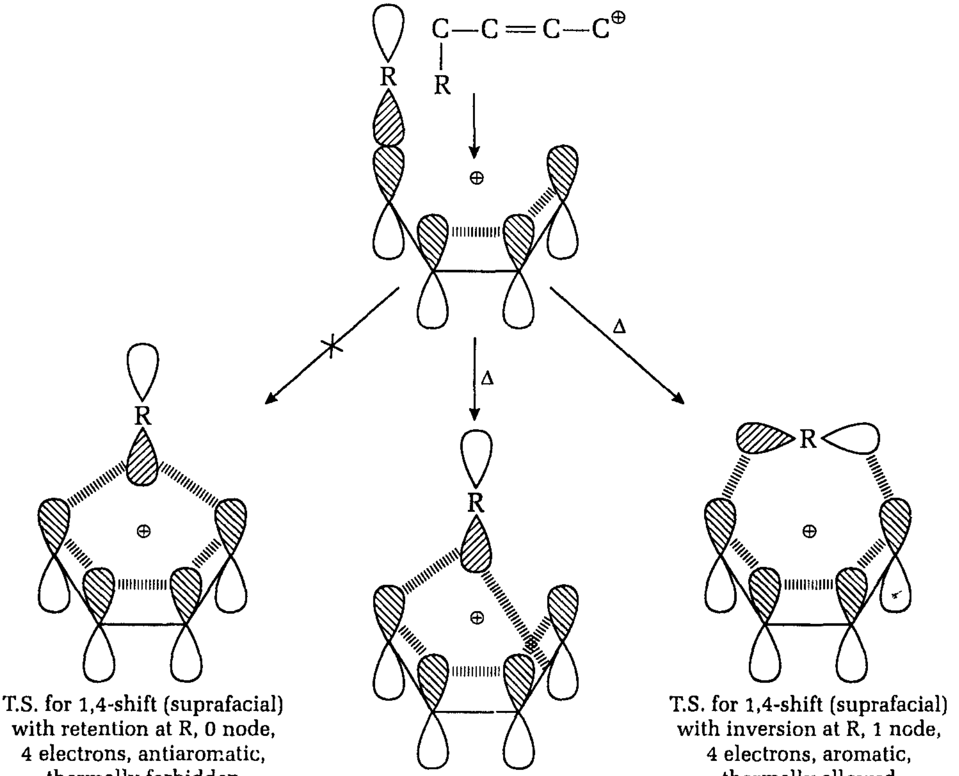
$$\overset{\displaystyle R}{\underset{}{\overset{|}{C}}}{-}C{=}C{-}\overset{\oplus}{C} \rightleftharpoons \overset{\oplus}{C}{-}C{=}C{-}\underset{\displaystyle R}{\underset{|}{C}}$$

But, [1, 4]-sigmatropic shifts are sterically prohibited. Thermal [1, 4]-shifts are thermally allowed through suprafacial mode of migration; this process involves inversion at the migrating centre.

[1, 5]-Sigmatropic shift in contrary proceeds with retention of configuration through suprafacial mode. PMO-analysis also reveals that [1, 4]-shift with inversion would be thermally allowed since transition state here is with four electrons, one node and is aromatic.

Analysis by PMO-method to predict feasibility of [1, 4]-shift is illustrated below :

[1, 4]-shift with carbocation (PMO-method)



T.S. for 1,4-shift (suprafacial) with retention at R, 0 node, 4 electrons, antiaromatic, thermally forbidden

T.S. for 1,4-shift (antarafacial) with retention at R, 1 node, 4 electrons, aromatic, thermally allowed

T.S. for 1,4-shift (suprafacial) with inversion at R, 1 node, 4 electrons, aromatic, thermally allowed

7.3 ELECTROCYCLIC AND SIGMATROPIC REACTIONS AS CYCLOADDITIONS

Electrocyclic and Sigmatropic reactions can be considered in terms of cycloadditions. It has been shown that it is possible if we consider sigma bond as a component of cycloaddition. Selection rules for cycloadditions can be applied to electrocyclic as well as sigmatropic reactions. Involvement of σ-bond in these reactions is possible in following manner :

(a) Addition of σ-bond is suprafacial if there is either retention or inversion on both terminal ends of σ-bond.

(b) Addition of σ-bond is antarafacial if at one terminal end there is retention and at other terminal end is inversion.

Classification of σ-bond as a component of cycloaddition came out of consideration of suprafacial and antarafacial addition to double bond which can be demonstrated by ball and stick-model. During retention there is interaction of **bonding lobe** (large one) of σ-bond with the other component of cycloaddition. During inversion interaction of smaller lobe takes place with other component of cycloaddition.

7.3.1 Electrocyclic Reactions

For conrotatory ring opening of cyclobutene there is retention at C_3 and inversion at C_4. Sigma bond thus participates in antarafacial manner. Addition across π-bond is then suprafacial and this pathway is classified as $\sigma^2 s + \pi^2 s$ type of cycloaddition (Fig. 7.3).

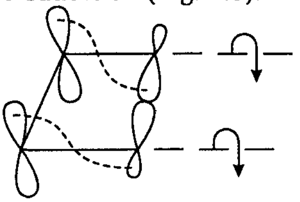


Fig. 7.3. $\sigma^2 a + \pi^2 s$ **ring opening and ring closure of cyclobutene-butadiene interconversion.**

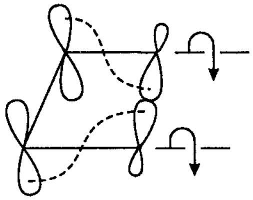
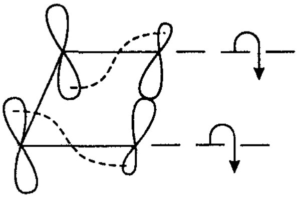


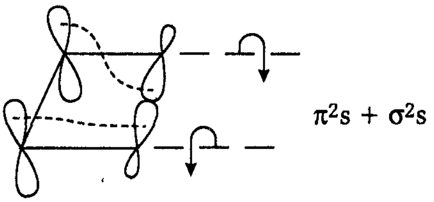
Fig. 7.4. $\sigma^2 s + \pi^2 a$ **ring opening and ring closure of cyclobutene-butadiene interconversion.**

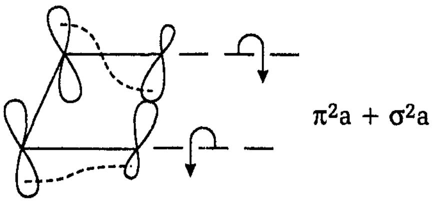
Similarly, when retention occurs at both the ends of σ-bond, it is involved in suprafacial manner and addition at π-bond occurs in antarafacial manner, pathway is classified as $\sigma^2 s + \pi^2 a$ cycloaddition (Fig. 7.4).

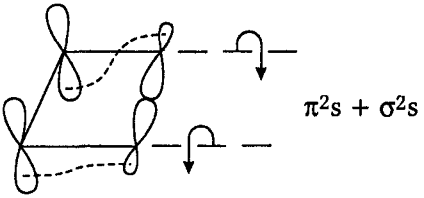
It is noteworthy that conrotatory opening always involves suprafacial involvement of one component and antarafacial involvement of other. Selection rule for cycloaddition is that this type of ring-opening must be allowed. Another conrotatory ring opening classified as $\sigma^2 s + \pi^2 a$ can be illustrated as given below :



Similarly, disrotatory ring opening can be classified as given below :







7.3.2 Sigmatropic Reactions

Sigmatropic reactions may be classified in terms of cycloadditions as given below :

(a) 1, 3-Sigmatropic shift :

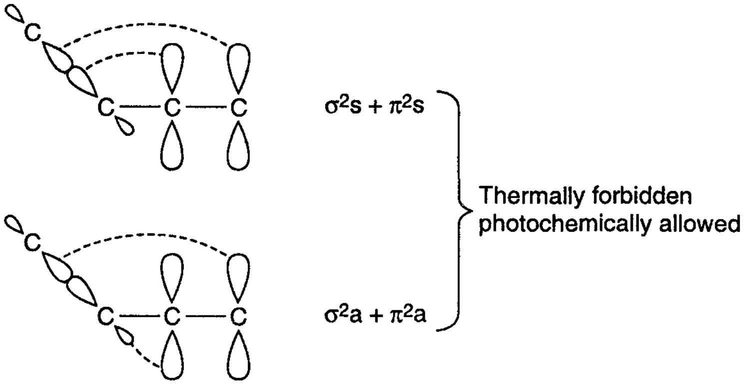


Fig. 7.5. [1,3]-sigmatropic shifts with retention at migratory atom as $(\sigma^2s + \pi^2s)$ and $(\sigma^2a + \pi^2a)$ cycloadditions.

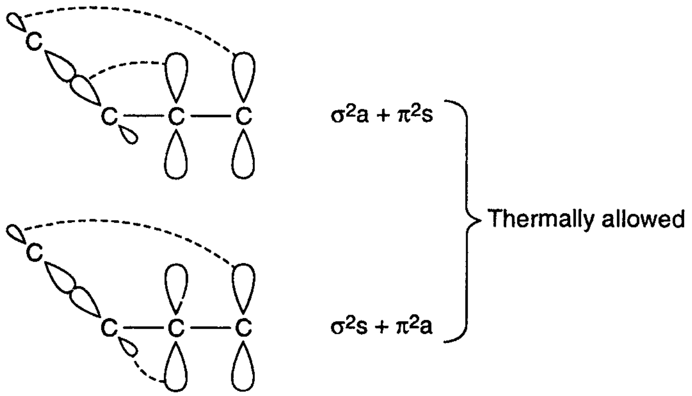


Fig. 7.6. [1,3]-sigmatropic shifts with inversion at migratory atom as $(\sigma^2a + \pi^2s)$ and $(\sigma^2s + \pi^2a)$ cycloadditions.

(b) 1, 5-Sigmatropic shifts :

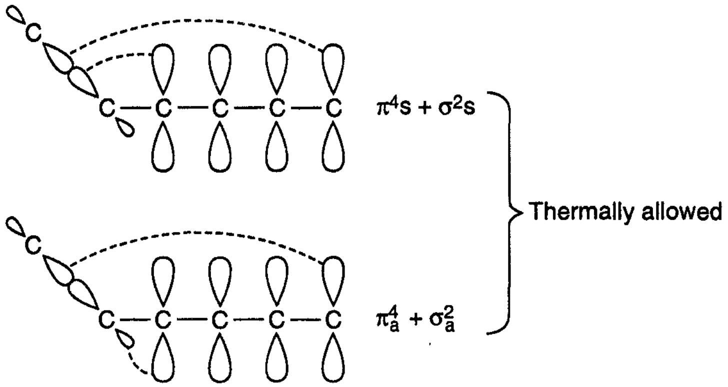


Fig. 7.7. [1,5] sigmatropic shift with retention at migratory atom as ($\pi^4s + \sigma^2a$) and ($\pi^4a + \sigma^2a$) cycloadditions.

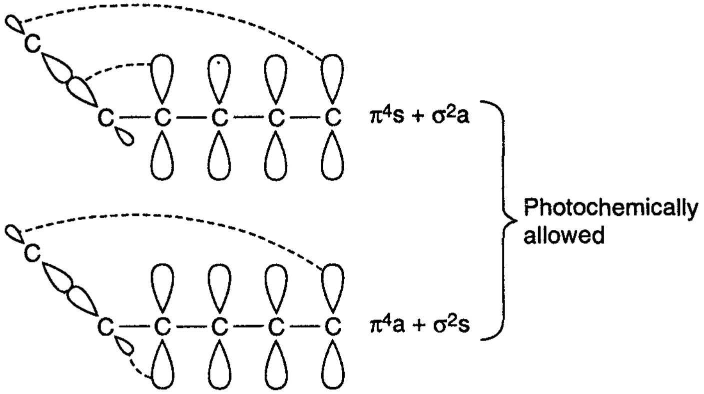


Fig. 7.8. [1,5] sigmatropic shifts with inversion at migratory atom as ($\pi^4s + \sigma^2a$) and ($\pi^4a + \sigma^2s$) cycloadditions.

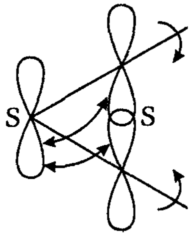
7.4 WOODWARD-HOFFMANN'S GENERALIZED RULES FOR PERICYCLIC REACTIONS

All pericyclic reactions in which all first order changes resulting in bonding reorganization occur in concerted manner through cyclic transition states can be treated in terms of cycloadditions. There are selection rules for two component systems; but selection rules for them can be made more comprehensive to include greater number of components. **Woodward and Hoffmann** made **generalized rules** for them. According to which **a ground state pericyclic reaction is symmetry allowed when total number of $(4q+2)s$ and $(4r)a$ components is odd** (where q and r are two integers including zero). The rules are reversed for excited state process in which total number of such components becomes zero or even number. This selection rule is equally effective for **single atomic orbital.**

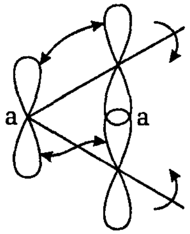
When $r = 0$, $4r$ component represents a vacant atomic orbital and if $q = 0$, $(4q+2)$ component is treated as an atomic orbital occupied by two electrons. A single atomic orbital is represented by Greek letter ω(omega) Vs σ-and π-molecular orbitals. $\omega^0 s$ and $\omega^0 a$, thus represent suprafacial and antarafacial addition to vacant single orbital. Suprafacial and antarafacial addition to doubly filled atomic orbitals are represented by the symbols $\omega^2 s$ and $\omega^2 a$, respectively. Generalized rules for electrocyclic reactions, cycloadditions and sigmatropic reactions are depicted below :

(i) **Conrotatory** electrocyclic ring-opening of cyclobutenes may be represented as $(\pi^2 s+\sigma^2 a)$ or $(\pi^2 a+\sigma^2 s)$ thermally allowed processes. Because, neither $\sigma^2 a$ nor $\pi^2 a$ represent $(4r)_a$ component, they may be ignored. Therefore, total number of $(4q+2)_s$ and $(4r)_a$ component in either case is odd (one), therefore, reaction is symmetry allowed.

(ii) **Disrotatory ring opening** of cyclopropyl cation to give allyl cation may be represented as $(\omega^0 s+\sigma^2 s)$ or $(\omega^0 a+\sigma^2 a)$ thermally allowed process. In this case $\omega^0 s$ or $\sigma^2 a$ may be ignored, thus total number of interacting components is odd and reaction is symmetry allowed.



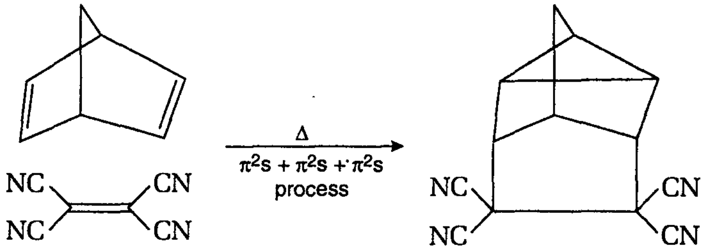
$(w^0 s + \sigma^2 s)$



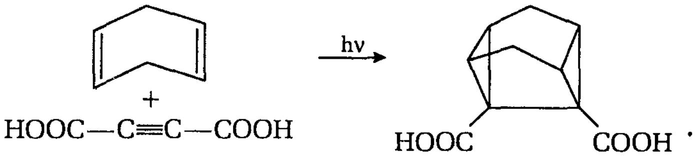
$(w^0 a + \sigma^2 a)$

(iii) **Diels-Alder reaction** is $(\pi^4 s+\pi^2 s)$ thermally allowed process. In this case we may ignore $\pi^4 s$, because, it represents neither $(4q+2)_s$ nor $(4r)_a$ component. Thus, total number of components here odd (one) and, therefore, reaction is symmetry-allowed.

(iv) **(2*s*+2*s*+2*s*) thermal process** given below is a thermally allowed process, because total number of $(4q+2)_s$ and $(4r)_a$ is three here. $(4r)_a$ is zero here.



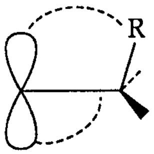
(v) **(2*a*+2*a*+2*a*+2*a*) cycloaddition** given below is symmetry allowed photochemically in which each one of participating ethylene unit has singly occupied antibonding orbital.



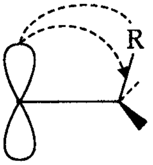
Here total number of $(4q+2)_s$ and $(4r)_a$ components is zero. This type of examples are very rare. This type of $(\pi^2 s+\pi^2 s+\pi^2 s+\pi^2 s)$ cycloadditions can be regarded as $(\pi^2 a+\pi^2 a+\pi^2 a+\pi^2 a)$ process, because $\pi^2 s+\pi^2 s$ is equivalent to $\pi^2 a+\pi^2 a$.

(vi) **Suprafacial [1, 3]-sigmatropic rearrangement** with inversion at migrating centre may also be accepted as symmetry-allowed $(\pi^2 s+\sigma^2 a)$ or $[\pi^2 a+\sigma^2 s]$ change.

(vii) **[1, 3]-Sigmatropic shift** within a cation cannot take place with inversion of migratory group, because $(\omega^0 a+\sigma^2 s)$ and $(\omega^0 a+\sigma^2 a)$ process are symmetry forbidden.

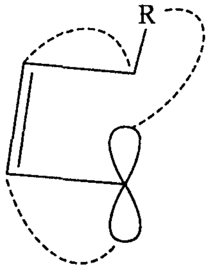


$(\omega^0 a + \sigma^2 s)$-process

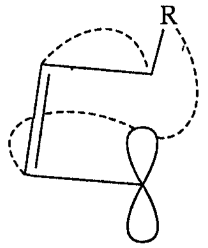


$(\omega^0 s + \sigma^2 a)$-process

(viii) **Suprafacial [1, 4]-sigmatropic shift** with inversion at migratory centre may be considered symmetry-allowed $[\pi^2 a+\omega^0 a+\sigma^2 a]$ process. There is allowed suprafacial process in which R migrates with retention. For instance, $\pi^2 s+\omega^0 s+\sigma^2 s$ pericyclic reaction is symmetry-forbidden.

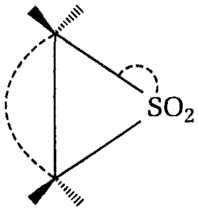


$(\pi^2 a + \omega^0 a + \sigma^2 a)$-process

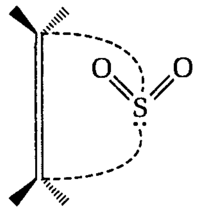


$(\pi^2 s + \omega^0 s + \sigma^2 s)$-process

(xi) **Non-linear cheletropic expulsion of SO_2** from episulfone is symmetry-allowed $(\sigma^2 s+\sigma^2 a)$ process; reverse of which is $(\pi^2 s+\omega^2 a)$-process.



$(\sigma^2 s + \sigma^2 a)$-process



$(\pi^2 s + \omega^2 a)$-process

These generalized rules should be used with following precautions :

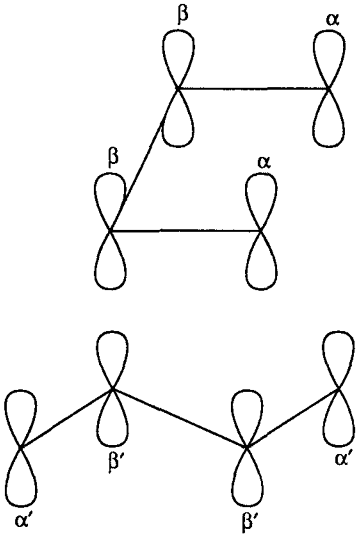
(a) Geometry of each individual case must be examined on its merits in order to ascertain whether process is physically realizable.

(b) In cases in which the reacting components are directly joined by non-participating bonds, forced ancillary off-circuit antibonding

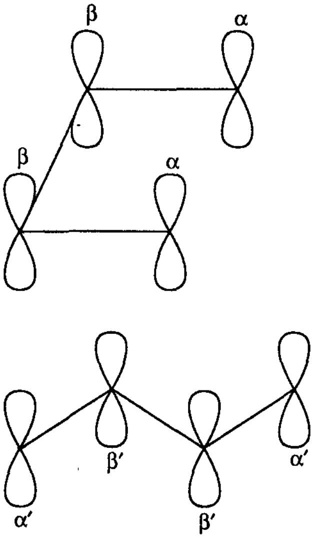
> interactions may render an otherwise allowed reaction symmetry-forbidden."
> —Woodward and Hoffmann

7.5 SECONDARY EFFECTS

Orbital symmetry concepts can be used to explain the origin of secondary conformational effects in concerted cycloaddition reactions. Let us explain Diels-Alder reaction which is $\pi^4 s+\pi^2 s$ cycloaddition. *Endo*-approach can be differentiated from *exo*-approach. In *endo*-approach there is proximity of a β-and a β′-orbital. "**Any secondary interaction among occupied dienes and dienophile molecular orbitals will contribute only in a minor way to the total energy of transition state, since such an interaction will increase the energy of some levels while decrease the energy of others**". Significant interaction arises by symmetry allowed mixing of occupied and unoccupied energy levels.



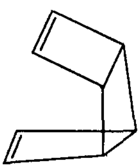
endo-Approach



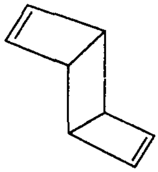
exo-Approach

Possibility of such mixing results in bonding, *i.e.*, lowering of energy by the interaction of proximate β and β′ orbitals as in *endo*-approach, therefore, its transition state is stablized in comparison to *exo*-approach by symmetry-controlled **secondary orbital interaction.**

In dimerization of cyclobutadiene examination of secondary orbital interaction reveals that *endo*-approach leads to *syn*-dimer in contrast to *exo*-approach which provides *anti*-dimer.

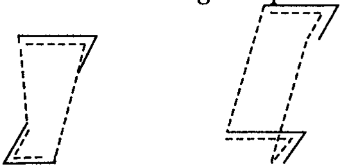


syn-dimer



anti-dimer

Orbital symmetry arguments are also applicable to sigmatropic-shifts. The [3, 3]-sigmatropic shift of 1, 5-hexadienes proceeds more easily through four-centered chair-like transition state rather than through boat-like. Orbital symmetry plays a major role in determining this preference.



Chair-like T.S. Boat like T.S.

A correlation diagram for molecular orbitals involved in this rearrangement is given below :

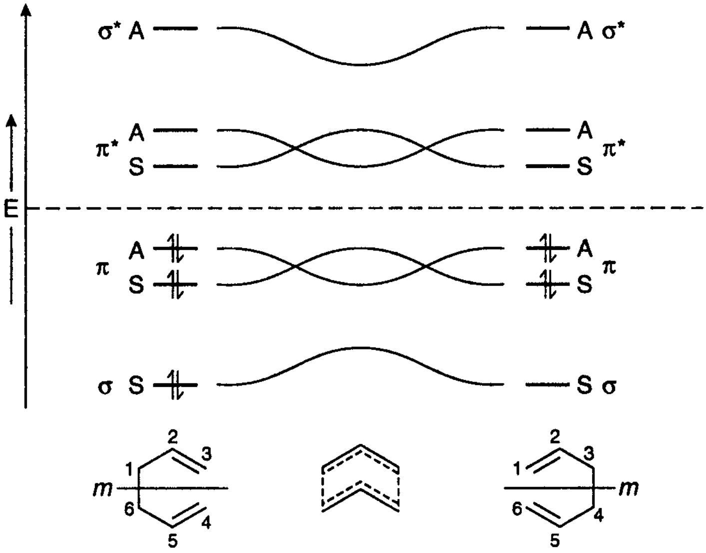
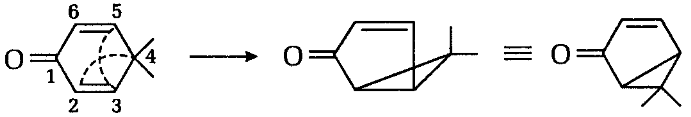


Fig. 7.9. Correlation diagram for [3,3] sigmatropic shift in 1,5-hexadiene.

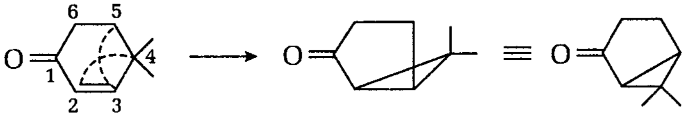
The M.O. levels are symmetric or antisymmetric w.r.t. mirror plane *m* in boat-like transition state or C_2-axis in chair like T.S. The correlation of reactant bonding levels with product bonding levels indicates process is symmetry allowed under thermal conditions. At half-way in the reaction level ordering is as two strongly interacting allyl radicals.

7.6 [2 + 2]-CYCLOADDITIONS IN THE PHOTOCHEMISTRY OF THE CYCLOHEXADIENONES AND CYCLOHEXENONES

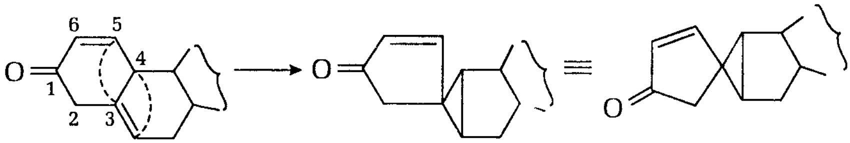
This primary isomerization process is of three types :



Class (I)



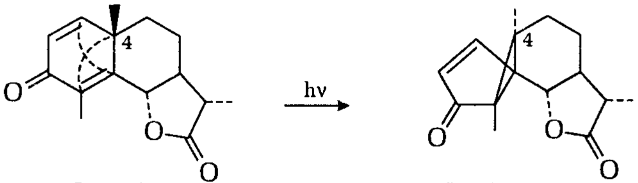
Class (II)



Class (III)

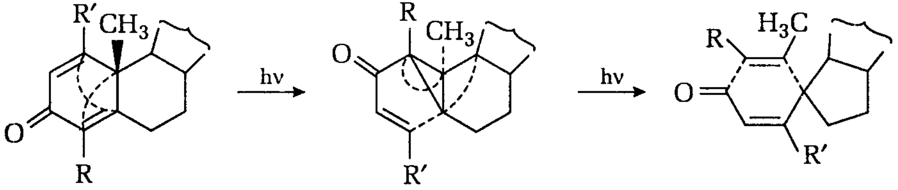
All the above reactions are ($\sigma^2 + \pi^2$)-cycloadditions. If they are concerted within excited states, they should be ($\sigma^2 s + \pi^2 s$) or ($\sigma^2 a + \pi^2 a$)-cycloadditions. In class(I) and (II), suprafacial participation of double bond 2, 3 is stereochemically impossible as it leads to *trans*-fused three-membered and five-membered rings. Hence, reaction must follow ($\sigma^2 a + \pi^2 a$)-path for which antarafacial addition to 2, 3-double bond is needed alongwith inversion at $C-4$. In class (III) both ($\sigma^2 a + \pi^2 a$) as well as ($\sigma^2 s + \pi^2 s$)-paths are possible.

During conversion of santonin to lumisantonin **antara**-addition at double bond occurs alongwith inversion at the migrating saturated carbon atom. In this conversion alternative symmetry-forbidden change will occur with retention at $C-4$ and will lead to sterically-forbidden *trans*-ring fusion. Therefore, path of the reaction will be decided by the geometry of the system.



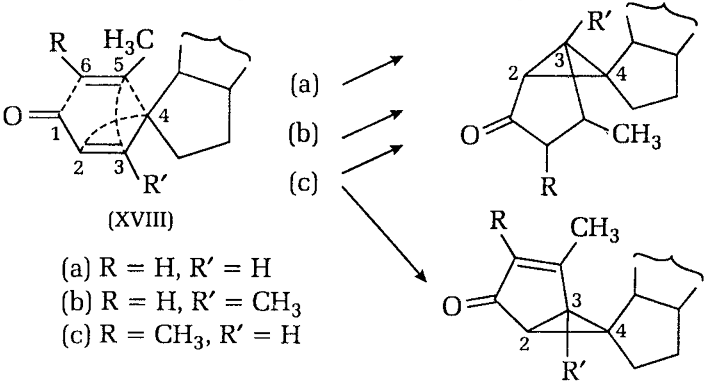
Santonin Luminsantonin

Photochemistry of 1-dehydrotestosterone acetate and its methyl derivatives begins with conversion of 2, 5-cyclohexadienones (XVI) into a bicyclo [3.1.0] hexenone (XVII) and then to new cyclohexadienone (XVIII) of assigned stereochemistry.



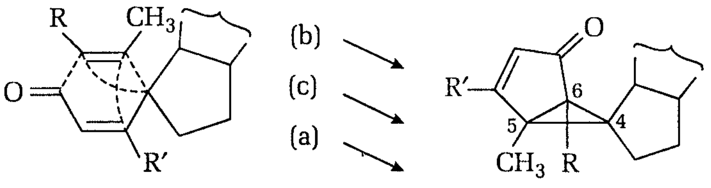
(XVI) (XVII) (XVIII)

On further photolysis (XVIII) yields two or three isomers, depending upon pattern of substitution. The products have been assigned structures (XIX)–(XXI).



(XVIII)

(a) R = H, R′ = H
(b) R = H, R′ = CH_3
(c) R = CH_3, R′ = H

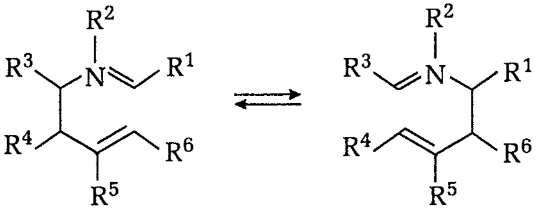


(XVIII) (XXI)

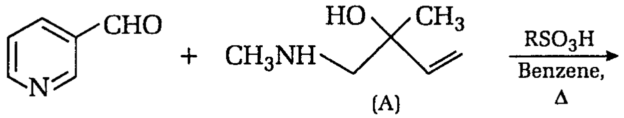
Above three products are results of $(\pi^2 a+\sigma^2 s)$-cycloadditions. Inversion at $C-4$ should occur during photoisomerizations. For substitution pattern (a) and (c) one product (XIX) from symmetry-allowed changes at 2, 3-double bond is formed. From (a) and (c) other product is (XXI). In case (b) all the three products (XIX)–(XXI) are formed from symmetry-allowed processes.

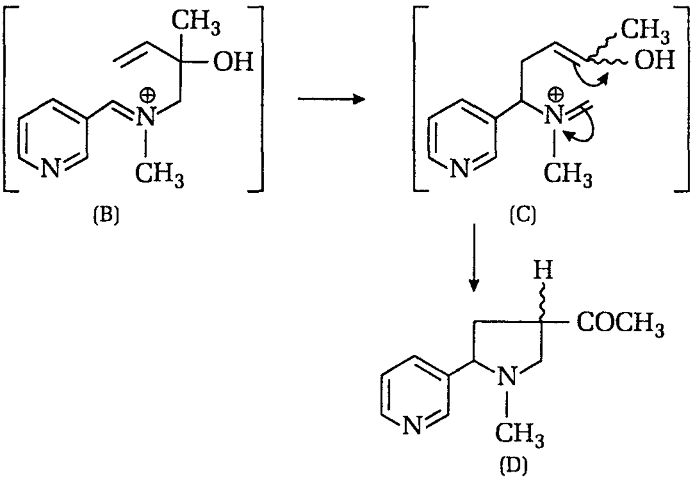
7.7 AZA-COPE REARRANGEMENT

Rearrangements of the compounds like N-allylic enamines $R_2C{=}CRNRCR_2CR{=}CH_2$, $ArNHCH_2CH{=}CH_2$, allylic iminoesters $RC(OCH_2{-}CH{=}CH_2){=}NR$ (these has often rearranged with transition metal catalysis), and of $RCH{=}NRCHRCH_2CH{=}CH_2$ are possible. **These rearrangements of nitrogen containing compounds are often called aza-cope rearrangements.** An example of aza-cope rearrangement is that of 4-butenyliminium ion as given below :



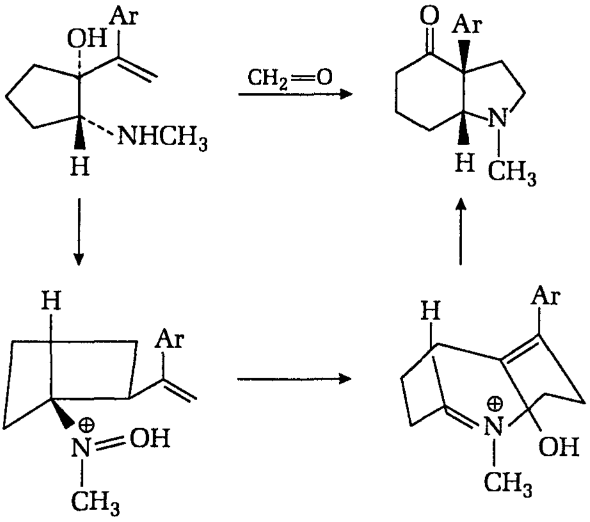
This carbon-carbon bond forming reaction takes place in mild condition. This reaction is not of much synthetic utility because of its reversible nature. However, reaction involving a properly placed —OH group or alkyl group at $C-3$ of butenyl group (for example, R^4 = —OH in above example) proceeds in forward direction is of much synthetic utility; this reaction involves intramolecular Mannich reaction through the capture of rearranged iminium salt and is excellant route for the synthesis of 2-substituted pyrrolidine derivatives. Thus, pyridine-3-aldehyde when heated in benzene solution with N-methyl-2-hydroxy-buteneamine (A) in presence of an acid catalyst (*e.g.*, camphor sulphonic acid) gives acetylnicotine derivative (*D*) in good yield (84%). The initial salt (*B*) rearranges to (C) which is irreversibly trapped in an intermolecular Mannich reaction to give (D) [Scheme 7.6].





Scheme 7.6

When —OH and —NH_2 groups are neighbouring substituents on the ring a bicyclic pyrrolidine derivative is formed. During the conversion original ring is expanded by one carbon. If —OH and —NH_2 groups are *cis* to each other in reactant, the reaction proceeds with high degree of stereospecificity and product is *cis*-fused bicyclic compound. Reaction with *trans* hydroxy amine is not so stereoselective. Both of above reactions are useful in the synthesis of natural products (Scheme 7.7).



Scheme 7.7

UNIT 8

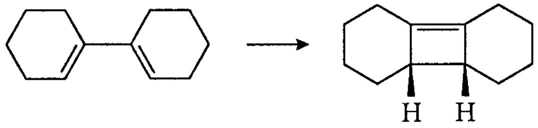
PROBLEMS AND SOLUTIONS

8.1 ELECTROCYCLIC REACTIONS

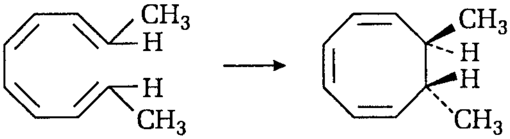
PROBLEMS

1. Predict if the following reactions proceed in conrotatory or disrotatory manner :

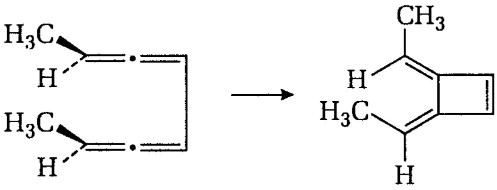
(a)



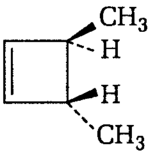
(b)



(c)

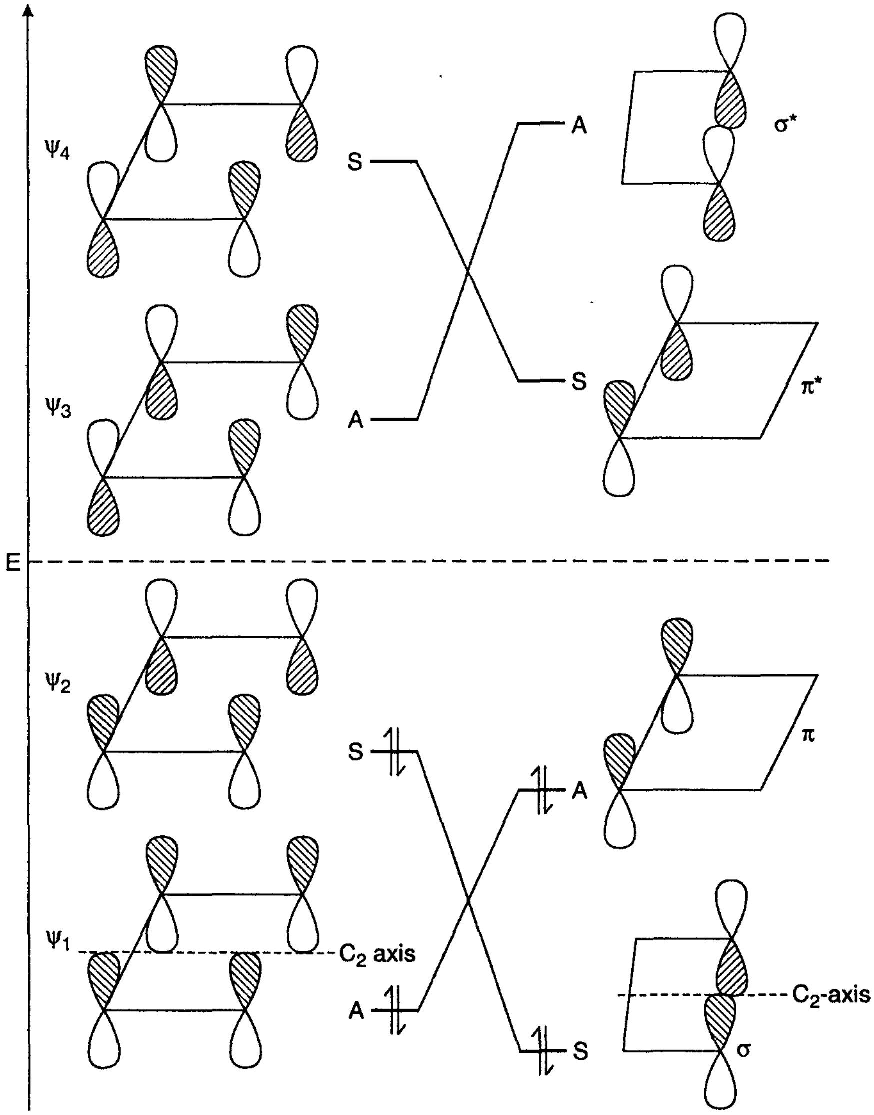


2. In question 1(a), 1(b) and 1(c) show if the reaction is thermally feasible or photochemically feasible.
3. In cyclobutene given below ring can open by two conrotatory modes. Predict the product in each case and also if two isomers must form is equal amounts?



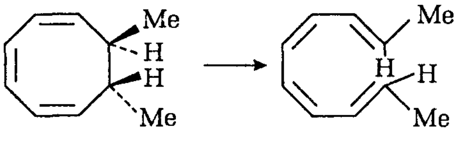
Cyclobutene

4. Discuss the rules for the construction of correlation diagrams. What precautions you will take during the process?
5. Predict reaction conditions and stereochemical mode from following correlation diagram.

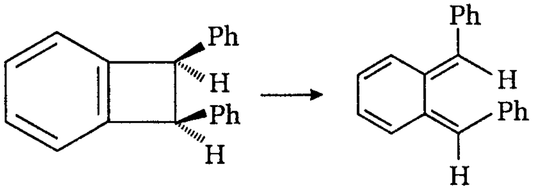


6. Draw correlation diagram for disrotatory interconversion of 1, 3-butadiene $\rightleftharpoons$ cyclobutene. Also decide if reaction is thermally allowed or photochemically feasible.
7. Predict reaction conditions for conrotatory and disrotatory interconversion of 1, 3, 5-hexatriene $\rightleftharpoons$ cyclohexadiene through correlation diagram method. Also write which symmetry is being conserved under which process.
8. Decide stereochemical modes for following transformations. Also, write the reaction conditions in each case.

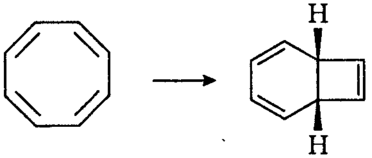
(a)



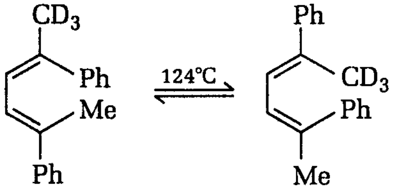
(b)



(c)

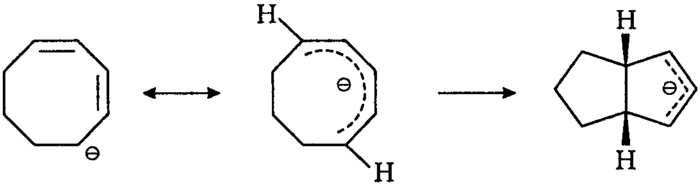


9. Butadienes (*A*) and (*B*) can be readily interconverted under thermal condition. Propose reaction mechanism for this interconversion.

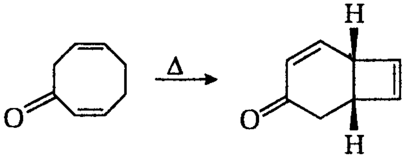


(A) (B)

10. Cyclo-octadienyl anion undergoes thermal ring closure. Explain.

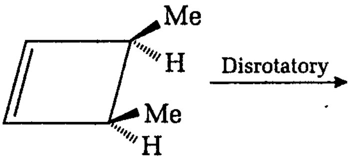


11. Discuss the mechanism of following electrocyclic reaction.

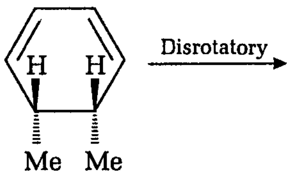


12. Two electrocyclic reactions are given below :

(a)



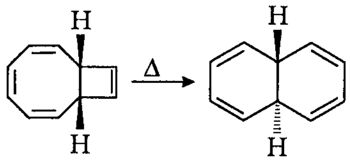
(b)

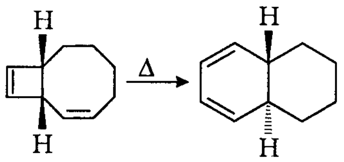


Predict the products formed with reasons.

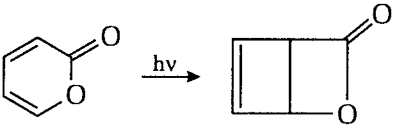
13. What will be the stereochemical course for thermal cyclization of (a) pentadienyl anion (b) pentadienyl cation?

14. Write down the mechanism for following electrocyclic reactions under thermal conditions :

(a) 

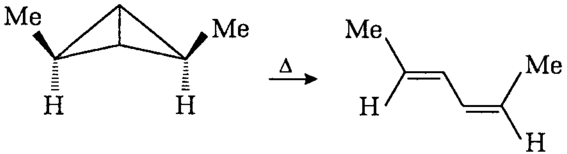
(b) 

15. Explain how α-pyrone undergoes photolytic ring-closure; also predict stereochemical structure of product :

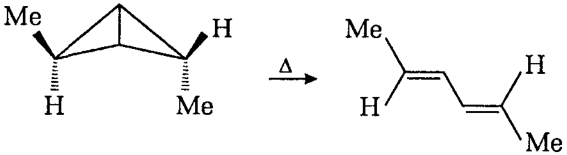


(A)

16. Following cycloreversions have been observed on thermolysis. Assuming these to be concerted reactions, show these are $\sigma^2 s + \sigma^2 a$ process :

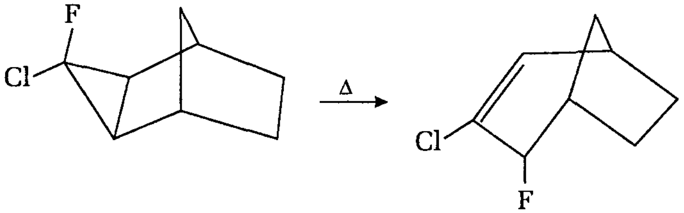
(a) 

Trans-cis

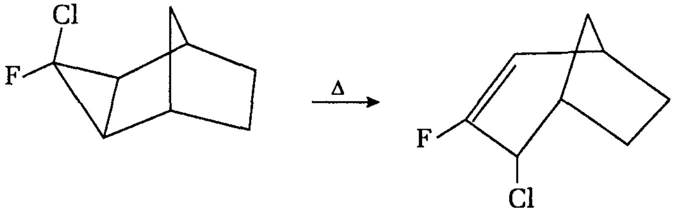
(b) 

Trans-trans

17. Suggest mechanism for following pyrolysis :

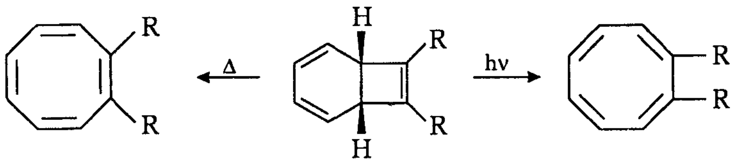
(i) 

(A) (C)

(ii) 

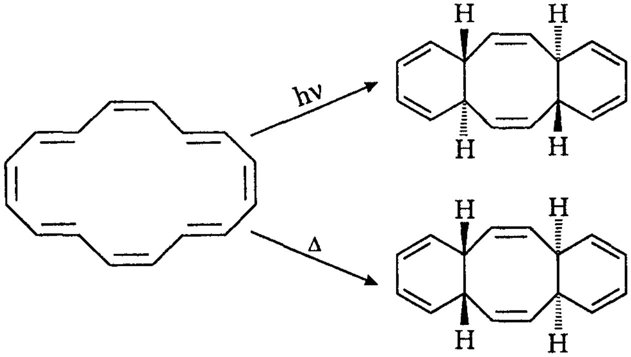
(B) (D)

18. How compound (i) can give (ii) and (iii) under thermal and photochemical conditions, respectively? Are they same or different?

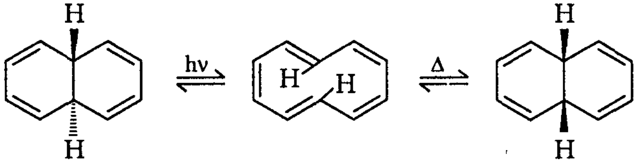


(ii) (i) (iii)

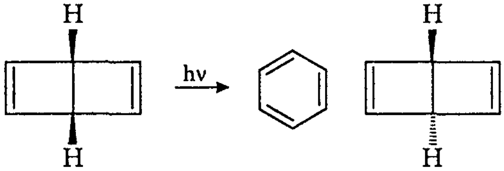
19. Explain the following isomerization of 16-annulene.



20. Suggest a mechanism for each of the following steps :



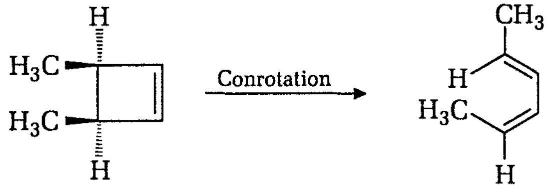
21. Dewar benzene [*cis*-bicyclo (2.2.0) hexadiene] undergoes thermal isomerization to benzenoid system with activation energy 37 K cal/mole, although the strain energy in the ring system (relative to benzene) is as high as 60 K. cals per mole. Explain and compair its stability with that of hypothetical *trans*-isomer.



Cis *Trans*

22. Whether following electrocyclic reactions are feasible thermally or photochemically :

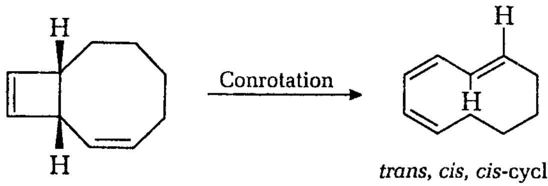
(a)



Cis, 3,4-dimethyl-cyclobutene

Cis, trans-2,4-hexadiene

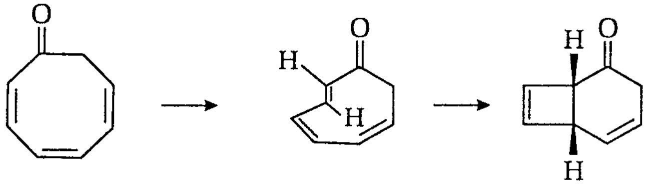
(b)



cis, bicyclo-[6.2.0] deca-2,9-diene

trans, cis, cis-cyclodeca-1,3,5-triene

(c)



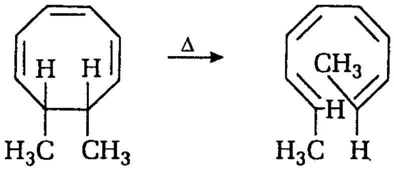
Cis, cis, cis-2,4,6-cyclooctatrienone

trans, cis, cis-2,4,6-cyclooctatrienone

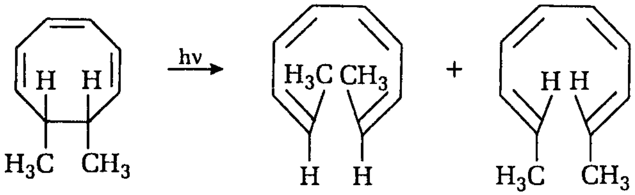
cis-bicyclo [4,2,0]-octa-4,7-dien-2-one

23. Predict whether following ring-openings will be conrotatory or disrotatory :

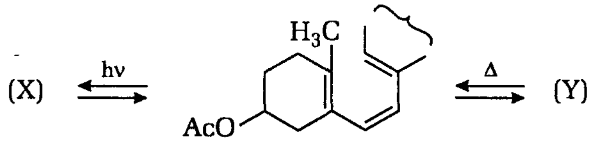
(a)



(b)



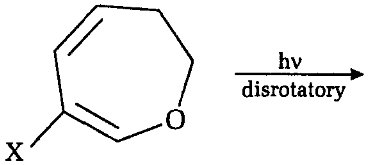
24. Predict the products of following ring closures :



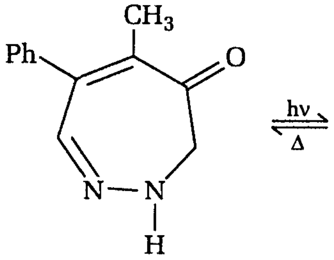
(A)

25. Show the products of following transformations :

(a)

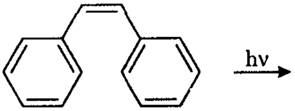


(b)

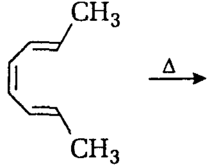


26. What will be the products in following ring closures :

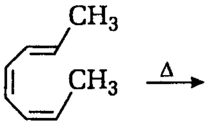
(a)



(b)

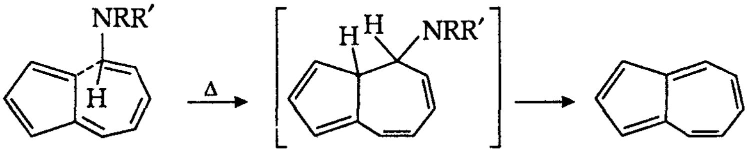


(c)

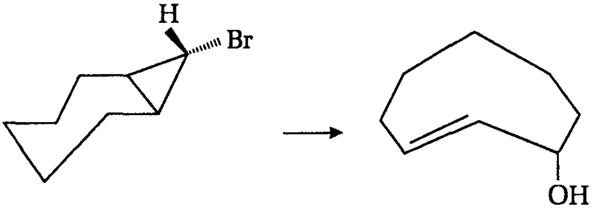


27. Explain following transformations :

(a)

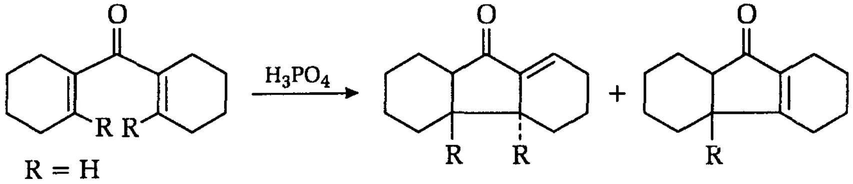


(b)

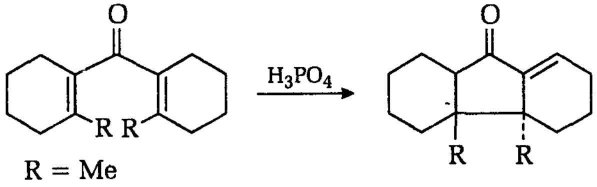


28. Predict mode of rotation :

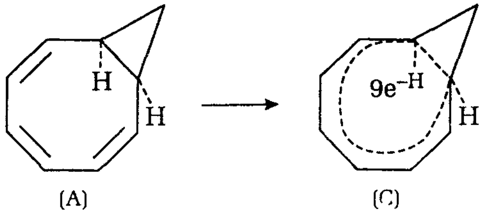
(a)

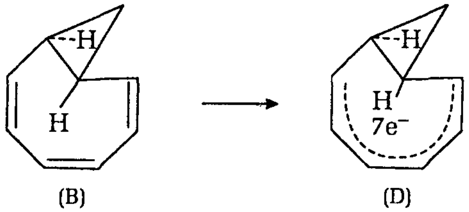


(b)

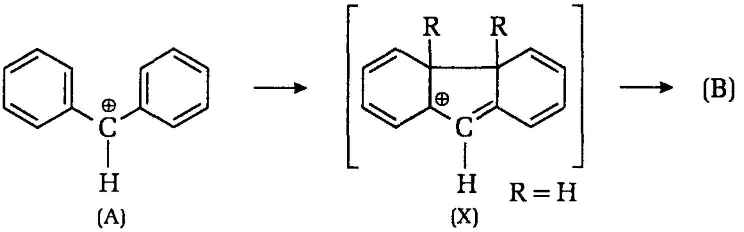


29. If following conversion paths are conrotatory or disrotatory when one electron is added to (*A*) and (*B*).



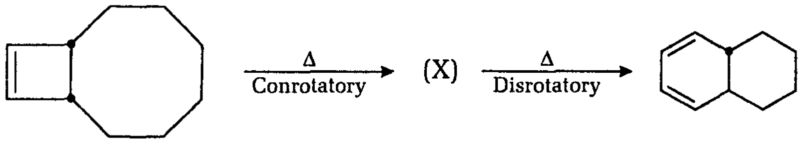


30. Predict the product of following symmetry allowed process :

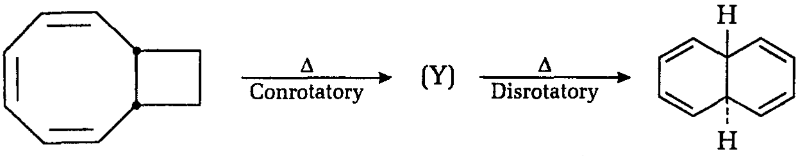


31. Write the intermediates in following transformations :

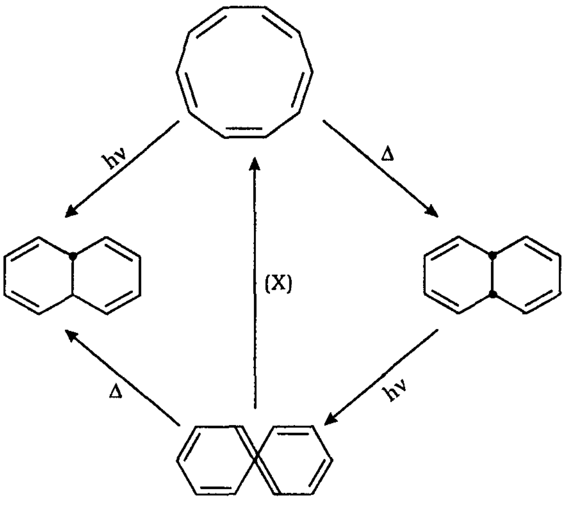
(a)



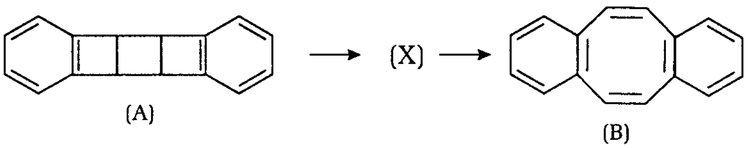
(b)



32. Write mode (X)

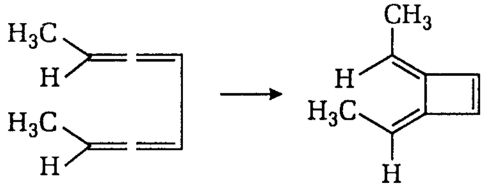


33. Write the intermediate for following electrocyclic reaction is presence of silver catalyst :

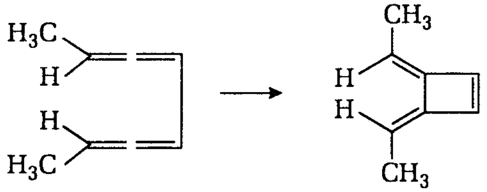


34. How many electrons are involved in the following electrocyclic processes :

(a)

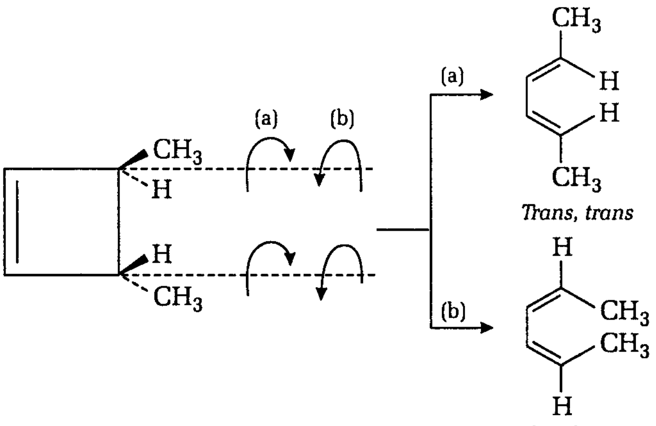


(b)



Solutions (Electrocyclic Reactions)

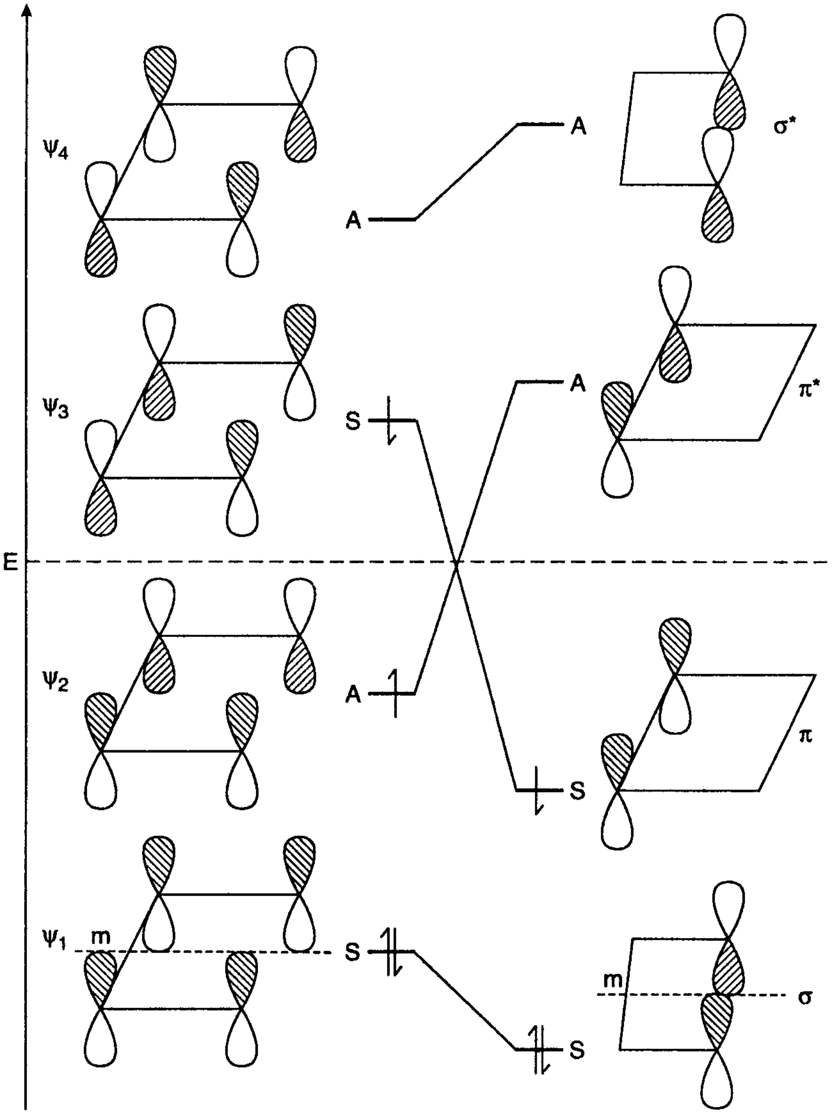
1. (a) Disrotatory, (b) Conrotatory, (c) Conrotatory
2. (a) Photochemically feasible, (b) Thermally feasible, (c) Thermally feasible
3. Two conrotatory modes of ring opening in the cyclobutene are (a) and (b) :



Process (a) leads to *trans-trans*-product, whereas, (b) results in *cis, cis*-product. Steric repulsion is there in the transition state for *cis, cis*-product, therefore, transition state for *trans,-trans*-product will be more stable. Hence, formation of *trans-*, *trans*-product will be favoured and it will be in larger amount.

4. See Unit III, *p*-24 to 28.
5. As correlation is taking place in ground state reaction is thermally feasible. Furthermore, c_2-axis of symmetry is being conserved, therefore, process is conrotatory process.

6. Correlation diagram for disrotatory 1, 3-butadiene $\rightleftharpoons$ cyclobutene interconversion is given below :



As correlation while conserving orbital symmetry is feasible is excited state, reaction is feasible under photochemical conditions while proceeding in concerted manner.

7. Please see Unit IV, *p*-40 to 42.

8. Predictions about stereochemical mode can be made on the basis of FMO as well as PMO-methods.

   (a) (i) **FMO-method** : HOMO of open-chain partner is ψ_4 with three nodes and c_2-axis of symmetry. Therefore, reaction follows conrotatory path under thermal conditions or in ground state. Upon irradiation one electron jumps from ψ_4 to ψ_5 which has mirror plane-symmetry. Hence, under photochemical conditions as HOMO has *m*-symmetry reaction follows disrotatory path. Structure of product-reveals that it is the product of conrotatory ring opening, therefore, reaction is symmetry allowed under thermal conditions.

(ii) **PMO-method** : The structure of product shows, it is a case of conrotatory ring-opening. The T.S. has 8-electrons, one node and is aromatic. Therefore, reaction is thermally allowed.

Same conclusion is reached by selection rule.

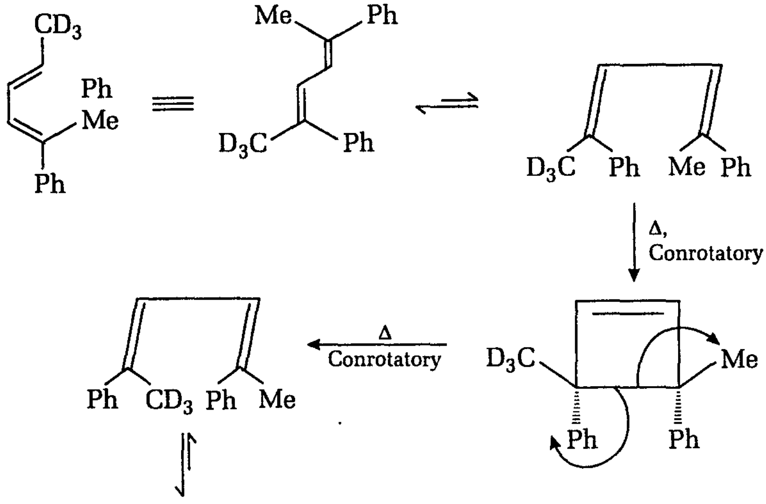
(b) (i) **FMO-method** : In this problem ring-opening is conrotatory process as HOMO of open chain partner is ψ_2 with c_2-symmetry. Hence, reaction is thermally feasible.

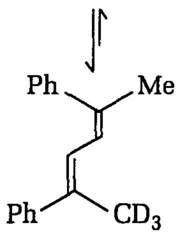
(ii) **PMO-method** : T.S. for ring opening with four electrons and one node is aromatic. Hence, reaction is thermally allowed by conrotatory process.

(c) (i) **FMO-method** : Reaction can be visualized in two ways. First a disrotatory ring-closure of two butadiene moieties to give *cis*-product which is photochemically allowed. Secondly, it is disrotatory ring-closure of 1, 3, 5-hexatriene to give same *cis*-product which is thermally allowed.

(ii) **PMO-method** : In first case T.S. involves four electrons without any node and is therefore antiaromatic making the reaction photochemically allowed. In case second T.S. involves 6 electrons, without any node, is therefore aromatic and therefore reaction proceeds under thermal conditions.

9. Both the steps are symmetry-allowed under thermal conditions, because HOMO of each of them possess c_2-axis of symmetry. Interconversion proceeds through cyclic-structure. Both, ring-closure as well as ring-opening

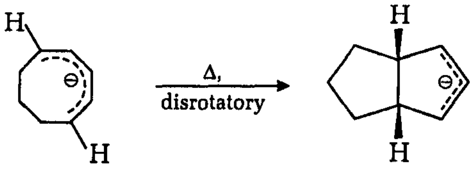




Mechanism of interconversion
of (A) to (B)

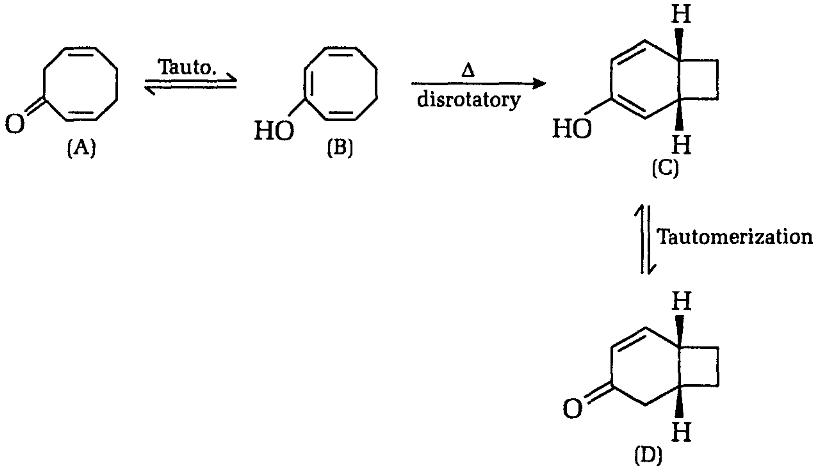
are conrotatory. It is worthnoting that CD_3 and Me groups never become *cis* in diene regardless of number of ring-closure and ring opening during the interconversion.

10. This is a pentadienyl system. Here disrotatory ring-closure is symmetry allowed under thermal conditions.

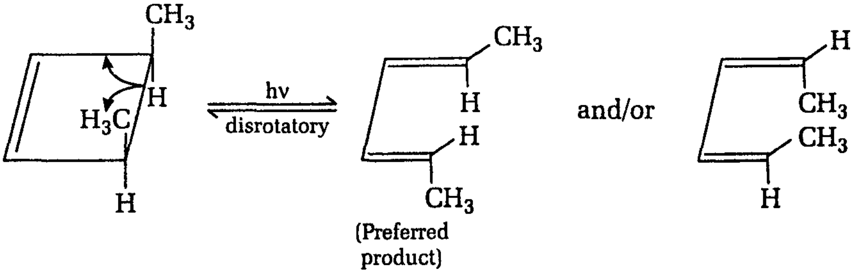


11. Following mechanism can be written for this transformation :

First keto-enol tautomerization takes place to give 1, 3, 5-hexatriene system which undergoes disrotatory ring closure under thermal conditions to give *cis*-fused ring system (c). (c) upon keto-enol tautomerization gives the product (*D*). As HOMO of 1, 3, 5-hexatriene moiety is ψ_3 with mirror plane symmetry cyclization proceeds is disrotatory manner. T.S. for disrotatory ring closure involves 6-electrons with 0-node and is therefore aromatic. Thus reaction is thermally allowed.

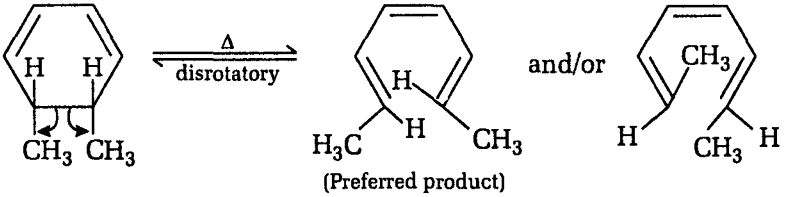


12. **(a)** In this cyclobutene system preferred mode of rotation can be shown by arrows as given below :



Preferred product is that in which transition state of formation have minimum steric hinderance.

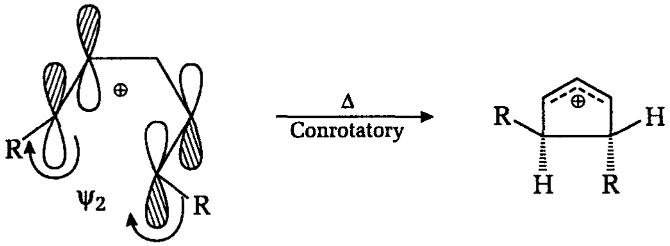
(b) For cyclohexadiene in (b) mode of rotation and preferred products can be as written below :



Reason for the formation of preferred product is again minimum steric repulsion in transition state of its formation which is responsible for its greater stability.

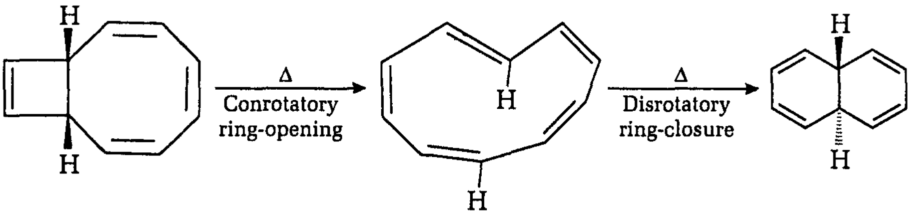
13. **(a)** **Stereochemical course of thermal cyclization of pentadienyl anion :** HOMO of ground state of pentadienyl anion is ψ_3 with *m*-symmetry, therefore, cyclization will follow disrotatory course under thermal conditions. Similar are predictions by PMO method. As transition state for disrotatory ring closure have 6 electrons with zero node, therefore, T.S. is aromatic and reaction is thermally allowed.

(b) **Thermal ring-closure of pentadienyl cation (stereochemical course) :** HOMO of ground state of pentadienyl cation is ψ_2 with c_2-symmetry. Therefore, thermal cyclization will follow conrotatory course.



Similar is prediction by PMO method. Transition state for conrotatory ring closure will involve 4 electrons, one node and is therefore aromatic. As reaction through aromatic. T.S., is thermally allowed, hene, under thermal conditions reaction proceeds by conrotatory mode.

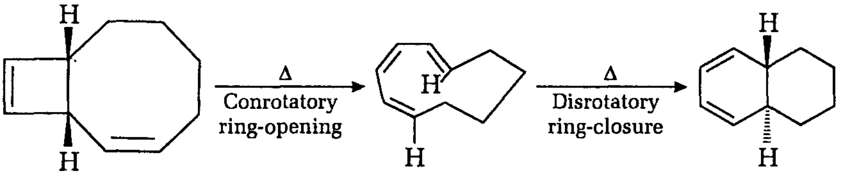
14. **(a)** Following mechanism can be written for this reaction :



10-Annulene

Ring opening will involve conrotatory process whether we take into consideration either cyclobutene or cyclooctatriene moiety. This ring opening will give 10 annulene which spontaneously undergoes disrotatory ring-closure through 1, 3,5-hexatriene moiety to give *trans*-product.

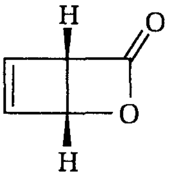
(b) For reaction (b) we can write following mechanism :



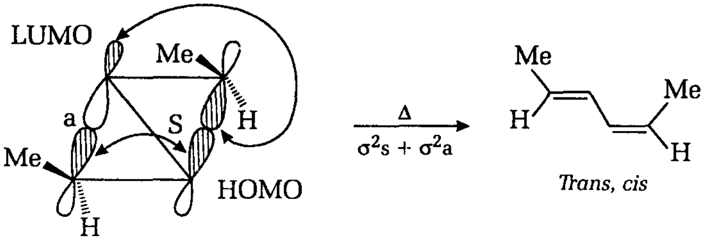
(A)

Ring-opening of this bicyclic compound under thermal conditions will follow conrotatory path to give macrocyclic compound (*A*) which through the involvement of 1, 3, 5-hexatriene moiety will undergo disrotatory ring-closure to give *trans*-product.

15. α-pyron given in problem has 1, 3-butadiene system which under photochemical conditions undergoes disrotatory ring closure, because HOMO of 1, 3-butadiene under excited state is ψ_3 which has similar sings of lobes at terminal ends. Therefore cyclization is disrotatory and product is *cis*.



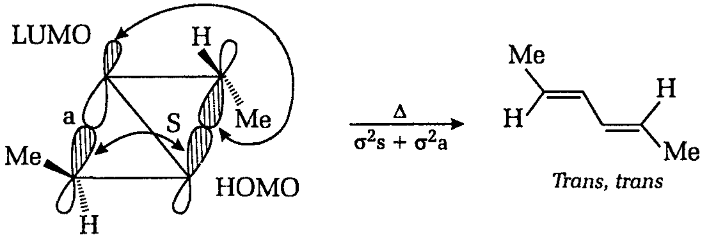
16. **(a)** This cycloreversion can be represented by the following diagram :



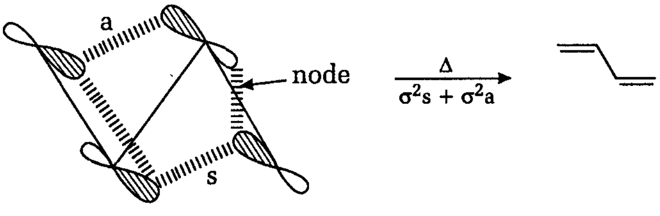
Trans, cis

It is thermally allowed $\sigma^2 s + \sigma^2 a$ process. The σ-bond (HOMO) opens by conrotatory mode and other σ-bond (LUMO) opens up by disrotatory mode to give *trans-cis*-isomer.

(b) Diagramatic representation of this cycloreversion is given below :

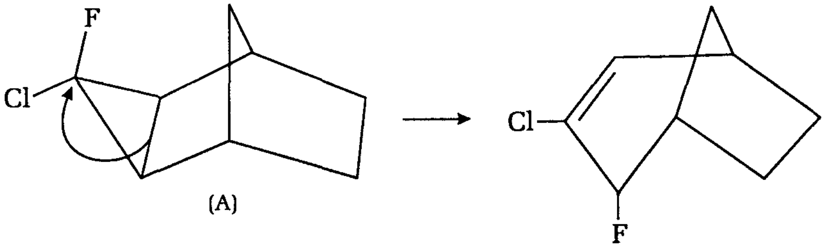


This is also $\sigma^2 s + \sigma^2 a$ thermal cycloreversion on the same grounds as (a). Furthermore, transition state is these cycloreversions has 4 electrons, 1 node and is aromatic. Therefore, reactions are thermally allowed.



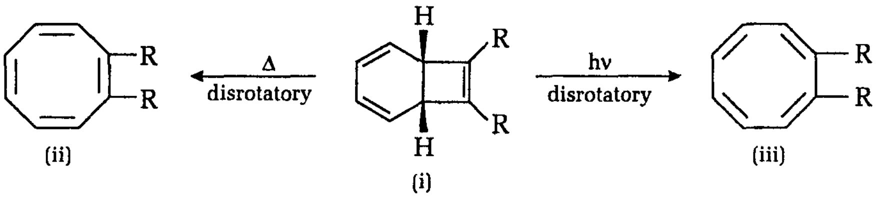
T.S.

17. Let us suppose that back-side attack of the opening σ-bond electrons on the halogen-bearing carbon takes place. If opening of the σ-bond is towards bridge, we shall get a cycloheptene system with *trans* double bond. First chlorine atom will be expelled and then will recombine at the adjacent position. On the other hand, if ring-opening takes place away from the bridge, fluorine atom is first expelled and then reunites to give cycloheptene system with *cis*-double bond. Like cyclohexene, cycloheptene system with a *trans*-double bond is very less stable in comparision to *cis*-system. Therefore, mechanism of conversion of (*A*) → (*C*) is as given below :



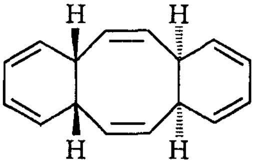
Mechanism of conversion of (*B*) → (*D*) is similar to above mechanism.

18. Compound (i) gives (ii) under thermal conditions by opening of six-membered ring of (i). But, (iii) may be obtained under photochemical conditions by the cleavage of cyclobutene ring. In both cases opening is disrotatory ring opening.

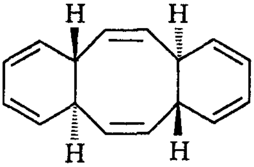


Both (ii) and (iii) are different.

19. 16-Annulene has two 1, 3, 5-hexatriene moieties. Each of the hexatriene moiety cyclizes by disrotatory mode under thermal condition, because HOMO of each of them has same signs at the terminal atoms and have *m*-symmetry. The product is therefore *cis* on each of condensed ring positions.



Under photochemical conditions, both the 1, 3, 5-hexatriene moieties undergo conrotatory ring-closure to give *trans* rings at both the ends.



20. In photochemical process, the cyclohexadiene system must open in conrotatory fashion giving 10-annulene having a 1, 3, 5-hexatriene moiety which undergoes thermal disrotatory ring-closure is a symmetry-allowed process to give *cis*-isomer. FMO and PMO explanations for the processes are given below :

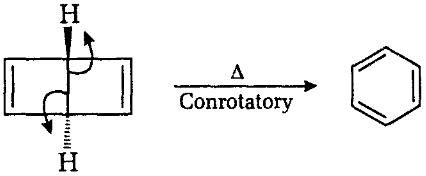
FMO Explanation : In ground state HOMO of 1, 3, 5-hexatriene is ψ_3 having *m*-plane symmetry. Hence, concerted cyclization should be disrotatory. In first excited state HOMO, is ψ_4 with c_2-axis of symmetry, hence, conrotatory ring closure is symmetry allowed under photochemical conditions.

PMO Explanation : For conrotatory ring-opening transition state for the first step has 6-electrons, 1 node and is antiaromatic, therefore, reaction is photochemically allowed. But, transition state for disrotatory ring closure of 1, 3, 5-hexatriene has 6-electrons, 0 node and is aromatic. Therefore, reaction is thermally allowed.

21. Dewar benzene is more stable than expected on the basis of its strain energy, as under thermal conditions. Fission of middle bond gives highly strained molecule cyclohexatriene with *trans*-double bond in the symmetry allowed process. Energy of this system is very high because of strain. But, under photochemical conditions disrotatory ring opening becomes symmetry

allowed and Dewar benzene spontaneously gives benzene. Thermal transformation must be through radicals and requires high energy than conrotatory process.

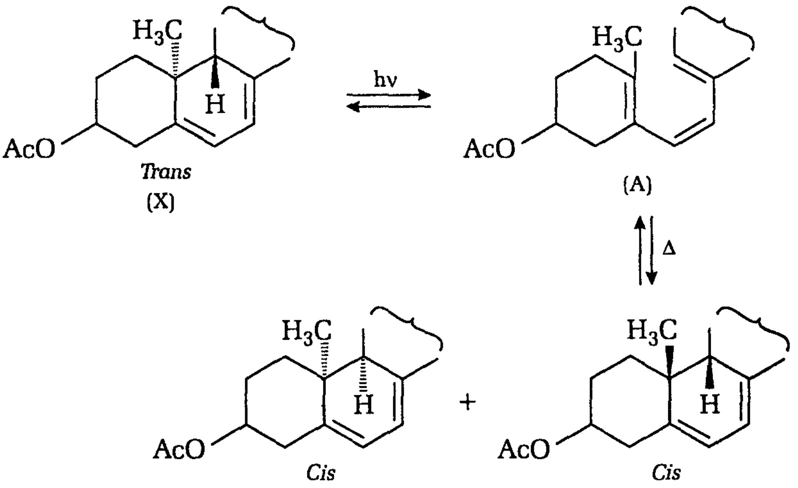
In case of *trans*-isomer conrotatory ring opening is symmetry allowed under thermal conditions giving rise to stable benzene. For this reason derivatives of *trans*-isomer of Dewar-benzene is not known even if they spontaneously undergo conrotatory ring-opening to give benzenoid system of all *cis*-double bond.



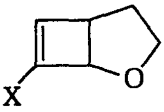
22. (a) Thermally (b) Thermally
(c) Ist step photochemically and 2nd step thermally.

23. (a) Conrotatory (b) Disrotatory

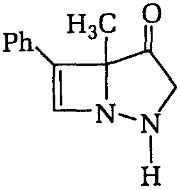
24. (A) undergoes electrocyclic ring-closure on UV-irradiation to form *trans*-product by conrotatory ring-closure. In contrast, on heating (A) yields two *cis*-isomers through disrotatory cyclization.



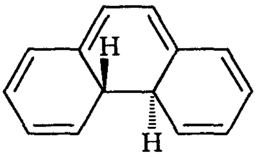
25. (a)



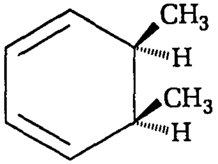
(b)



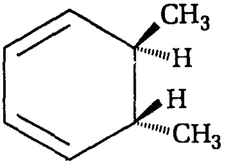
26. (a)



(b)



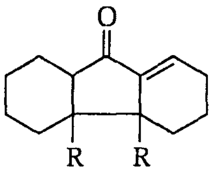
(c)



27. (a) This reaction is Ziegler-Hafner synthesis of azulene. It is ten-electron electrocyclic reaction involving disrotatory cyclization.

    (b) In this reaction solvolysis of exo-8-bromobicyclo [5.1.0] octane gives expected *trans*-cyclooctenol.

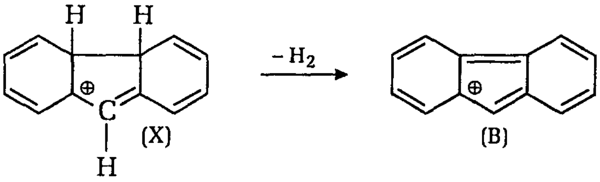
28. In the case (b) conrotatory mode of cyclization has been followed. Irradiation of [*R* = *H*] gives the product by disrotatory cyclization; but with H_3PO_4 conrotatory mode is followed. Product on irradiation of (*a*) is a ketone (*A*).

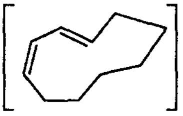
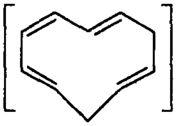


(A)

29. If one electron is added to *cis*-bicyclo [6.1.0] nona-2, 4, 6-triene (*A*) anion radical (*C*) is produced in an symmetry allowed disrotatory geommetrical displacement. One more electron can be added to it to give doubly charged anion. Addition of an electron to (*B*) does not involve delocalization of cyclopropane electrons. Here, steric factor does not permit disrotatory displacement and seven-electron ion radical (*D*) is produced.

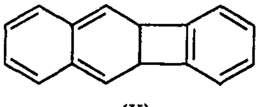
30. Excited state of cation (*A*) undergoes symmetry allowed electrocyclic reaction giving *cis*-product (*X*) which loses hydrogen to give product (*B*) :



31. (a) (X) is  (b) Y is 

32. Photochemical condition.

33. Dibenzotricyclooctadiene (*A*) undergoes thermal isomerization to dibenzocyclooctatetraene (*B*) when heated at 180°C for 4-5 hrs. But, at room temperature, in presence of silver ions, isomerization takes place in 10 seconds. Intermediate (*X*) is first formed in a forbidden disrotatory opening, which is made allowed by the extra orbitals and electrons of metal ions of silver.



(X)

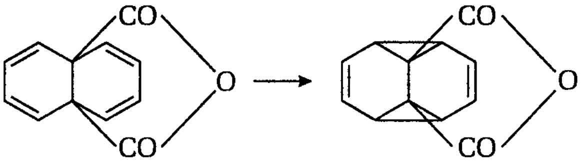
34. Both the reactions are four electron conrotatory electrocyclic processes.

8.2 CYCLOADDITION REACTIONS

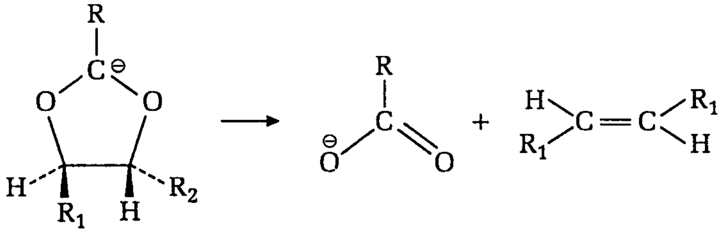
PROBLEMS

1. Predict the product of cycloaddition of ethylene and *cis*-2-butene, addition being suprafacial on both the component. Is the reaction symmetry-allowed under thermal or photochemical condition?
2. Draw correlation diagram for the cycloaddition of two ethylene molecules.
3. Classify the following as [$m+n+$...] cycloaddition reactions :

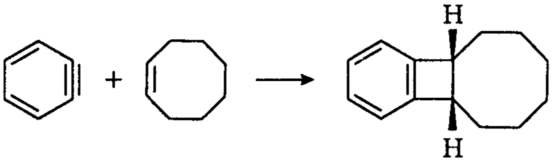
(a)



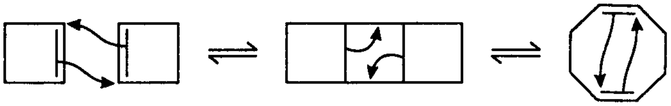
(b)



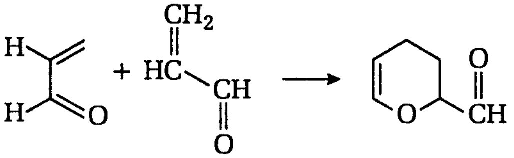
(c)



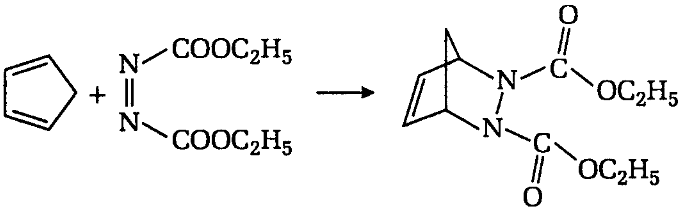
(d)



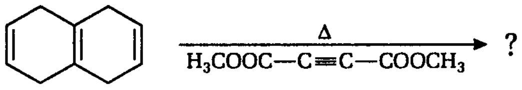
(e)



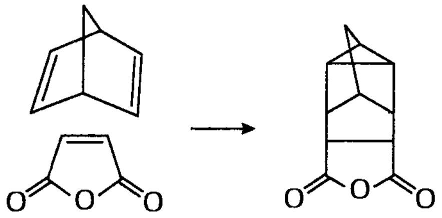
(f)



4. Suggest structure of anticipated products of the reaction of isotetralin with dimethyl acetylene dicarboxylate.

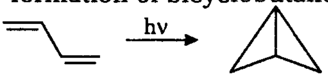


5. Classify the following reaction and predict whether reaction is thermally or photochemically allowed :



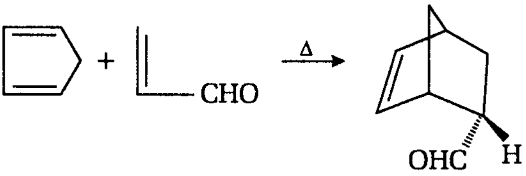
6. Cycloaddition of two molecules of *cis*-2-butene may produce different stereoisomers. Write the structures of (i) *supra-supra* (ii) *supra-antara* and (iii) *antara-antara* products alongwith reaction conditions.

7. Irradiation of butadiene in addition to cyclobutene derivatives also gives bicyclobutanes. Show formation of bicyclobutane is cycloaddition process.

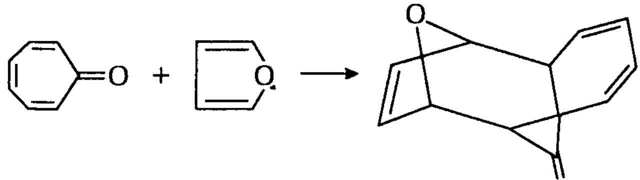


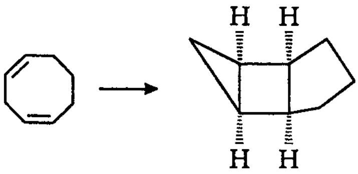
8. Discuss if the following *supra-supra* cycloadditions are thermally allowed or photochemically allowed :
   (a) Pentadienyl cation + ethylene → cycloheptenyl cation.
   (b) Pentadienyl anion + ethylene → cycloheptenyl anion.

9. Thermal cycloaddition between cyclopentadiene and acrolein gives *endo* product as the main product. Explain.

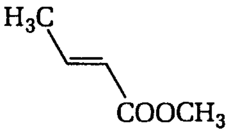


10. Considering following reactions concerted, predict the stereochemical modes involved and classify them.

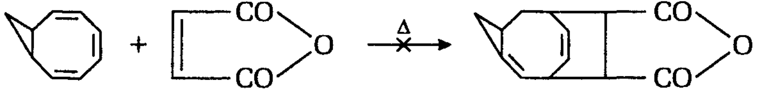
(a) 

(b) 

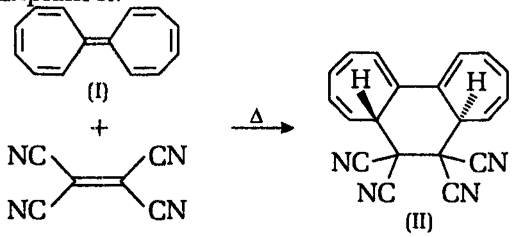
11. How many cyclohexene derivatives are possible from the cycloaddition of following two compounds by the suprafacial addition of each partner. Under kinetically controlled condition which of these may be major product?



12. Observation has been that following $\pi^4 s + \pi^2 s$ cycloaddition does not occur. Explain it.



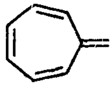
13. Heptafulvalene (I) and Tetracyanoethylene undergo cycloaddition under thermal conditions to give *trans*-product (II) indicating cycloaddition is antara on (I). Explain it.



(I) (II)

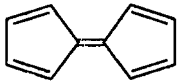
14. Assuming that all the following reactions are concerted and proceed to give symmetry allowed products, predict the stereochemistry of each of the product. Where more than one product is possible by symmetry allowed process, draw all possible products.

(a)



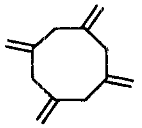
$+ H_3COOC—C \equiv C—COOCH_3 \xrightarrow{\Delta}$ 1 : 1 adduct

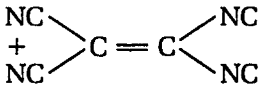
(b)



$+ NC—C \equiv C—CN \xrightarrow{\Delta}$ 1 : 2 adduct

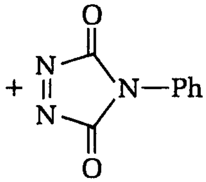
(c)





$+ (NC)_2C = C(NC)_2 \xrightarrow{\Delta}$ 1 : 1 adduct

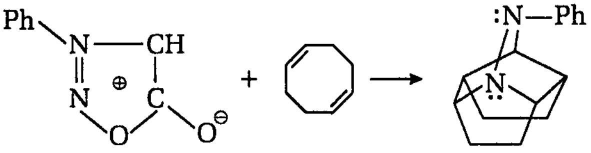
(d)



$\xrightarrow[-78°C]{CH_2Cl_2}$ 1 : 1 adduct containg two conjugated C — C double bonds

15. Thermolysis of cycloheptatriene gives a dimer containing two carbon-carbon double bonds. Suggest a structure for this dimer and a mechanism for its formation.

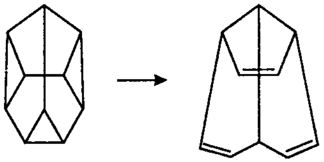
16. Sydnones are mesoionic compounds which display aromatic properties. They may undergo cycloadditions. For example, 3-phenylsydnone (*A*) upon cycloaddition with *cis, cis*-cycloocta-1, 5-diene gives system (*B*). Suggest a symmetry allowed mechanism for this transformation.



(A) (B)

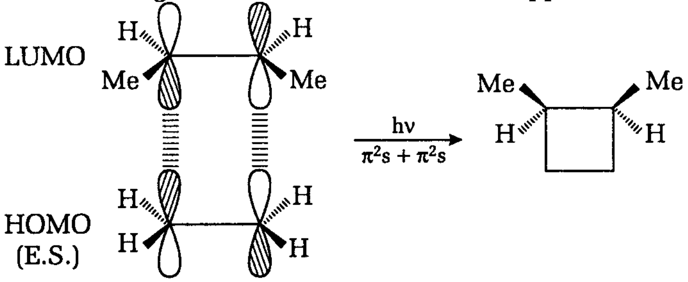
17. Indene with a four times excess of 2-bromofluorobenzene followed by hydrolysis gives a compound (A), $C_{15}H_{10}$. But, when hydrolysis is carried out in D_2O instead of H_2O, molecular formula of product becomes $C_{15}H_9D$. Suggest structure of (*A*) and a mechanism for its formation which is consistent with the deuterium inclusion. What position deuterium occupies in the molecule.

18. Show by PMO method that following cycloreversion is thermally allowed $\sigma^2s+\sigma^2s+\sigma^2s$ process.

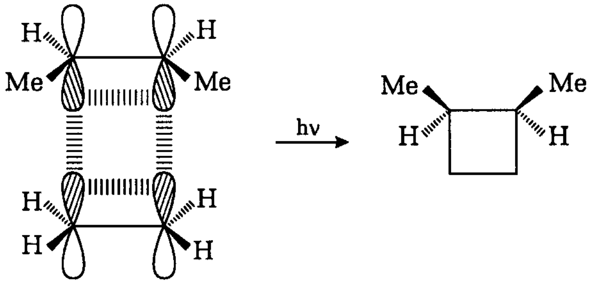


Solutions (Cycloaddition Reactions)

1. (a) **FMO method :** As the reaction is suprafacial on both the components, the product of reaction is *cis*-1, 2-dimethylcyclobutane. This is $\pi^2s+\pi^2s$ process and is symmetry allowed under photochemical condition according to frontier molecular orbital approach.



(b) **PMO-method :** In the transition state of reaction there are four electrons and zero node, therefore, transition state is antiaromatic under thermal condition. Hence, according to PMO method also reaction is photochemically allowed as T.S. for it has 4 electrons, one node and is aromatic.



T.S. : 4 electrons, 0-node, antiaromatic, hν-allowed

2.

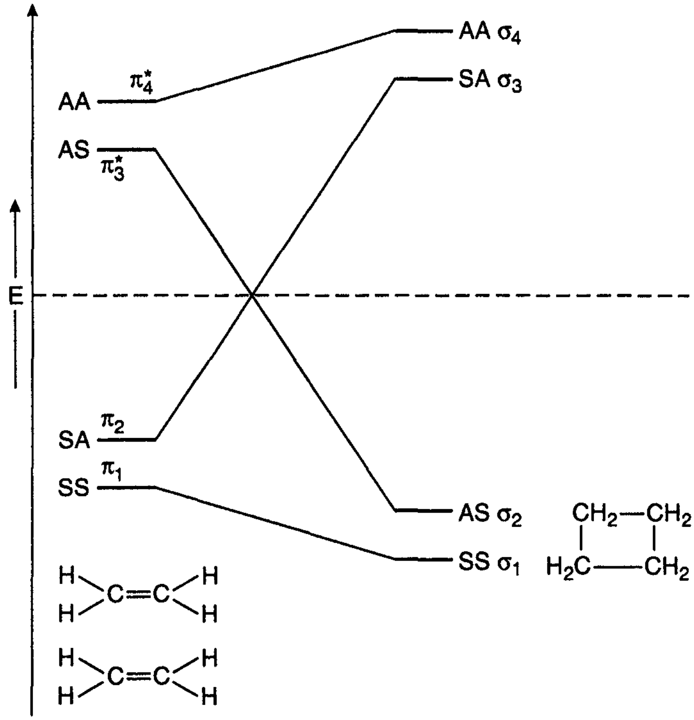
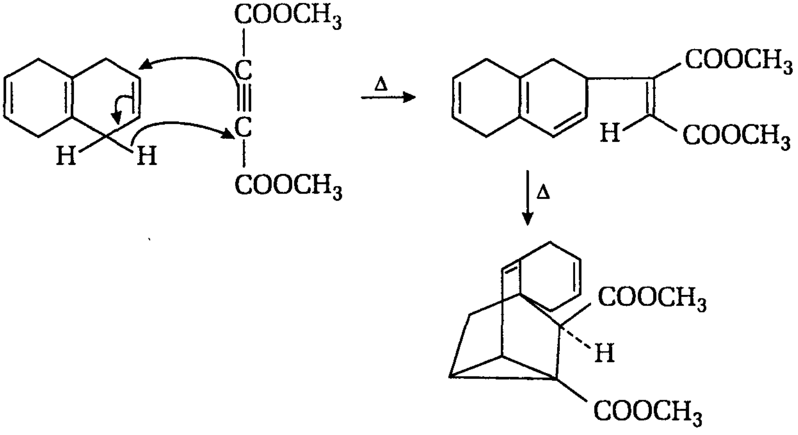


Fig. Correlation diagram for the cycloaddition of two molecules of ethylene.

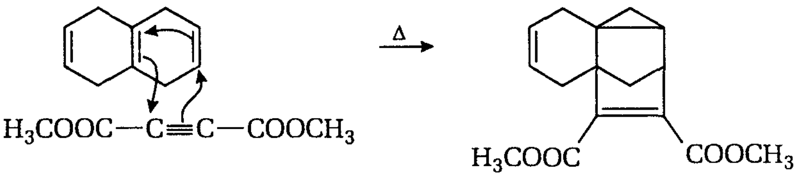
3. (a) (4+4) cycloaddition (b) (4+2) cycloaddition
(c) (2+2) cycloaddition (d) (2+2) cycloaddition
(e) (4+2) cycloaddition (f) (4+2) cycloaddition

4. Following product may be formed :

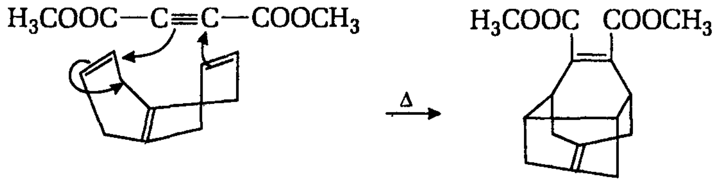


Two other possibilities are given below :

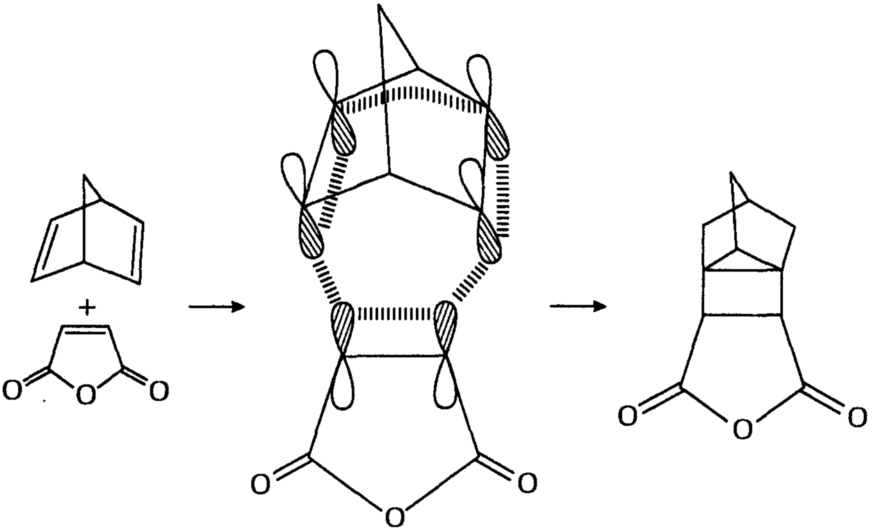
(i)



(ii)

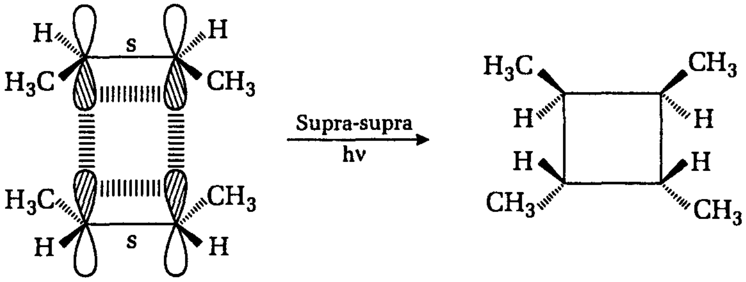


5. Structure of product indicates that this cycloaddition reaction is *supra* on all the three double bonds. It is $\pi^2s+\pi^2s+\pi^2s$ reaction and is thermally allowed. PMO-approach also predicts same thing as it proceeds through 6-electron, 0-node, aromatic transition state.



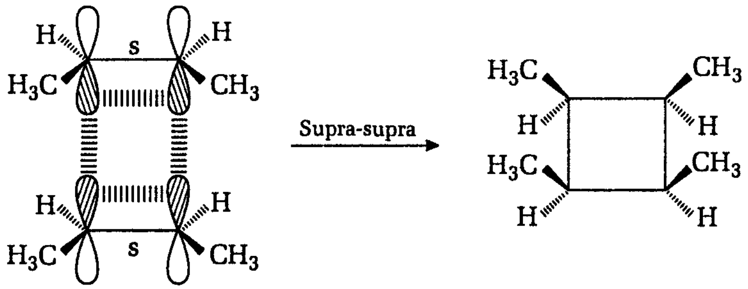
6. (i) Components can add to each other in *supra-supra* mode in following two ways :

(a)



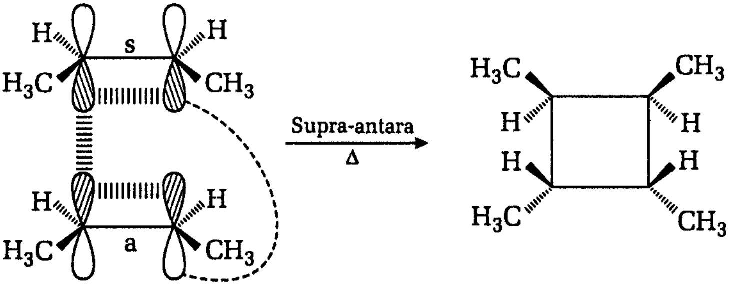
T.S.; 4 electrons, 0 node, antiaromatic; photochemically allowed

(b)



T.S. four electrons, 0-node antiaromatic; photochemically allowed

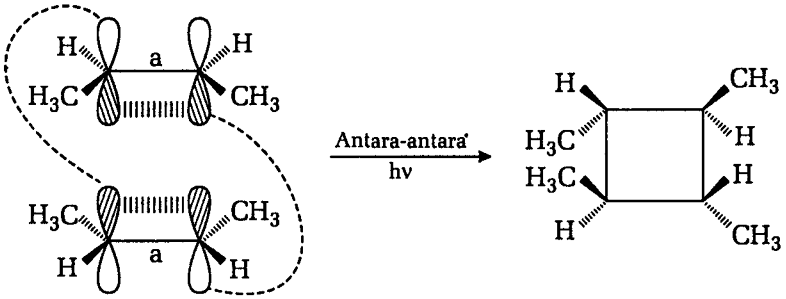
(ii) In *supra-antara* fashion ($\pi^2s + \pi^2a$) molecules may add as given below :



T.S.; 4 electrons, one node, aromatic thermally allowed

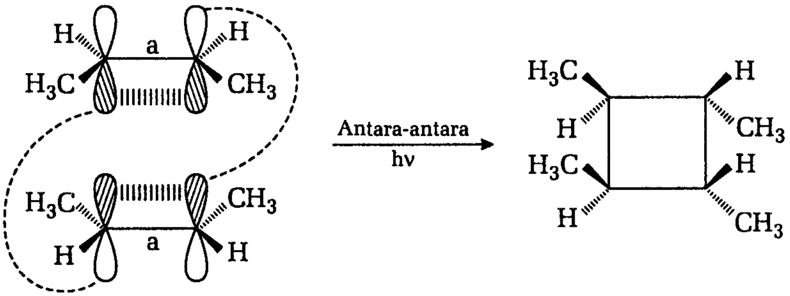
(iii) ***antara-antara*** cycloaddition can also proceed in two ways as given below :

(a)



T.S.; 4 electrons, 2 nodes, antiaromatic photochemically allowed

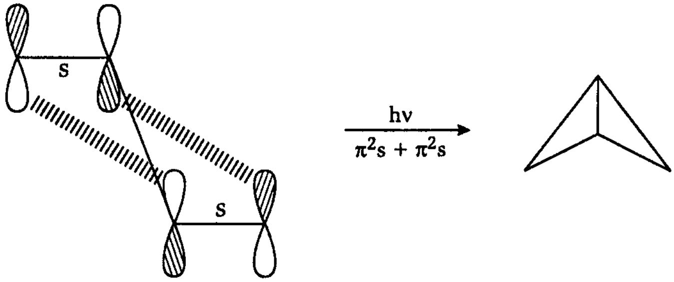
(b)



T.S.; 4 electrons, 2 node, antiaromatic, photochemically allowed

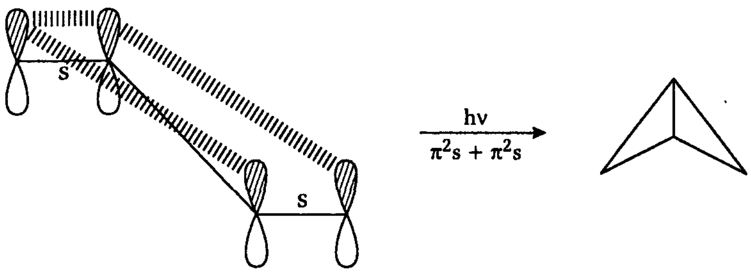
7. By the partition technique, the two ethylenic bonds may be regarded as independent components. Under photochemical condition we have to consider interaction of HOMO of excited part with the LUMO of unexcited part. Upper lobe of one is to overlap the lower lobe of other to give bicyclobutane by $\pi^2s+\pi^2s$ cycloaddition. This cycloaddition is symmetry allowed under photochemical condition.

   (a) HOMO of excited part



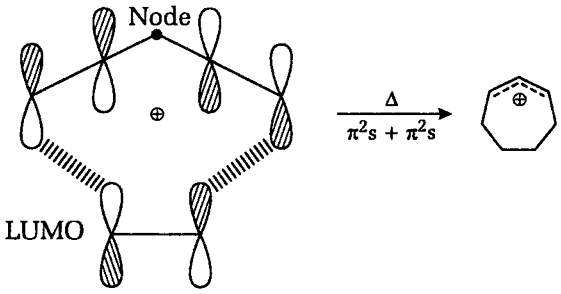
LUMO of unexcited part

   (b)

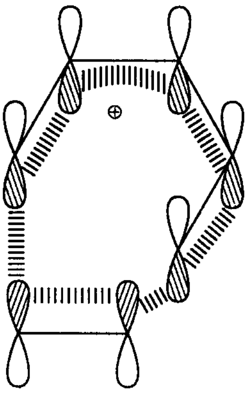


T.S. : 4 electrons, 0 node, antiaromatic, photochemically allowed

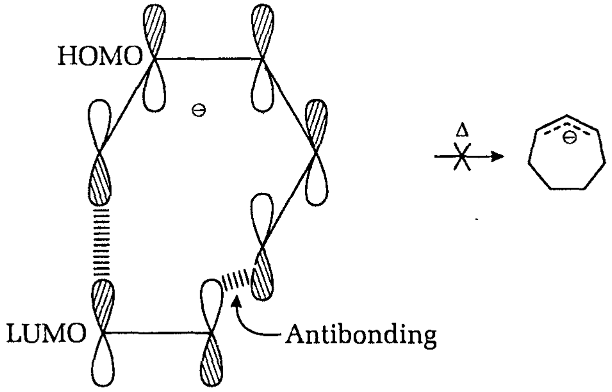
8. (a) It is symmetry allowed as it is $\pi^2s+\pi^2s$ cycloaddition. FMO method for it can be depicted as given below :



According to PMO method *supra-supra* addition transition state involves 6 electrons, 0 node and is therefore aromatic and reaction is thus thermally allowed.



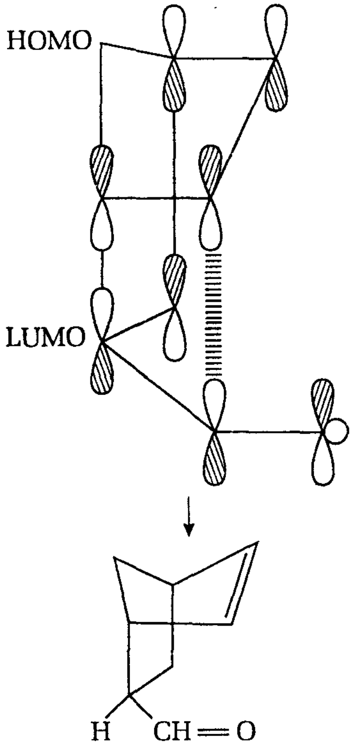
(b) Addition of pentadienyl anion to ethylene by *supra-supra* mode is allowed photochemically as is clear by the following representation :



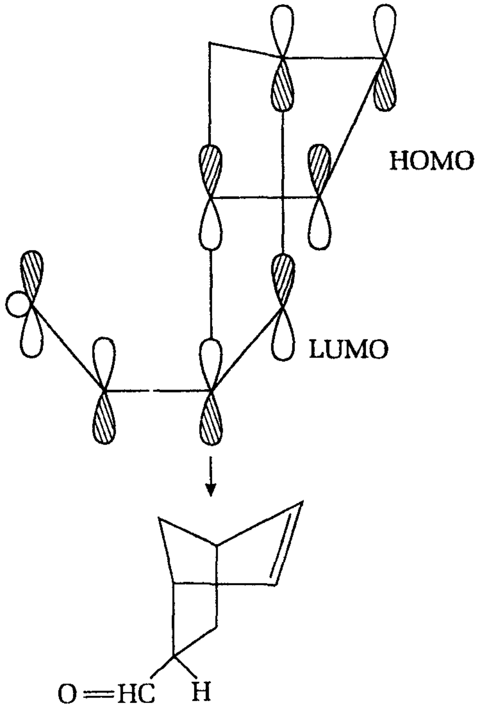
PMO method also gives same result. *Supra-supra* cycloaddition of these two species must proceed through 8 electrons transition state with 0 node, *i.e.*, antiaromatic transition state. Therefore, it is photochemically allowed.

9. Cycloaddition between cyclopentadiene and acrolein is $\pi^4 s + \pi^2 s$ process and is therefore thermally allowed. This conclusion is reached by both FMO as well as PMO-method.

It proceeds through 6-electrons transition state with zero-node, *i.e.*, aromatic T.S. and is, therefore, thermally allowed. This consideration alone can not



Endo

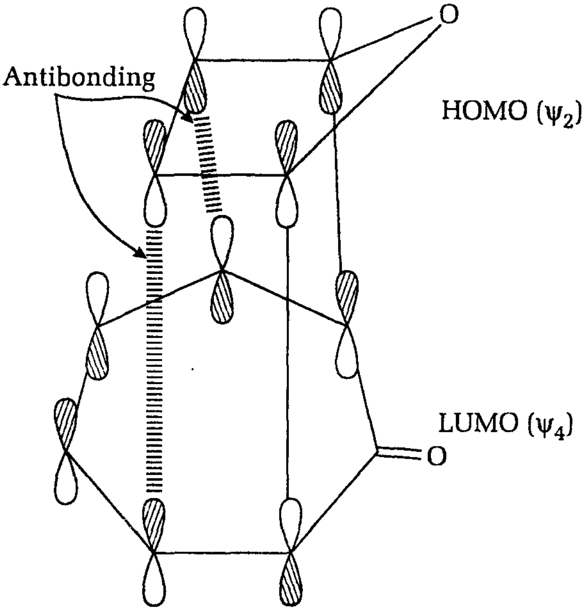


Exo

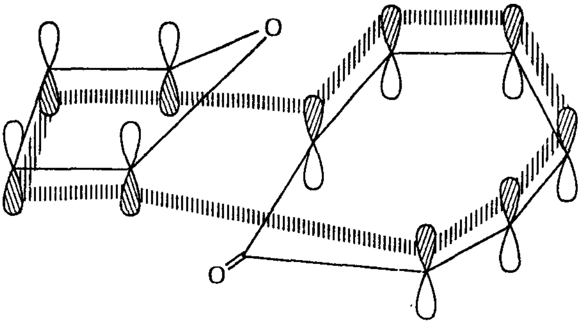
distinguish between *exo* and *endo* addition. We have to consider secondary interactions in the FMOs of reactants. Let us consider HOMO and LUMO for two reactants for both *endo* and *exo* additions.

Favourable secondary interactions favour the formation of *endo*-product. But, under equilibrium condition, *exo*-product will predominate as it is more stable then *endo*. Under kinetically controlled condition *endo*-product will predominate.

10. (a) **FMO Method** : It is $\pi^6 s + \pi^4 s$ cycloaddition and is symmetry-allowed under thermal conditions since total number of electrons is 10, *i.e.*, $(4\pi + 2)$. Another possible *endo*-product can not be obtained since secondary interaction shown by dotted lines are antibonding. Therefore, more stable *exo*-product is formed.



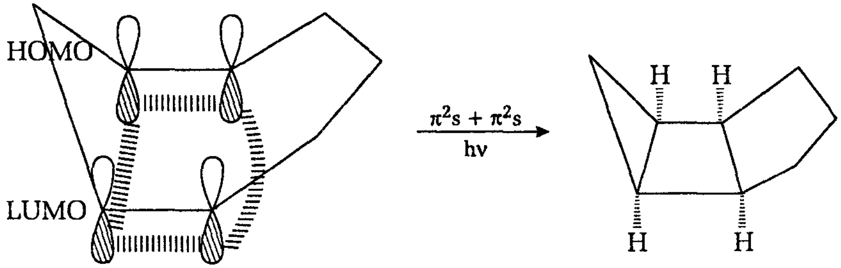
PMO method : The transition state for the reaction can be written as given below :



Transition state for exoaddition : 10 electrons, 0 node, aromatic, thermally allowed

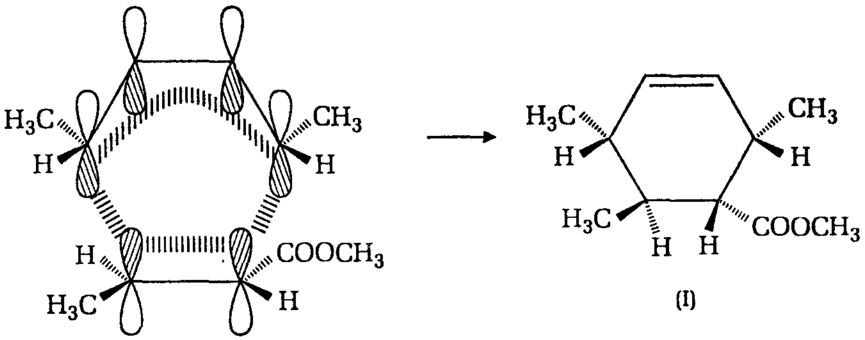
(b) **FMO-method :** From the structure of the product it is clear that it is $\pi^2s + \pi^2s$ cycloaddition of two double bonds. Therefore, it is symmetry allowed under photochemical conditions.

PMO method : It proceeds through 4 electrons transition state without any node, *i.e.*, antiaromatic transition state, therefore, it is photochemically allowed.

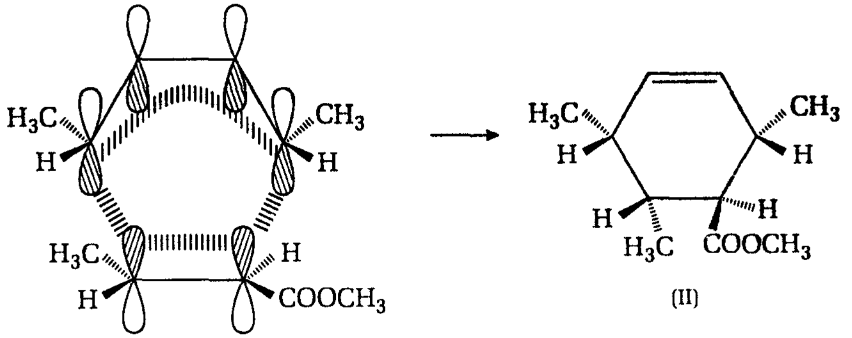


11. Following two possibilities are there :

Prediction by PMO-method :



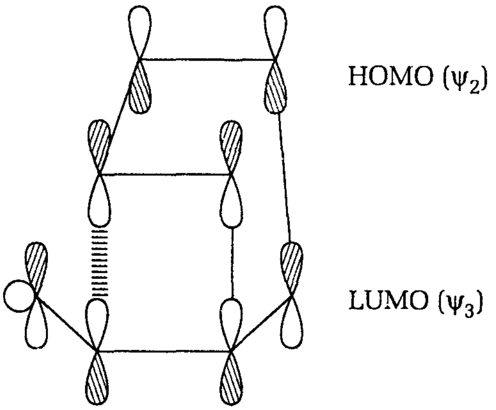
(I)



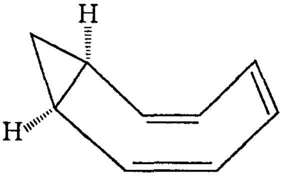
(II)

Transition state : 6 electrons, 0-node, aromatic, thermally allowed.

Prediction by FMO-method : Both the possibilities involve $\pi^4s + \pi^2s$ cycloaddition and are thermally allowed. (I) may be major product as in its transition state, there are favourable secondary interactions.

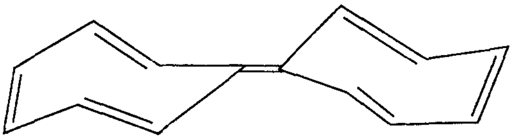


12. Cyclopropane ring possesses double bond character, therefore, reactant hydrocarbon has tub-shaped structure. Double bonds are not conjugate enough to react with maleic anhydride which is not much reactive.



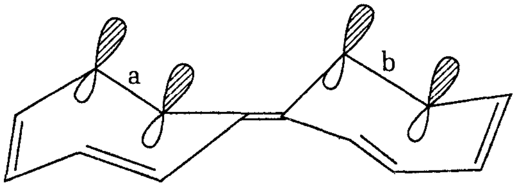
13. **FMO method :** Interaction of HOMO of one component with the LUMO of other involves either $\pi^{14}s+\pi^{2}a$ or $\pi^{14}a+\pi^{2}s$ cycloaddition. But structure of product indicates that process is $\pi^{14}a+\pi^{2}s$. Overlapping between HOMO of heptafulvalene and LUMO of tetracyanoethylene (TCNE) makes the interaction possible. HOMO of heptafulvalene (ψ_7) possesses mirror plane (m) symmetry and LUMO of TCNE (ψ_2) possesses c_2-symmetry. Therefore, overlapping is not feasible in *supra-supra*-fashion. This cycloaddition is thermally feasible only if overlapping is *antara* on one of the component which is heptafulvalene.

    PMO method : Transition state for this $\pi^{14}a+\pi^{2}s$ cycloaddition involves 16 electrons and one node. Therefore, transition state is aromatic and reaction is thermally allowed. Why approach is *antara* on heptafulvalene can only be understood on the basis of its structure which has been settled as (X) on the basis of X-ray crystallography.

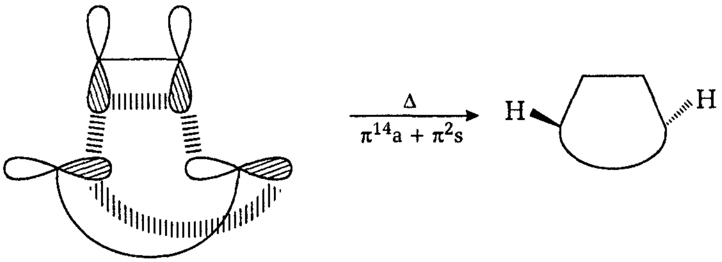


(X)

Partial orbital picture of heptafulvalene (Y) shows upper π-lobes (a) and lower π-lobes (b) are close together and can easily overlap with π-lobes of tetracyanoethylene with one node in transition state.

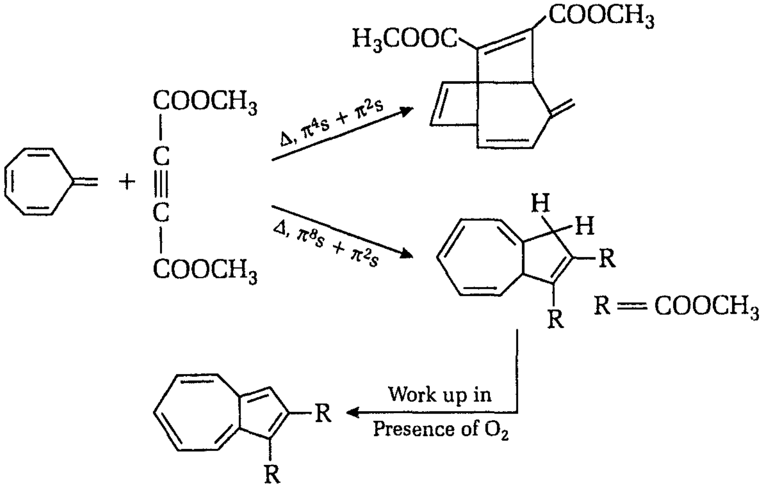


(Y)



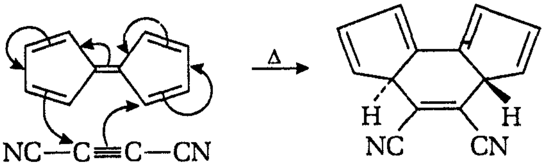
Transition state with one node and 16 electrons is aromatic.

14. (a) Two thermally allowed processes can be considered : a $[\pi^4s+\pi^2s]$ cycloaddition and a $[\pi^8s+\pi^2s]$ cycloaddition.

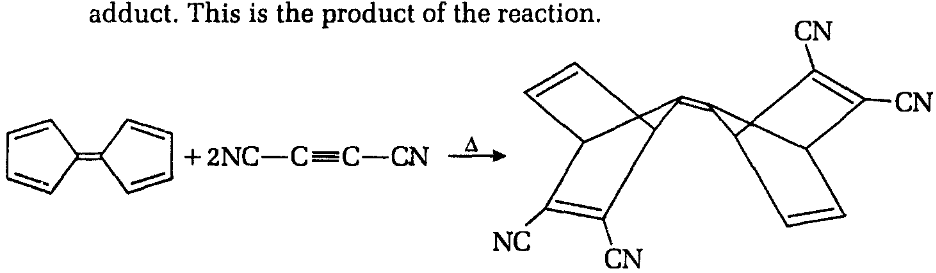


The $\pi^8s+\pi^2s$ cycloaddition product is actual product which is formed by the air oxidation of adduct. This is substituted azulene which possesses some aromatic character.

(b) Here too two thermally allowed processes are possible. One process will result in the formation of 1 : 1 adduct via *trans*-$[\pi^{10}a+\pi^2s]$ cycloaddition which is not observed.

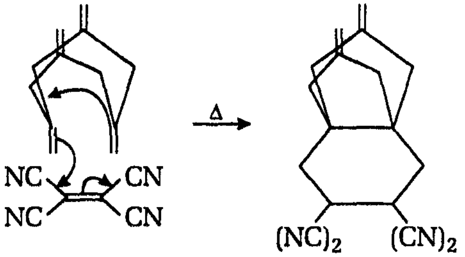


The second process is double Diels-Alder reaction and gives 1 : 2 adduct. This is the product of the reaction.

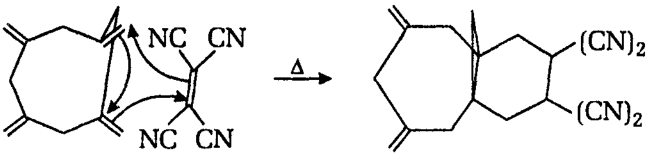


(c) Two $[\pi^2 s+\pi^2 s+\pi^2 s]$ cycloadditions may be considered :

(i)

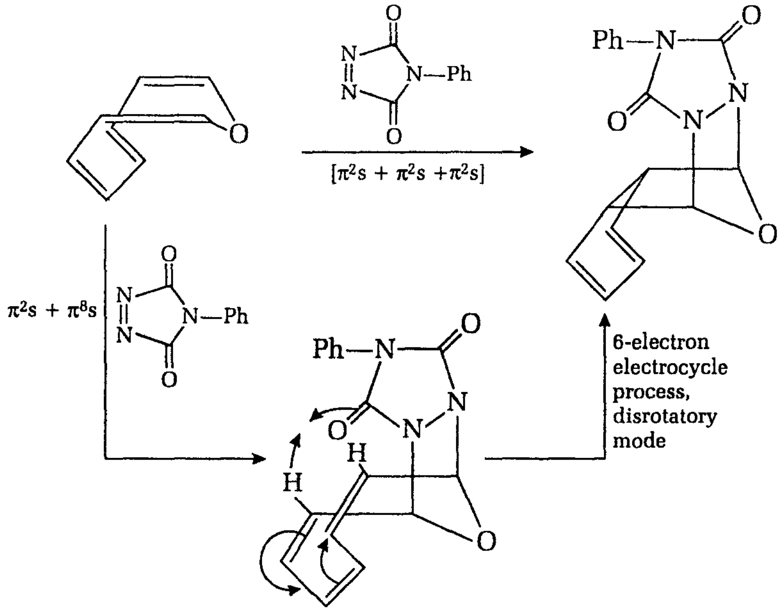


(ii)

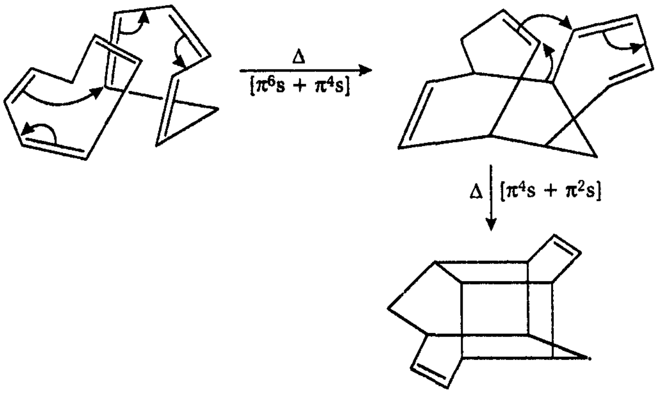


Considering strain effect product should form through path (ii).

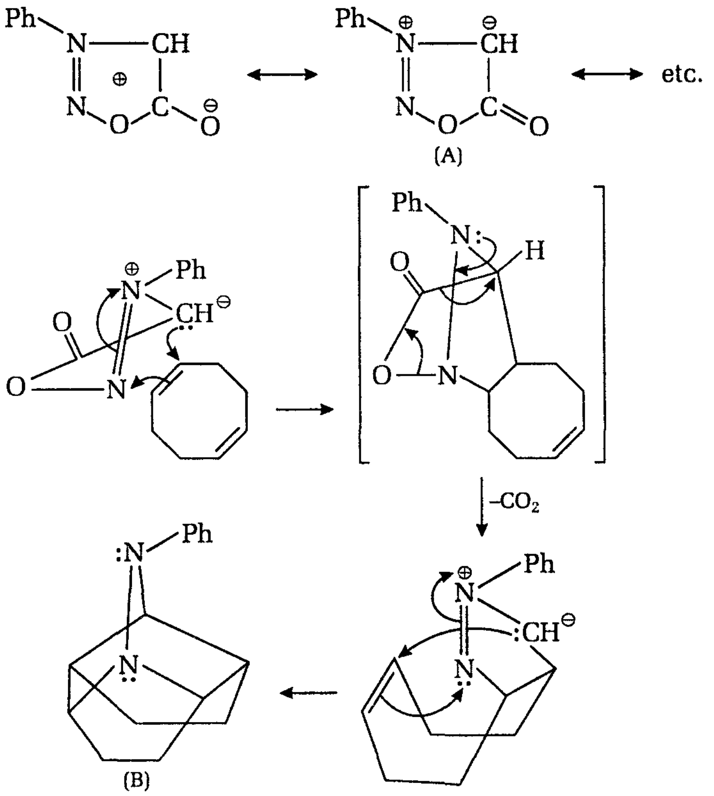
(d) 1 : 1 addition product should form by either of the two thermally allowed processes.



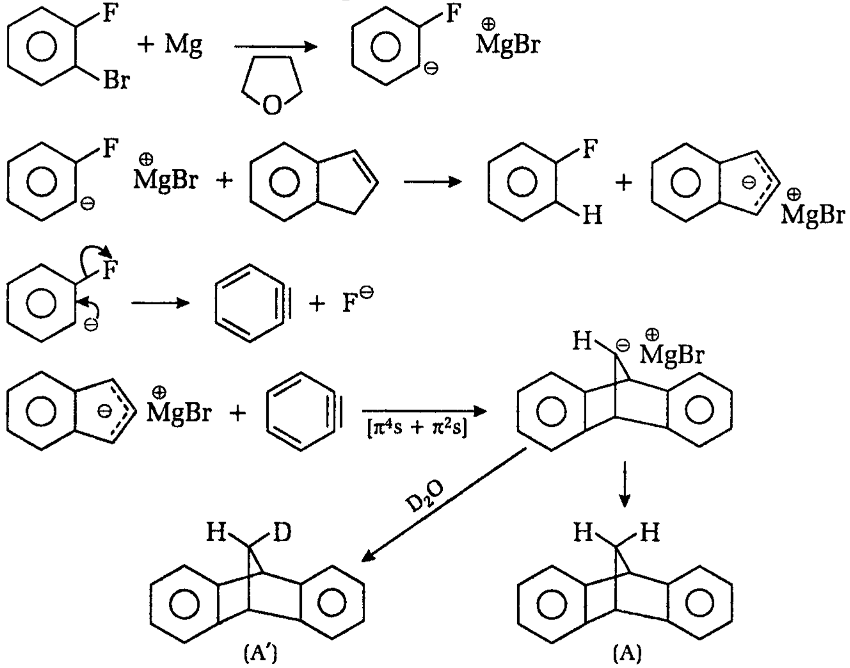
15. A dimer is produced in this reaction under thermal conditions is two steps : a symmetry allowed [$\pi^6 s+\pi^4 s$] cycloaddition followed by intramolecular Diels-Alder reaction :



16. In this transformation first step is 1, 3-dipolar cycloaddition, which is isoelectronic with [$\pi^4 s+\pi^2 s$] cycloaddition and is therefore symmetry allowed under thermal conditions. Second step of this reaction is, 1, 3-dipolar cycloreversion involving elimination of CO_2 too and the product (B).

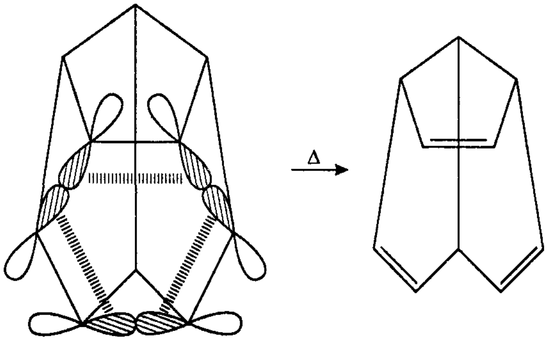


17. Structure and mechanism are given below :



The fact that deuterium uptake is observed upon hydrolysis in D_2O (to give A') confirms that (A) is formed by $[\pi^4 s + \pi^2 s]$ cycloaddition of benzyne to Grignard reagent of indene rather than to give isoindene. Deuterium occupies position on bridge.

18. The transition state for $\sigma^2 s + \sigma^2 s + \sigma^2 s$ cycloreversion possesses 0 node and 6 electrons, *i.e.*, is aromatic transition state. Hence, the process is thermally allowed.



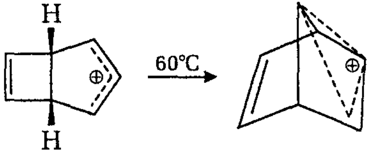
Transition state

8.3 SIGMATROPIC REARRANGEMENTS

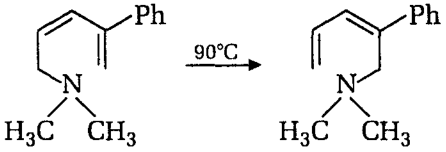
PROBLEMS

1. Concerted 1, 3-sigmatropic shift of hydrogen is thermally forbidden. Explain.

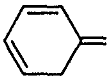
2. Suggest mechanism for following thermal conversion :



3. Suggest mechanism for following irreversible rearrangement :

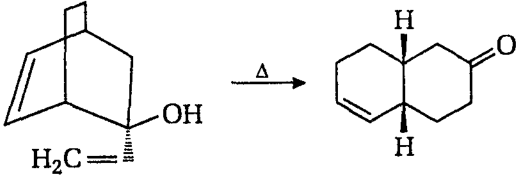


4. The following isomer of toluene though much less stable than toluene has long life. Explain.

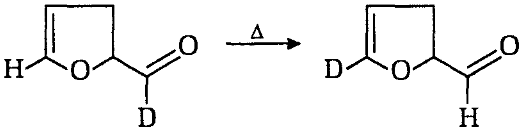


5. Explain following concerted rearrangements :

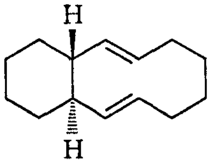
(a)



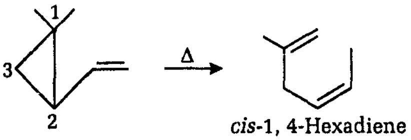
(b)



6. Following diene racemizes with half life of 24 hrs at 50°C. Give the mechanism.

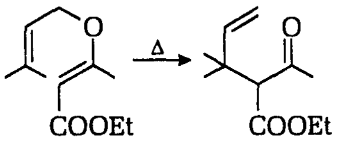


7. Thermal reaction of 1, 1-dimethyl-2-vinyl cyclopropane gives exclusively *cis*-1, 4-hexadiene. Suggest mechanism.

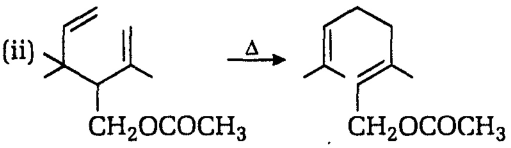


8. Following steps are involved in the synthesis of geraniol. Suggest the mechanism for them.

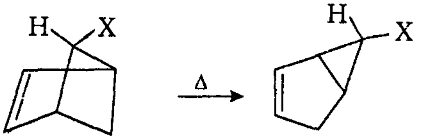
(i)



(ii)

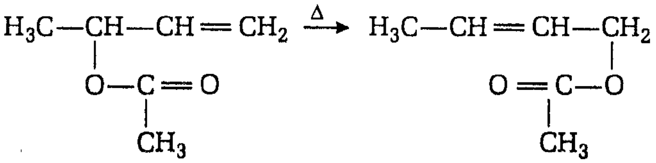


9. Explain, following thermal transformation is 1, 3-sigmatropic-rearrangement :

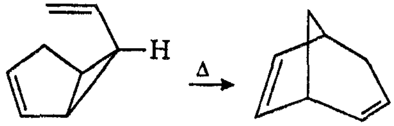


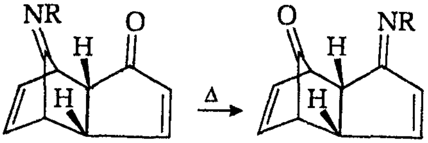
$X = CH_3$, $CH_3O—$, $—CH_2COO$, CH_3COO or N_3

10. Explain following concerted rearrangements :

(a)


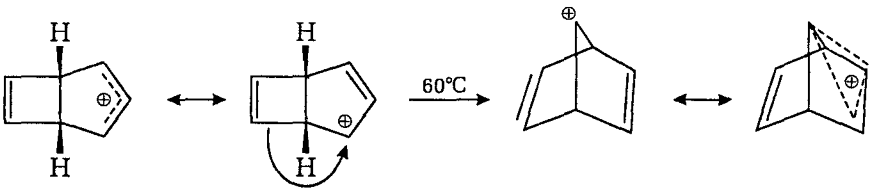
$$\begin{array}{c}H_3C—\underset{\underset{\underset{CH_3}{|}}{O—\underset{|}{C}=O}}{\underset{|}{CH}}—CH=CH_2\end{array} \xrightarrow{\Delta} \begin{array}{c}H_3C—CH=CH—\underset{\underset{\underset{CH_3}{|}}{O=\underset{|}{C}—O}}{\underset{|}{CH_2}}\end{array}$$

(b)


(c)


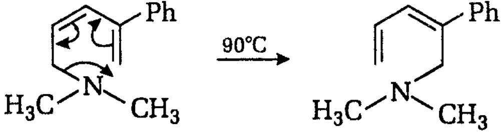
Solutions (Sigmatropic Rearrangements)

1. Concerted 1, 3-sigmatropic shift is feasible only if it proceeds **antarafacially** or **suprafacially** with inversion at migration centre. **Suprafacial** 1, 3-migration of hydrogen is thermally forbidden as there is no question of inversion at this atom which is bonded to carbon through spherically symmetrical 1S orbital. **Antarafacial** 1, 3-concerted shift is forbidden because of steric inhibition of such a process.
2. This thermal conversion is 1, 2-sigmatropic shift of cationic species :



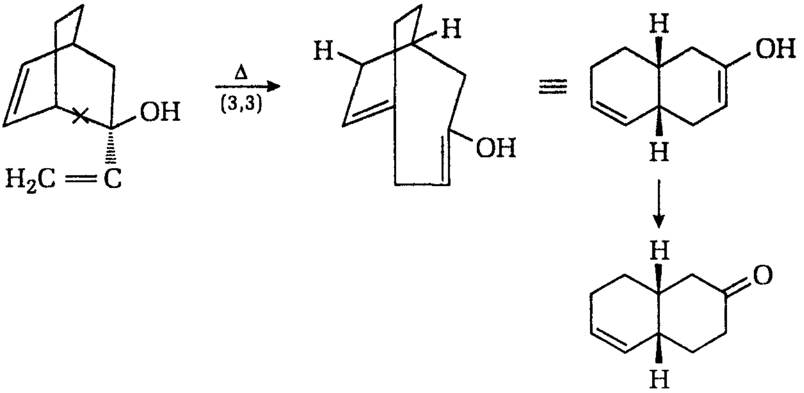
The HOMO of the π-framework is a radical cation $C=C^{+\bullet}$, having *m*-symmetry. That is why symmetry allowed process is suprafacial migration. Similar are the results with PMO-method, because the T.S. possesses 2-electrons and 0-node and is therefore aromatic, predicting the reaction thermally allowed. The positive charge on apical carbon is delocalized through space by one of the double bonds (homoallylic delocalization).

3. This is symmetry-allowed 1, 5-sigmatropic rearrangement under thermal conditions. It must be **suprafacial**; although stereochemical mode of shift can not be ascertained in absence of molecular dissymmetry in this case. Driving force may be extended conjugation in product.

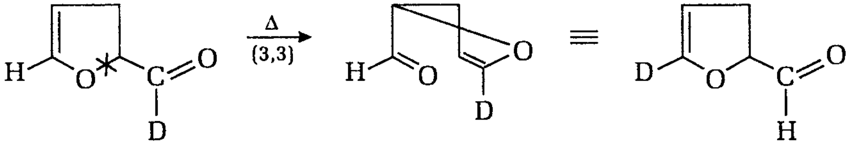


4. This is explained by the fact that 1, 3-shift of any two methylene hydrogen is symmetry-forbidden. If isomer of toluene is to be transformed to toluene it can not do so through facile symmetry-allowed concerted process. Therefore, there is resistance to isomerization and it has long life.
5. Both (a) and (b) are sigmatropic rearrangements of the order (3, 3), *i.e.*, Cope or Claisen rearrangements which are symmetry allowed under thermal condition as they proceed through six-membered aromatic transition state. For explanation, we need σ-bond flanked by two allylic systems.

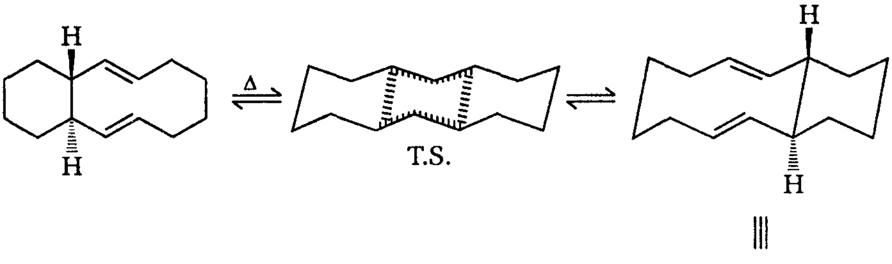
(a)

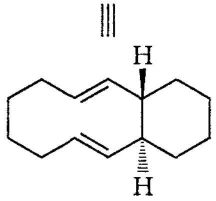


(b)



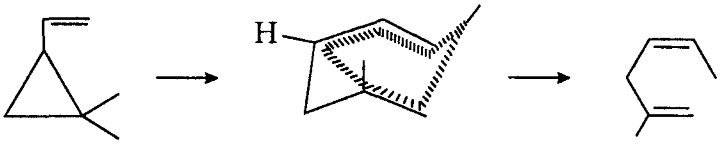
6. This optically-active diene undergoes 3,3-sigmatropic rearrangement through chair like transition state which is symmetrical. The dissymmetry which was present in optically active compound has been lost in symmetrical T.S.





Furthermore, isomer formed after 3,3-sigmatropic rearrangement is mirror image of the starting compound. Therefore, racemization takes place even at 50°C.

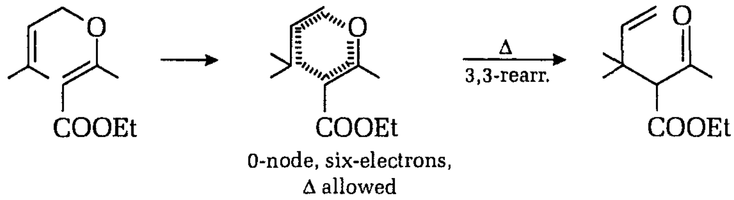
7. This thermolysis reaction represents 1, 5-H-shift across a HOMO conjugated diene in which cyclopropane ring replacess one of the double bond of the diene system. Formation of *cis*-product is explainable by the chair like T.S. during H-shift.



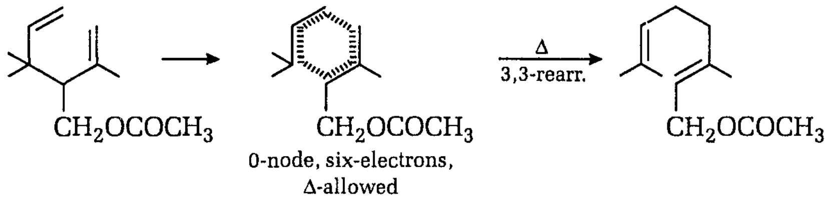
Cis
1,4-Hexadiene

8. In both the steps there is 3, 3-sigmatropic shift. First, there is Claisen rearrangement which is followed by Cope-rearrangement.

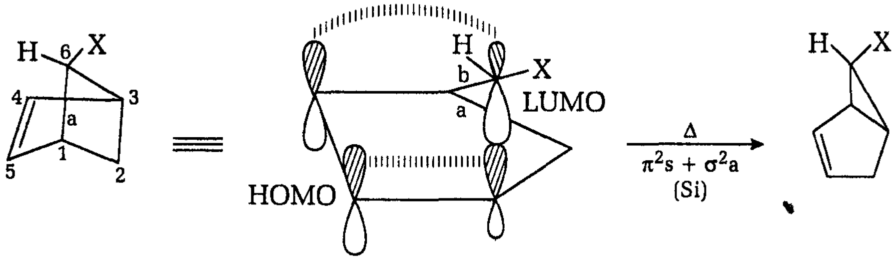
(i)



(ii)



9. Since, it is 1, 3-sigmatropic rearrangement, hence, on the basis of orbital rules there should be inversion at migrating centre.

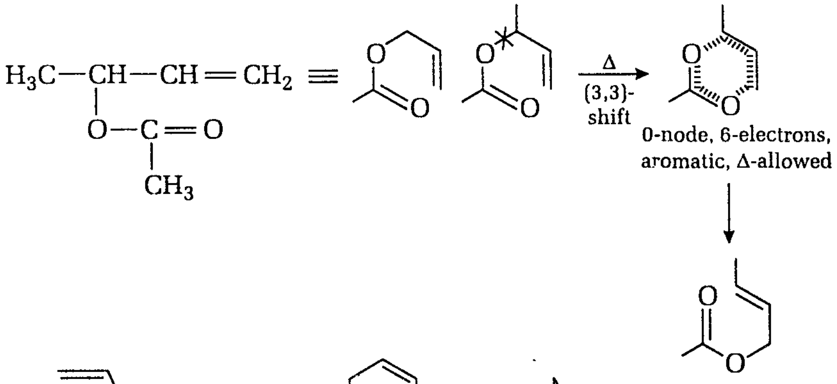


The migrating centre is apical carbon C_6. Both, σ-bond '*a*' as well as '*b*' can migrate to give same product as the molecule is symmetrical. Migration should be **suprafacial**. If migration is with retention of configuration (*Sr*) at C_6; H-atom at C_6 will become *exo* and group X endo to cyclopentene ring. But, fact is opposite of it, *i.e.*, X-is *exo* and H is *endo*. Therefore, migration has taken place with inversion of configuration (*Si*) at migrating centre C_6.

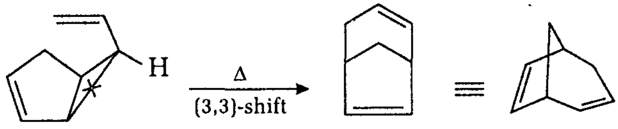
PMO method concludes that the reaction is thermally allowed as transition state for 1, 3-shift with inversion contains 4-electrons, 0-node, therefore is aromatic.

10. These are all 3, 3-sigmatropic rearrangements which are symmetry allowed under thermal condition as they proceed through aromatic transition state.

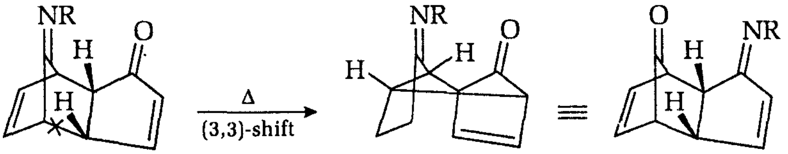
(a)



(b)



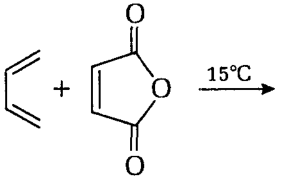
(c)



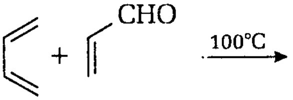
8.4 MISCELLANEOUS PROBLEMS

1. Write down the products of following transformations :

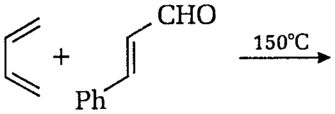
(a)



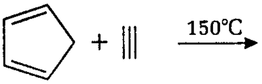
(b)

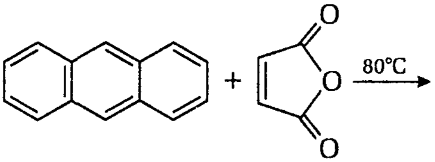


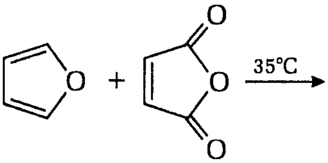
(c)



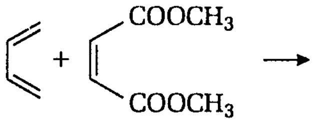
(d)

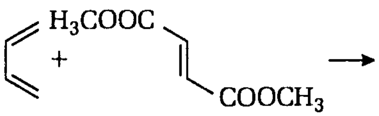


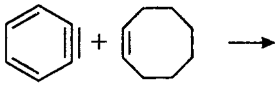
(e) 

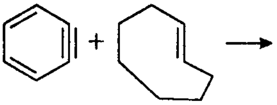
(f) 

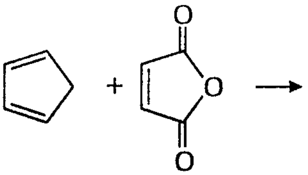
2. Predict the stereochemistry of following reactions :

(a) 

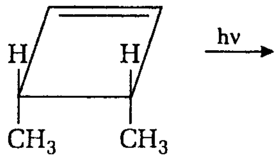
(b) 

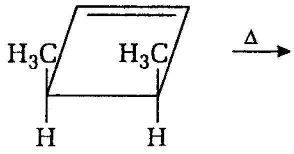
(c) 

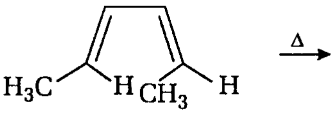
(d) 

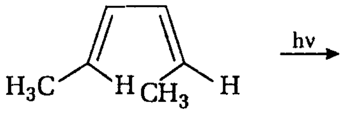
(e) 

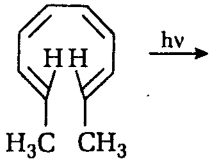
3. Give the stereochemistry of products in the following reactions :

(a) 

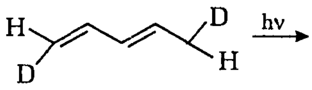
(b) 

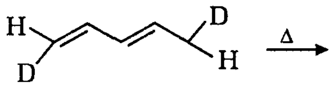
(c) 

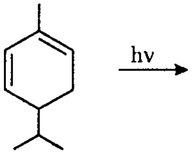
(d) 

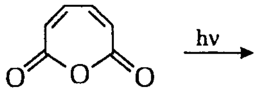
(d) 

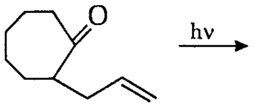
4. Predict the product of following reactions :

(a) 

(b) 

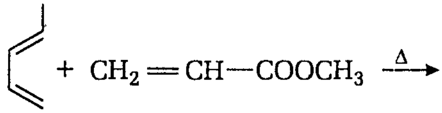
(c) 

(d) 

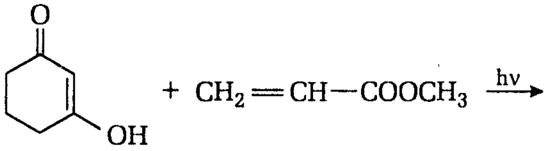
(e) 

5. Complete the following reactions :

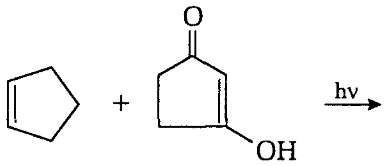
(i)



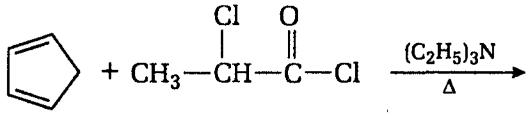
(ii)



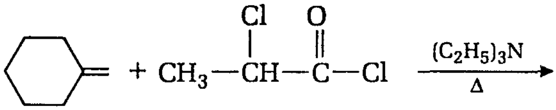
(iii)



(iv)

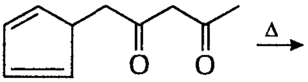


(v)

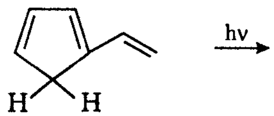


(vi) $CH_2N_2 + CH\equiv CH \xrightarrow{\Delta}$

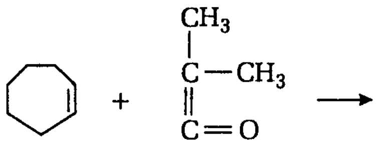
(vii)



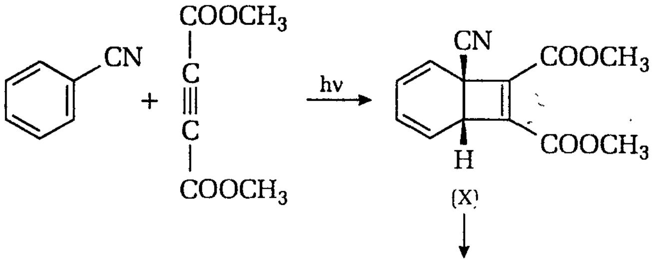
(viii)

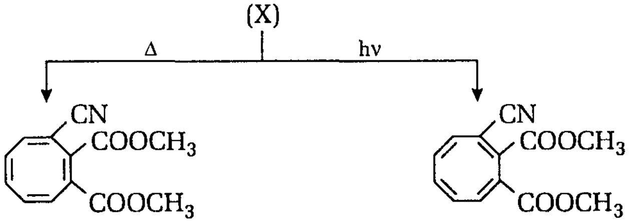


(ix)



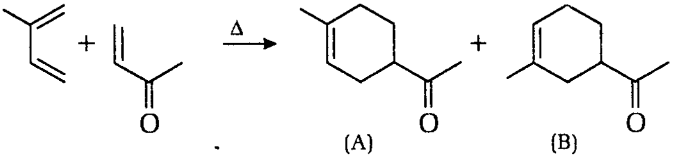
6. Classify the following transformation :



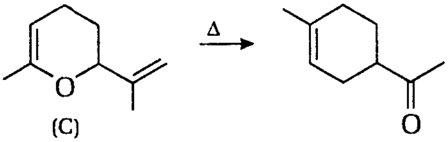


7. Cycloaddition (a) given below gives a mixture of isomeric *A* and *B*. But *C* gives only *A*. Give the mechanism for these reactions.

(a)

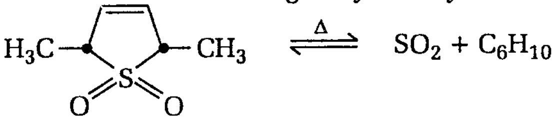


(b)

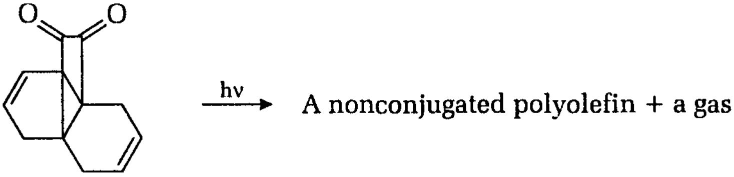


8. Predict the stereochemistry of each of following reactions assuming reaction is concerted in each case to give symmetry allowed product :

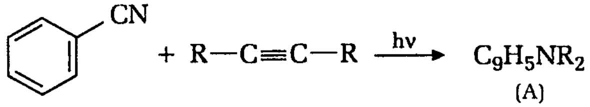
(i)



(ii)

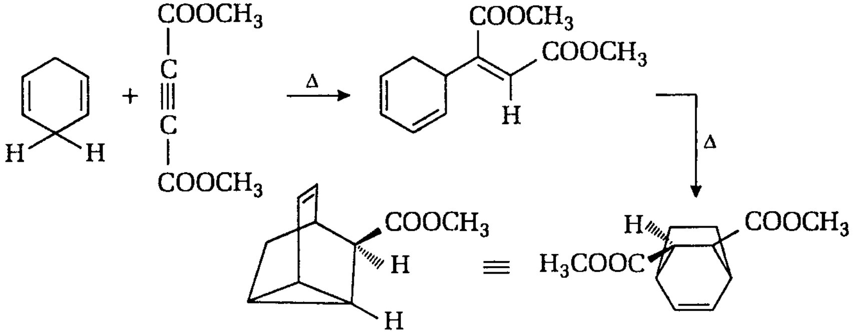


(iii)

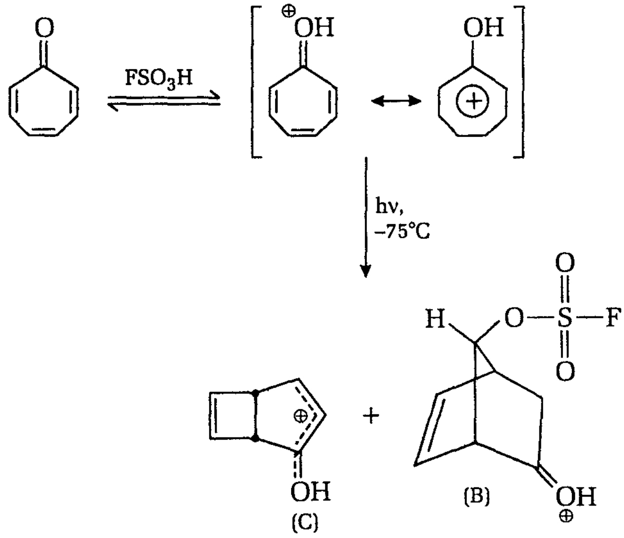


Compound (A) contains four double bonds.

9. Classify each step in following transformation :

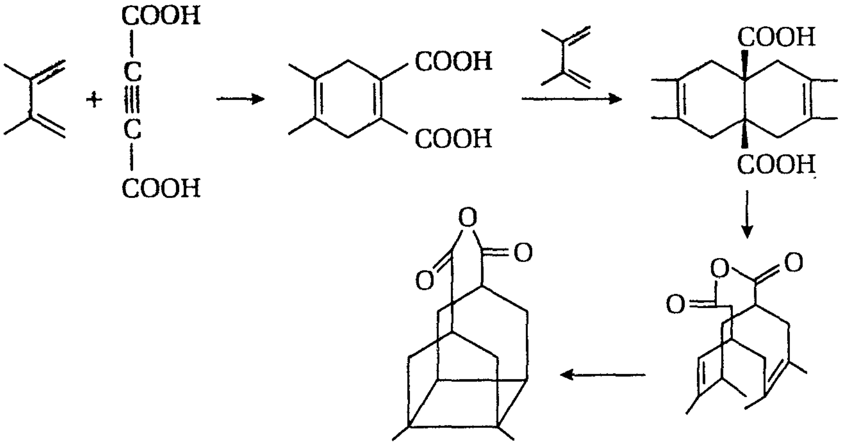


10. Stable carbonium ion solution can be prepared in fluorosulphonic acid. Stable carbonium ion in FSO_3H when subjected to photolysis at low temperature ($T < -60°C$) following type of transformation takes place.

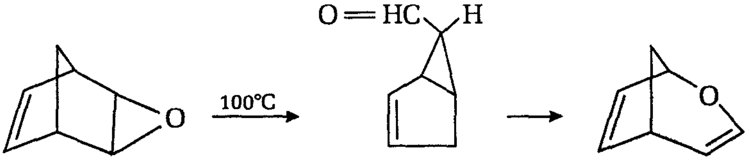


Products (B) and (C) have been found to be stable in FSO_3H at −76°C, they do not undergo rearrangement. Suggest mechanism of above transformation.

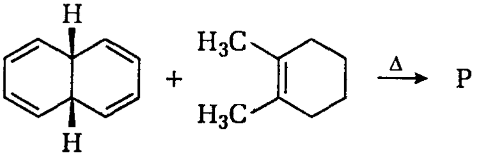
11. View the following reaction sequence, classify each step and determine the reaction condition for it.



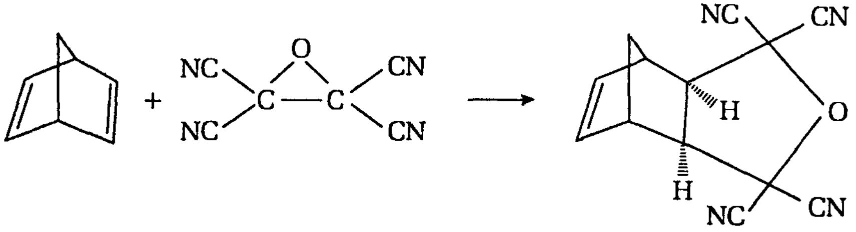
12. Analyse the following transformation and predict if it is thermally feasible or photochemically allowed :



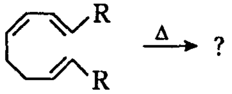
13. Using PMO method predict structure of the product in following transformation :



14. Predict the feasibility of following reaction :

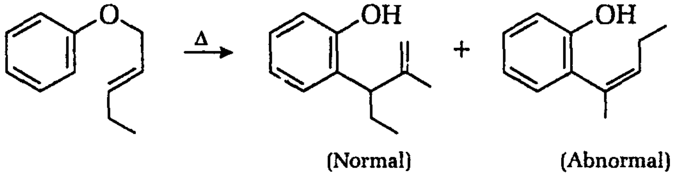


15. Predict by PMO method the structures of two possible products in following thermal rearrangement :



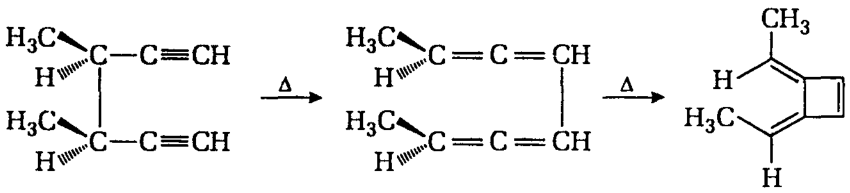
Trans, trans

16. Explain by PMO method formation of abnormal product in following Claisen rearrangement :

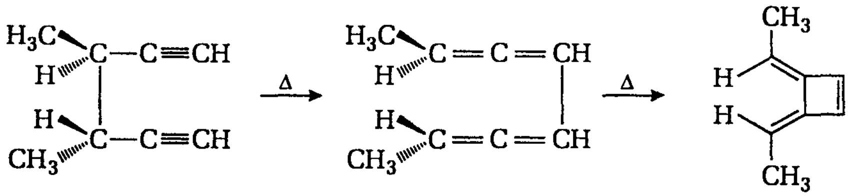


17. Explain each step in the following sequence of concerted reactions :

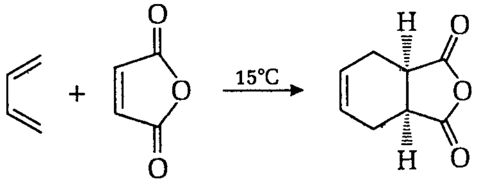
(a)

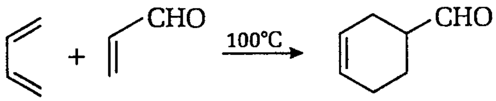


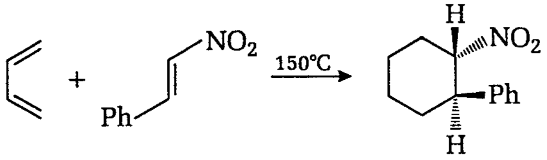
(b)

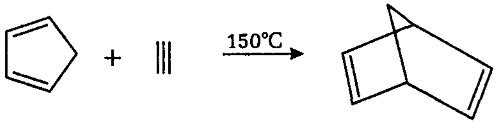


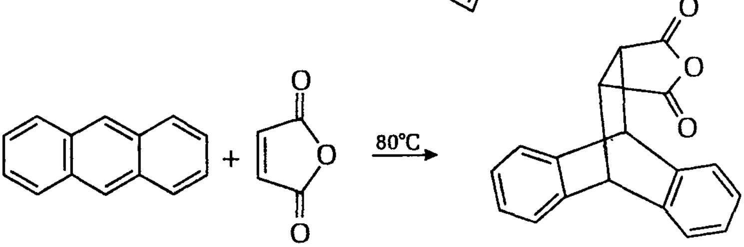
Solutions (Miscellaneous Problems)

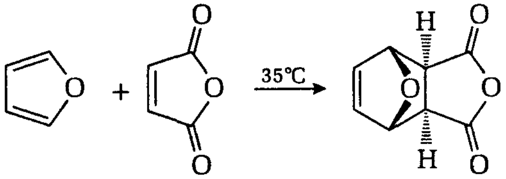
(a) 

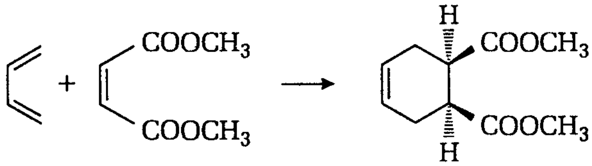
(b) 

(c) 

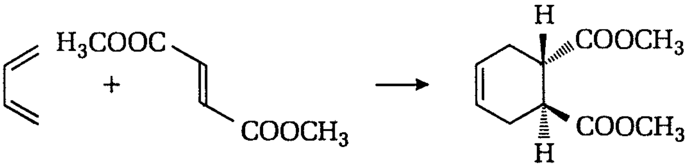
(d) 

(e) 

(f) 

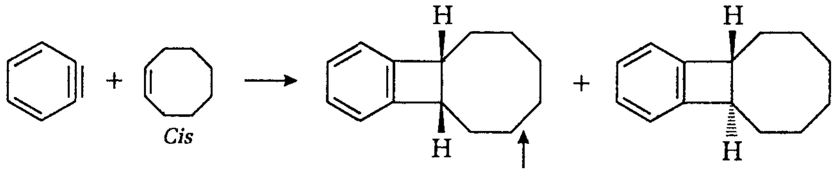
2\. (a) 

Cis-dimethyl cyclohexene-4,5-dicarboxylate

(b) 

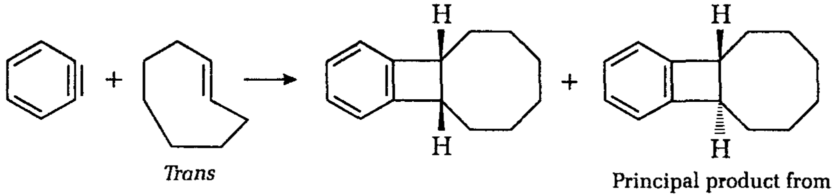
Trans-dimethyl cyclohexene-4,5-dicarboxylate

(c)



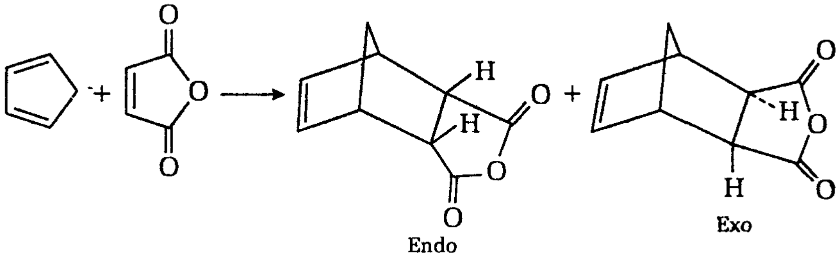
Principal product from *Cis*-cyclooctene

(d)

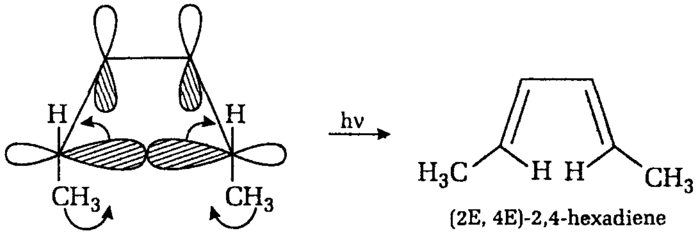


Principal product from *trans*-cyclooctene

(e)

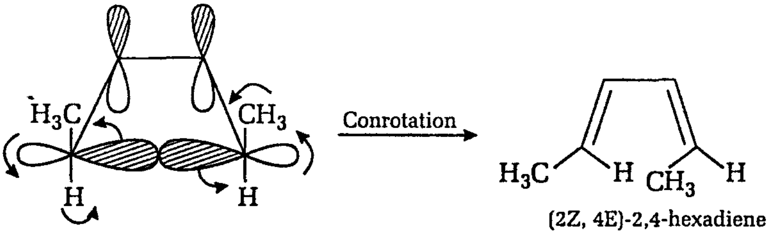


3. (a) This is 4π-electron system in which ψ_3 is HOMO under excited (photochemical) conditions which has *m*-symmetry in σ-bond, therefore, it should also have *m*-symmetry in π-bond of product. This ring opening should proceed through disrotation.



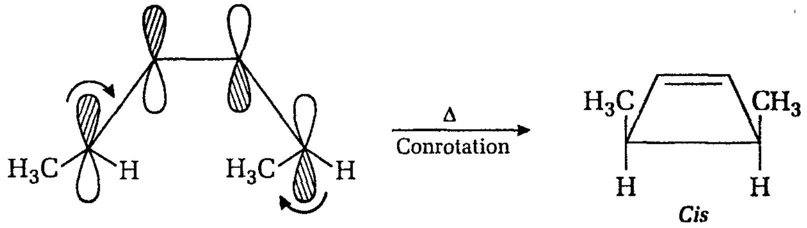
(2E, 4E)-2,4-hexadiene

(b) Given system is 4π-electron system in which ψ_2 is HOMO under thermal condition. ψ_2 has c_2-symmetry is σ-bond. Therefore, product should also have c_2-symmetry. This transformation proceeds through conrotation.

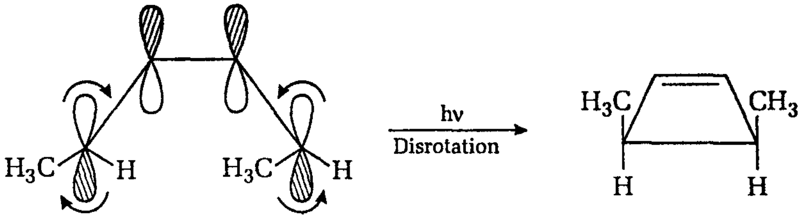


(2Z, 4E)-2,4-hexadiene

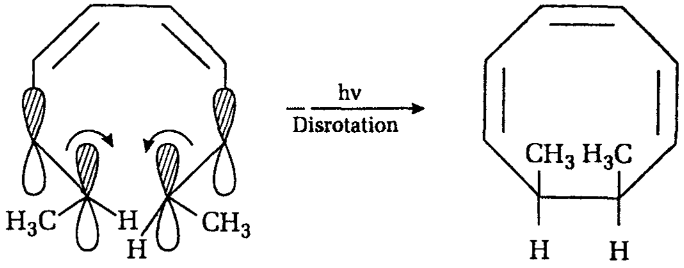
(c) This is 1, 3-butadiene system in which HOMO under thermal condition is ψ_2 which has c_2-symmetry. In it cyclization is possible by conrotatory mode.



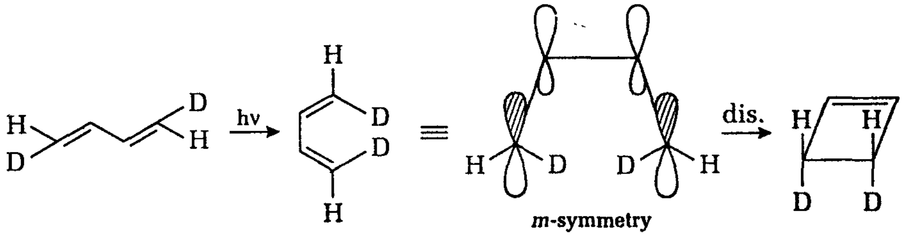
(d) In butadiene derivatives ψ_3 is HOMO under photochemical conditions which has *m*-symmetry. Therefore, cyclization proceeds through disrotation.



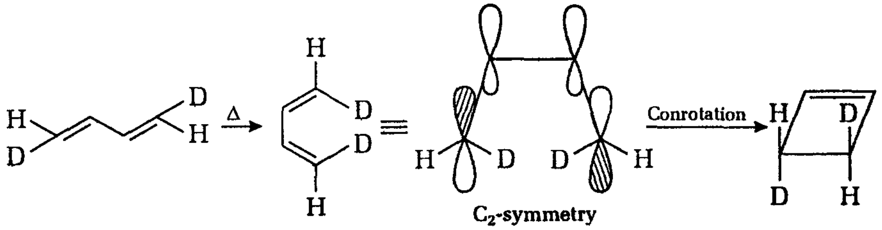
(e) Octatetraenes are also 4π-systems. Here ψ_5 is HOMO with *m*-symmetry under photochemical condition. Therefore, photochemical reaction should proceed through disrotation.



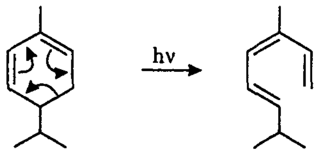
4. (a)



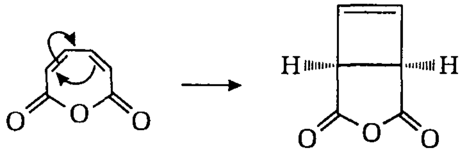
(b)



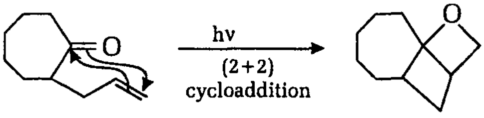
(c)



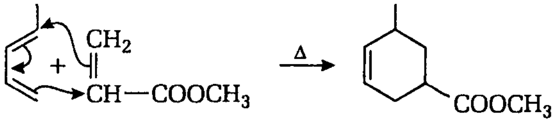
(d)



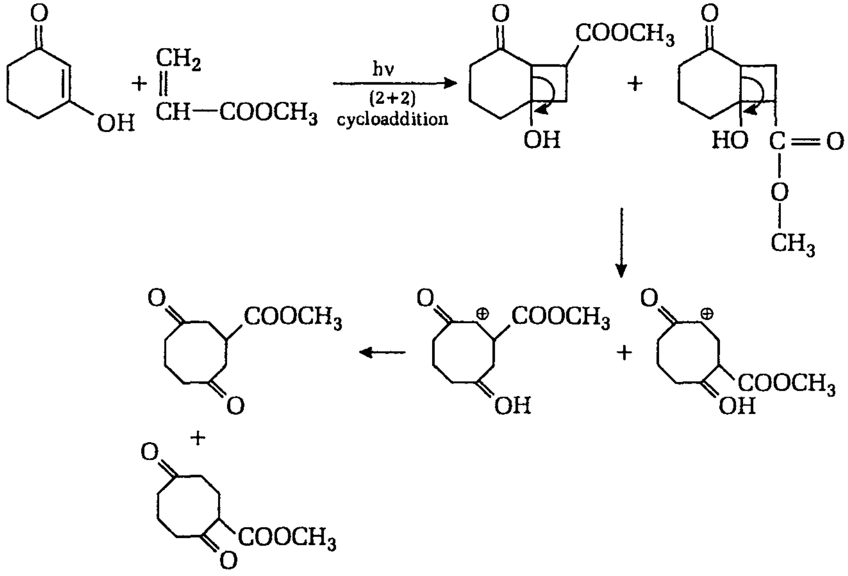
(e)



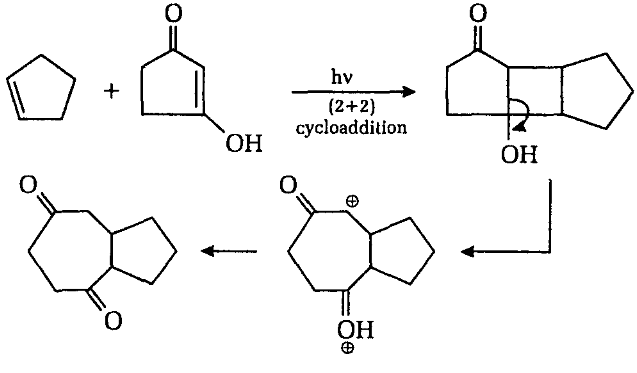
5. (i) This is Diel's-Alder transformation under thermal conditions :



(ii)



(iii)



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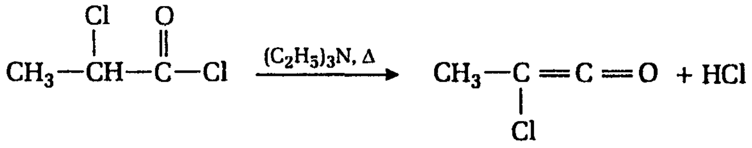
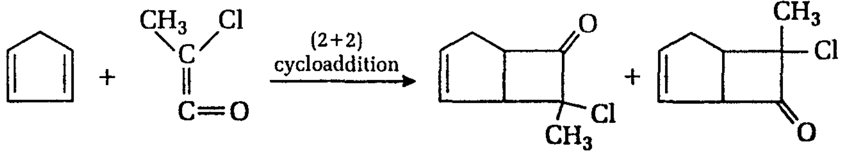
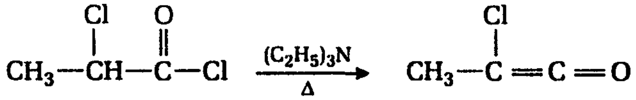


$$CH_3-\overset{Cl}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{(C_2H_5)_3N,\ \Delta} CH_3-\underset{Cl}{\underset{|}{C}}=C=O + HCl$$

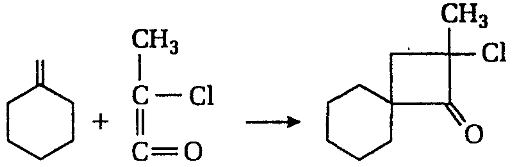
(A Ketene)



(v)

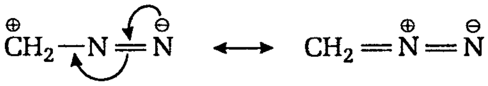


$$CH_3-\overset{Cl}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\Delta]{(C_2H_5)_3N} CH_3-\overset{Cl}{\overset{|}{C}}=C=O$$

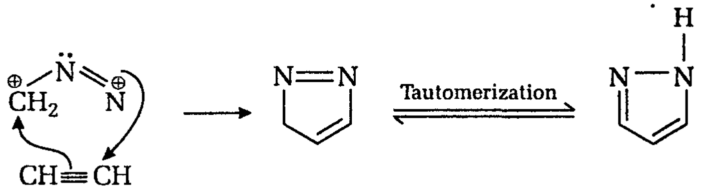


This is also an example of (2+2) cycloaddition

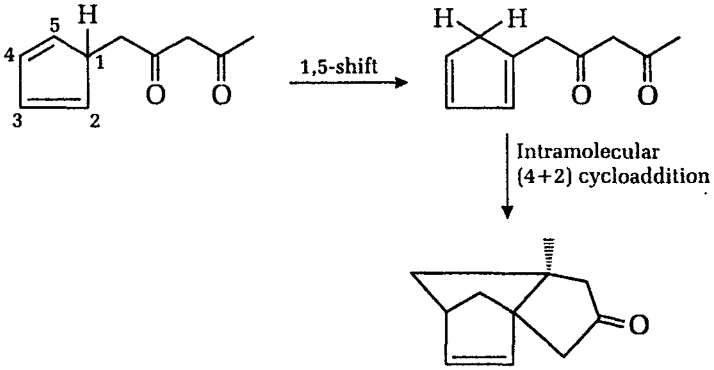
(vi)



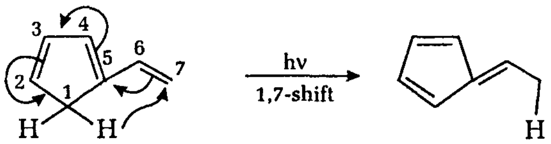
$$\overset{\oplus}{C}H_2-N=\overset{\ominus}{N} \longleftrightarrow CH_2=\overset{\oplus}{N}=\overset{\ominus}{N}$$



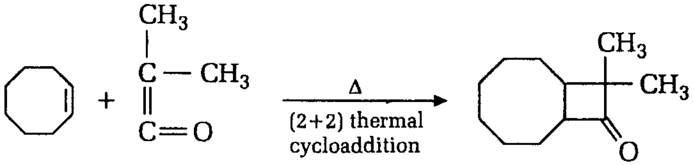
(vii)



(viii)



(ix)



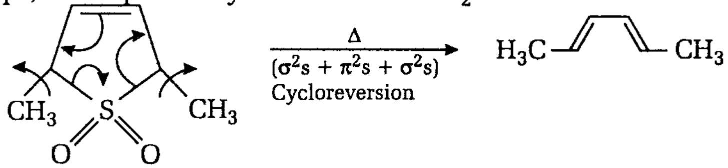
6. From the stereochemistry of the product of first step (X) it is clear that $\pi^2s+\pi^2s$ process in this transformation is symmetry allowed under photochemical conditions. PMO method predicts that transition state in it is antiaromatic as it has 4-electrons with 0-node. Therefore, reaction is photochemically allowed.

   Second step is symmetry allowed under thermal as well as photochemical conditions. If we consider cyclobutene moiety of (X), the opening ot middle bond of it will be disrotatory under photochemical conditions by $\pi^2s+\sigma^2s$-process. But, under thermal condition cyclohexadiene moiety will open in disrotatory manner by $\pi^4s+\pi^2s$ method giving a double bond isomer of photolytic product. However, conrotatory ring-opening will give unstable cyclooctatetraene derivative with *trans*-double bond.

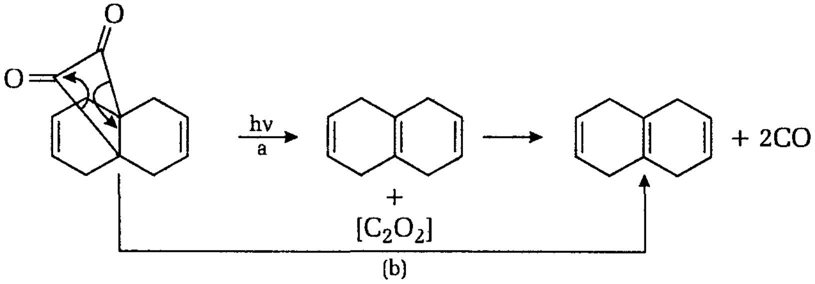
7. (a) This reaction is $\pi^4s+\pi^2s$ cycloaddition which is symmetry allowed under thermal condition. Because, isoprene molecule is unsymmetrical it can condense with methylvinyl ketone is two ways, therefore, we get two isomers of product (*i.e.*, *A* and *B*). Both, the processes are $\pi^4s+\pi^2s$ cycloadditions, therefore, are thermally allowed.

   (b) This is (3, 3)-sigmatropic rearrangement $(\sigma^2s+\pi^2s+\pi^2s)$ which is symmetry-allowed thermally. Its transition state has 6-electrons with 0-node, therefore is aromatic and reaction is thermally allowed. Because, reaction is stereospecific, therefore, we get only one product. In other words, in this case as there is only one reactant with fixed geometry, condensation is feasible is only one way, *i.e.*, reaction becomes stereospecific and we get only one product.

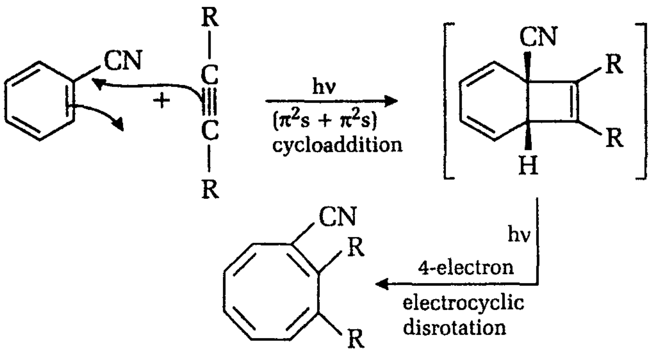
8. (i) This thermal transformation is six-electron, linear **cheletropic cycloreversion**. This takes place through disrotatory motion of methyl groups, accompanied by elimination of SO_2.



   (ii) Here probably $(\sigma^2s+\sigma^2s)$ photochemical cycloreversion occurs :

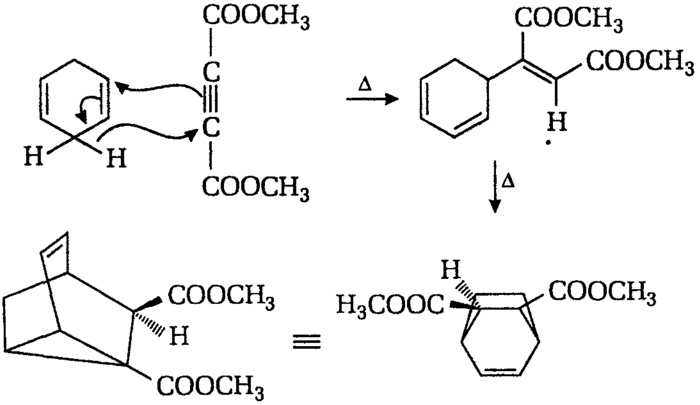


(iii)

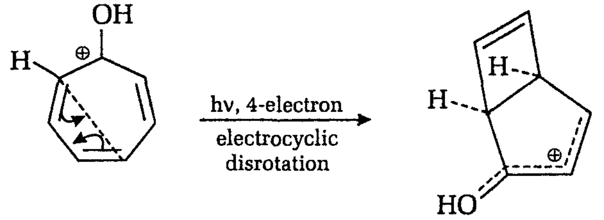


9. First step in this transformation is an **ene**-reaction which is symmetry allowed under thermal condition. Second step is intramolecular Diels-Alder reaction which is symmetry-allowed by $\pi^4s+\pi^2s$ mode under thermal condition.

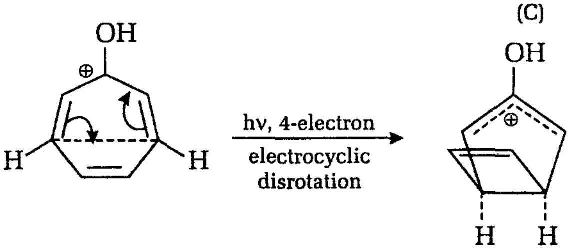
Alternative PMO-approach predicts that each step has 6-electrons with 0-node, therefore, proceeds through aromatic transition state and is thermally allowed.

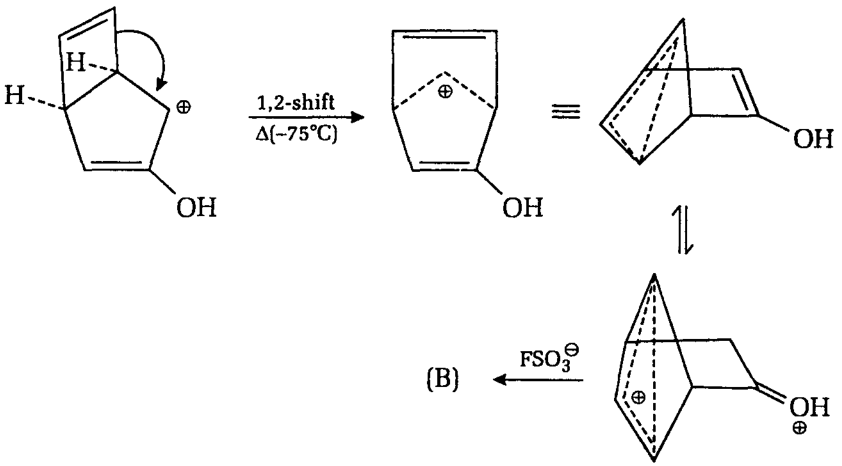


10.



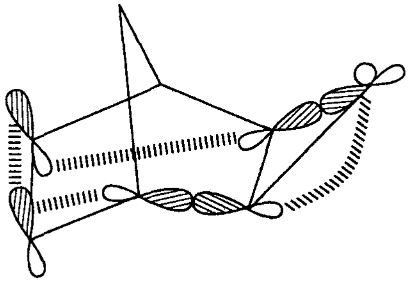
(C)



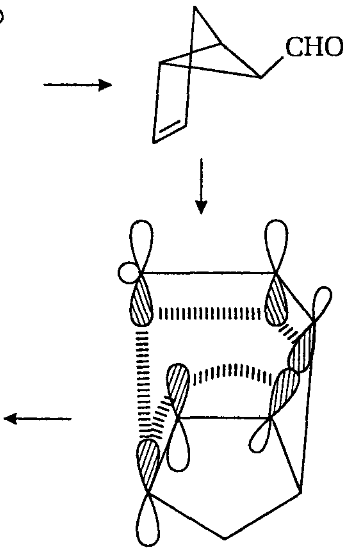


11. As per FMO-method first step is $\pi^4s+\pi^2s$ cycloaddition which is thermally allowed. Second step is again $\pi^4s+\pi^2s$ process which is also thermally allowed. Third step is thermal dehydration which is facile as two —COOH groups are *cis*-to each other. In fourth step intramolecular cycloaddition of $\pi^2s+\pi^2s$ takes place which is photochemically allowed to give all *cis*-substituted cyclobutane ring.

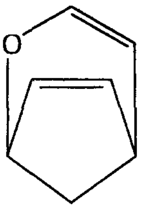
    According to PMO method T.S. of first step and also second step has 6-electrons, 0-node and therefore aromatic. Thus, both the steps are thermally allowed. T.S. of fourth step has 4-electrons, 0-node and is therefore **antiaromatic** indicating this step is photochemically allowed.
12. First step is a $(\pi^2a+\sigma^2s+\sigma^2a)$ thermal rearrangement of *exo*-epoxide to bicyclic aldehyde through aromatic transition state as shown below :



T.S. (epoxide) : 6 electrons, 2-nodes, aromatic, thermally feasible

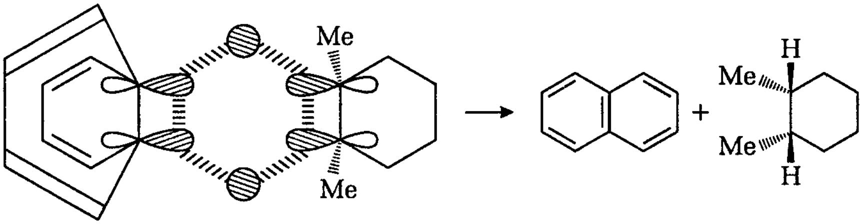


T.S. : 6 electrons, 0-nodes, aromatic, thermally feasible



Second step is Cope-rearrangement ($\pi^2s+\pi^2s+\sigma^2s$). As both the steps proceed through aromatic T.S., therefore, are thermally feasible.

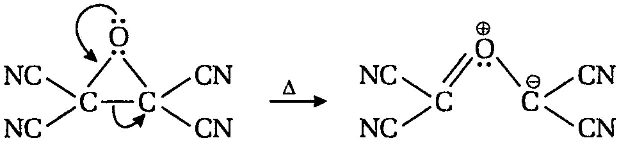
13. This reaction involves stereospecific hydrogen transfer and proceeds through aromatic transition state, hence is thermally allowed as given below :



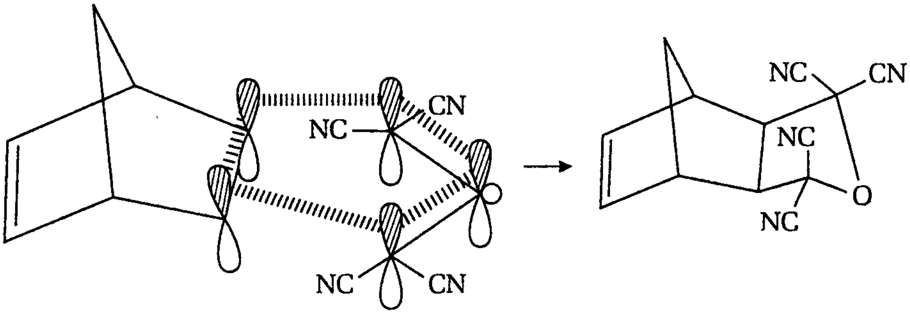
T.S. : 6-electrons, 0 node, aromatic

Products are naphthalene and *cis*-1, 2-dimethylcyclohexane.

14. Under thermal condition epoxide becomes polar as given below :

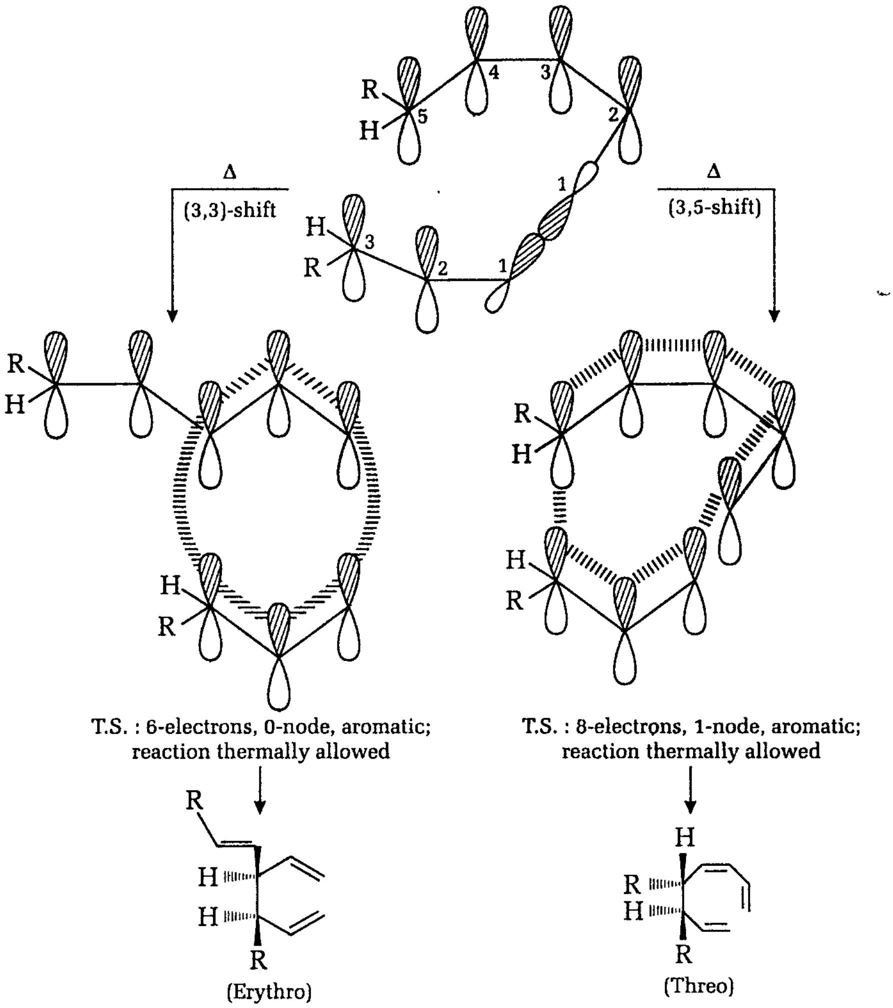


Dipole has 4-electrons which can add to one of the double bond of substrate through 6-electron aromatic transition state. Hence, reaction is thermally feasible.



T.S. : 6 electrons, 0-nodes, aromatic; reaction thermally feasible

15. In this compound one σ-bond is flanked by a π-system on either side. It is possible that 3, 5-sigmatropic (supra-antara) might have taken place to give a *threo*-product. On the other hand 3, 3-sigmatropic shift (Cope-rearrangement) may give an *erythro*-product. Transition states for both the possibilities are given below (Fig. 8.1.).

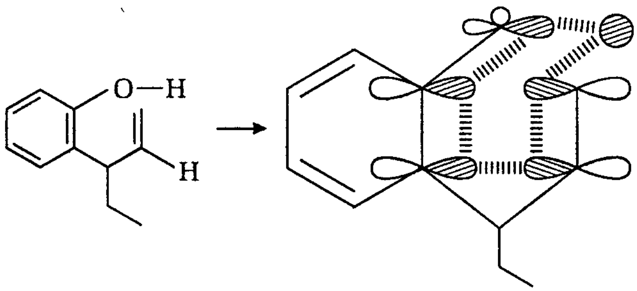


T.S. : 6-electrons, 0-node, aromatic; reaction thermally allowed

T.S. : 8-electrons, 1-node, aromatic; reaction thermally allowed

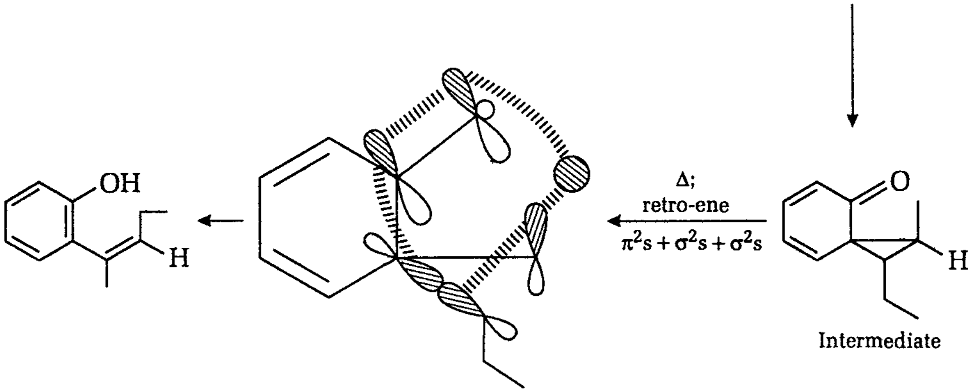
Fig. 8.1.

16. Formation of abnormal product can be explained on the basis of thermally allowed *ene*-reaction involving the normal product followed by retro-*ene* reaction of intermediate as shown below :



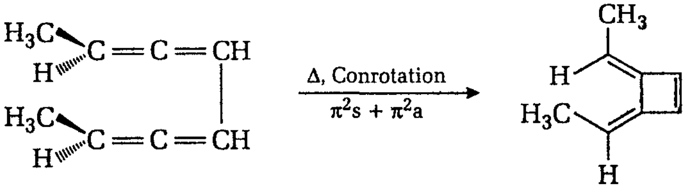
T.S. : 6 electrons,
0 node, aromatic Δ, allowed

$\Delta \Big\downarrow \pi^2s + \pi^2s + \sigma^2s$



T.S. : 6 electrons, 0 node, aromatic, thermally allowed

17. (a) The first is 3, 3-sigmatropic shift, symmetry allowed under thermal condition as it proceeds through 6-electron aromatic transition state (with 0-node). Second step is electrocyclic reaction involving butadiene moiety. The structure of product indicates that **conrotatory** cyclization of butadiene part of molecule according to selection rule takes place under thermal condition.



(b) Arguments similar to (a) hold good for (b) also.

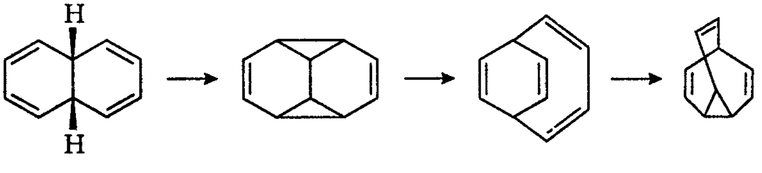
8.5 SYNTHETIC APPLICATIONS OF PERICYCLIC REACTIONS

Problems and Solutions

Pericyclic reactions are of stereospecific nature. This trait is of great value to synthetic organic chemists, because through a judicious choice specific chemical conversion can be carried out in which products have definite stereochemistry. Some problems related to these aspects are discussed in this unit.

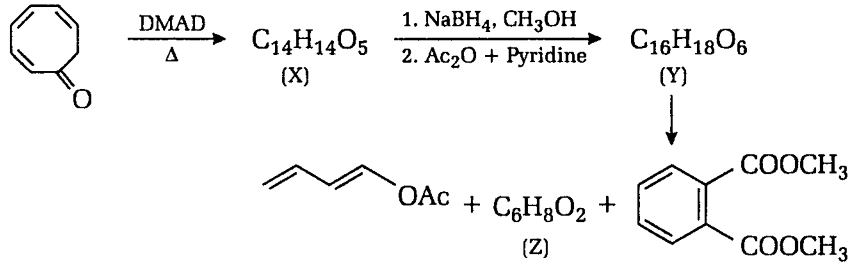
PROBLEMS

1. Conversion of *cis*-9, 10-dihydronaphthalene to bullvalene go through the steps given below :



Classify each step and predict if reaction is feasible thermally or photochemically.

2. Following sequence of reactions has been reported.

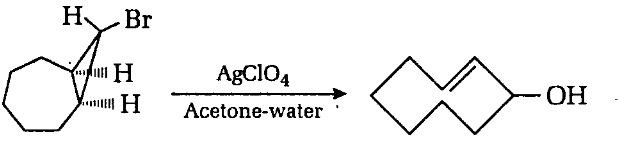


Comment on the mechanism of each thermolytic step and assign the structure of *X*, *Y* and *Z*. What is the source of butadienyl acetate?

3. Devise a procedure for synthesis of dimethyl furan-3, 4-dicarboxylate starting from furan and dimethyl acetylene dicarboxylate.

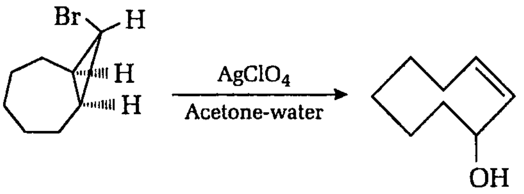
4. Following solvolysis reactions are reported in literature :

(a)



(*Trans*-double bond)

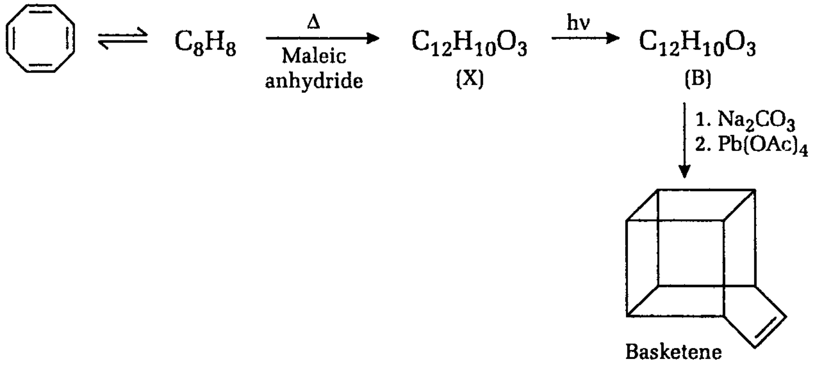
(b)



(*Cis*-double bond)

Suggest mechanism for them. Which reaction should occur rapidly?

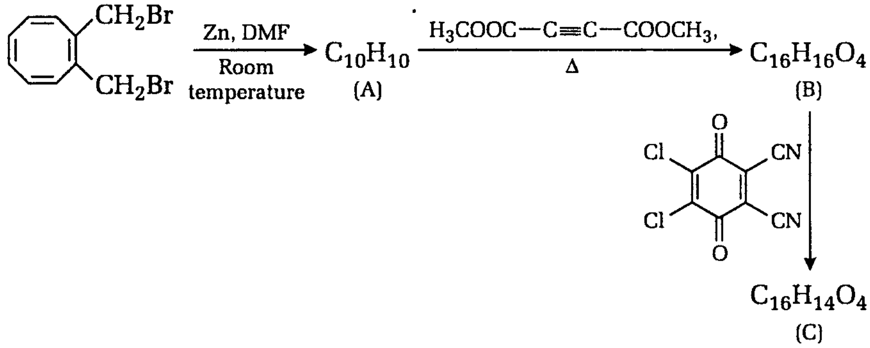
5. Cyclooctatetraene is used in the preparation of a number of highly strained cage compounds. Basketene is a Cage system with molecular formula $C_{10}H_{10}$. Following steps are involved in the synthesis of basketene :



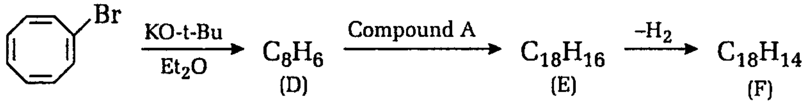
Assign structures to (A) and (B).

6. Suggest the structures of *A, B, C, D, E* and *F* in the following reaction sequences :

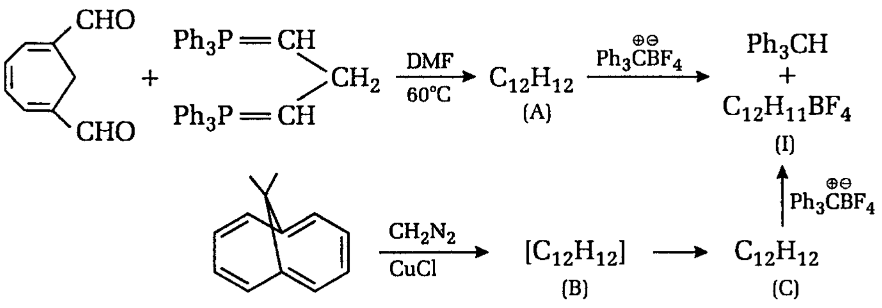
(a)



(b)

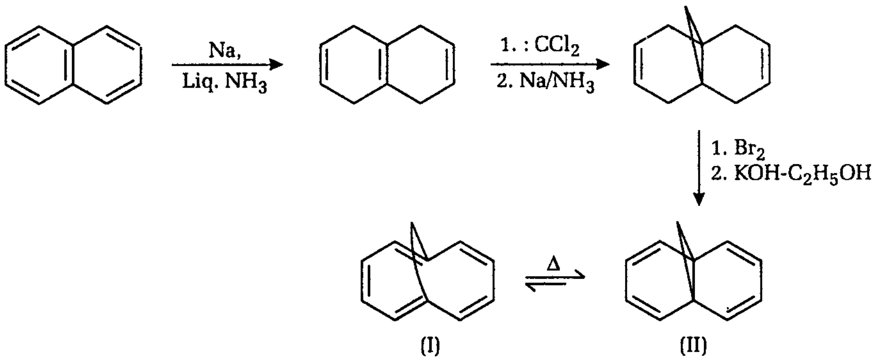


7. Two methods of preparation for the synthesis of a 10-π-electron system (I) are sequenced below :



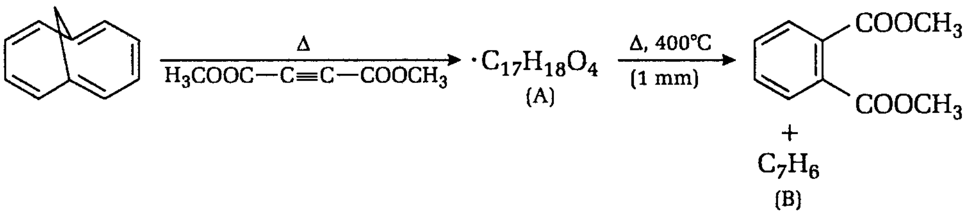
Assign the structures to (A), (B), (C) and (I).

8. A 10-π-electron system 1, 6-methanocyclodecapentaene (I) can be synthesised through *cis*-9, 10-dihydronaphthalene (II) which spontaneously rearranges to (I) according to following reaction sequence :

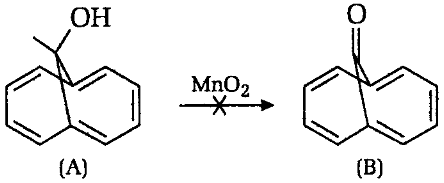


Suggest mechanism for thermal rearrangement II $\rightleftharpoons$ I.

9. Identify the compounds *A* and *B* in the following reaction sequence :



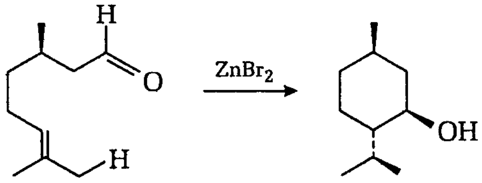
10. It is expected that alcoholic compound *A* upon oxidation should give ketone *B*. But this reaction failed.



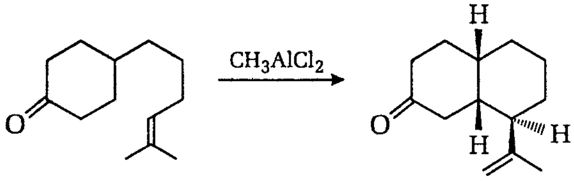
What other product might have formed. Also, explain the reason for the instability of (*B*).

11. Suggest the mechanism of following reactions :

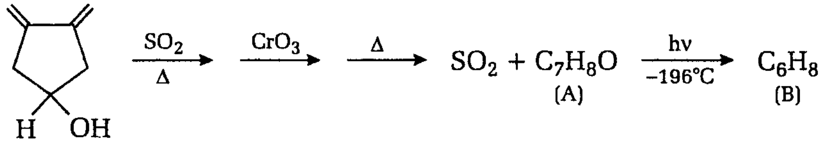
(i)



(ii)

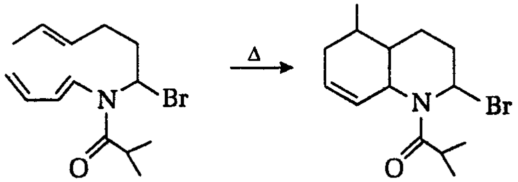


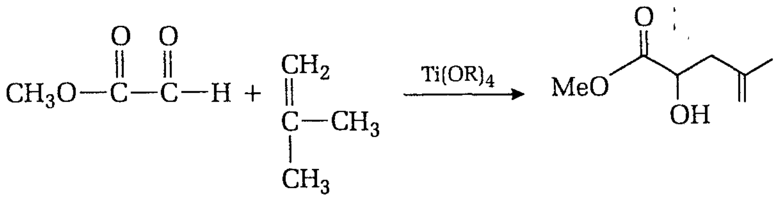
12. Study the following conversion and suggest the structures of compounds lettered (*A*) and (*B*) if (*B*) is very unstable and possesses triplet electronic state and obtained upon irradiation of (*A*).



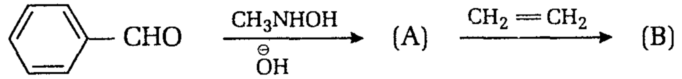
13. How following products are formed :

(a)



(b) 

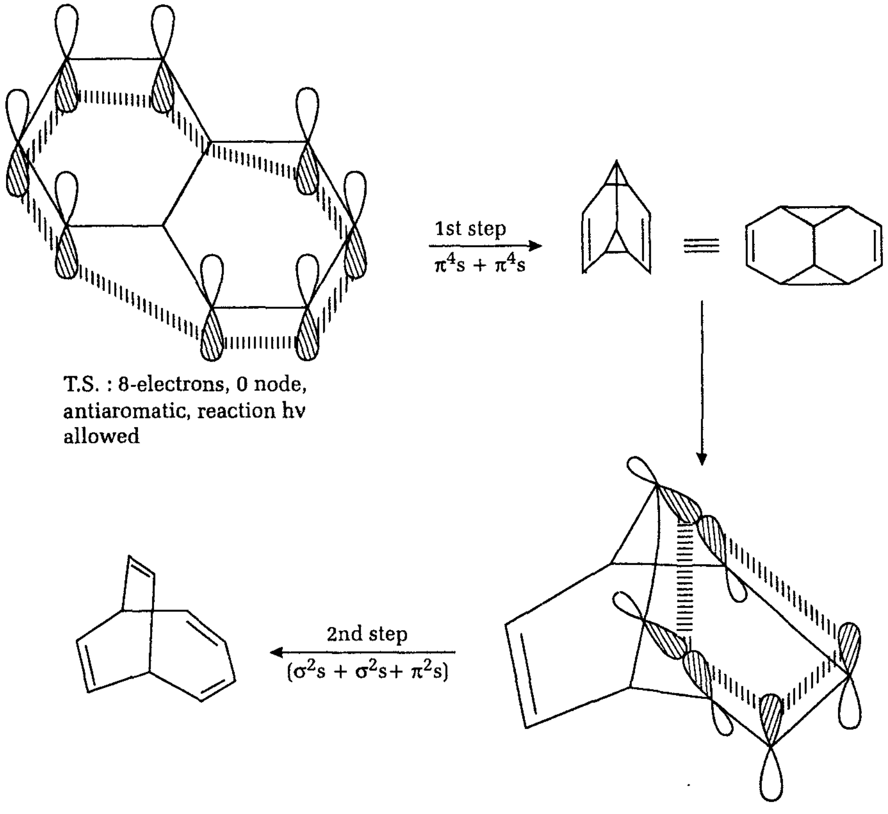
14. Give the products of following reactions. Also, discuss mechanism :

(a) 

(b) $C_6H_5-\overset{\oplus}{N}-N=\overset{\ominus}{N}+CH_3CH_2CH_2CH_2-O-CH=CH_2 \longrightarrow$

Solutions (Synthetic Applications of Pericyclic Reactions)

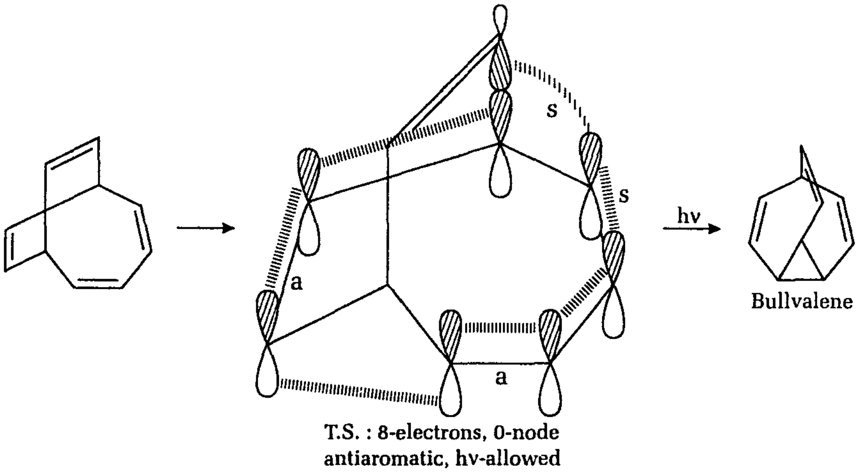
1. First step in this transformation is $\pi^4s+\pi^4s$ cycloaddition which is photochemically allowed. Its transition state contains 8-electrons and 0-node, therefore, is antiaromatic. Thus PMO-method also advocates it is symmetry allowed photochemically.
Second step is retro Diels-Alder cycloreversion of $\sigma^2s+\sigma^2s+\pi^2s$ type which is allowed thermally. T.S. of second step contains 6-electrons and 0-node, therefore, is aromatic predicting reaction is thermally allowed.



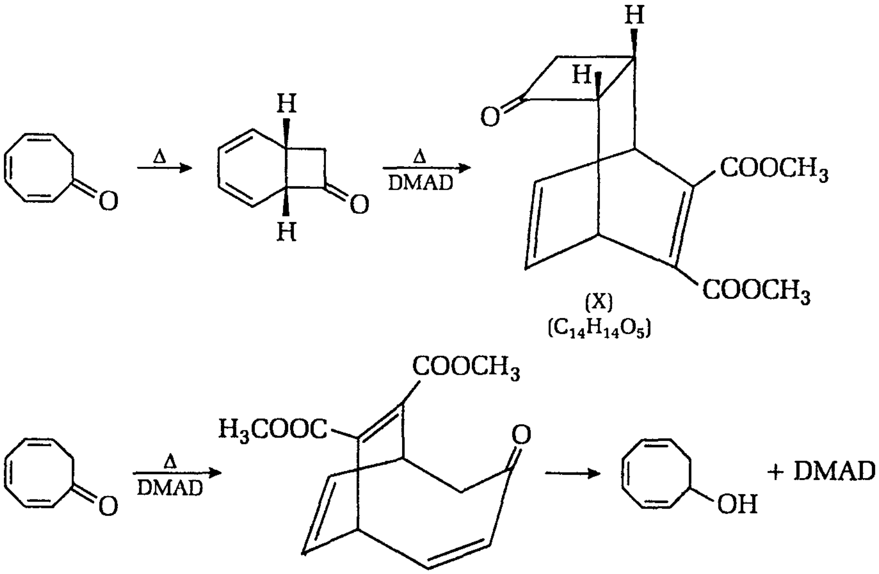
T.S. : 8-electrons, 0 node, antiaromatic, reaction hv allowed

T.S. : 6-electrons, 0-node, aromatic, Δ-allowed reaction

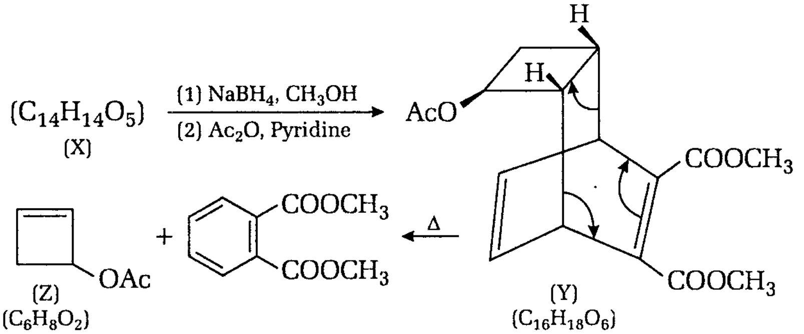
Last step gives bullvalene through 8-electron transition state with 0-node. As T.S. is antiaromatic, reaction is photochemically allowed.

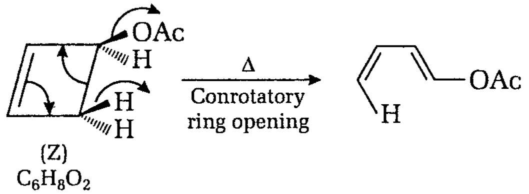


2. Cyclo-octatrienone gives X in two thermally allowed steps. Dimethyl acetylene-dicarboxylate (DMAD) can not add to three double bonds of cyclooctatrienone because in that case it will be $\pi^6 s + \pi^2 s$ cycloaddition which is symmetry forbidden under thermal condition. Alternatively DMAD may add to butadiene moiety to give (X) [Mol. formula $C_{14}H_{14}O_5$), but it will give alcohol of cyclooctatrienone and DMAD after reduction and thermolysis.



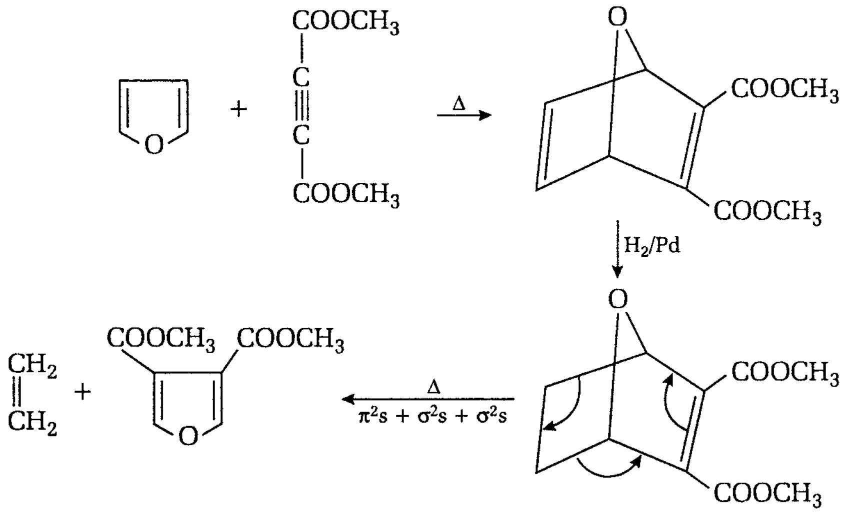
Keto group of condensed ketodiester may be reduced by $NaBH_4$ to alcohol leaving ester group unaffected. Alcoholic group may undergo acetylation with acetic anhydride and pyridine. The acetate on pyrolysis gives final product as a result of **retro-Diels-Alder reaction** (cycloreversion) as given below :





trans-Acetoxybutadiene is formed under thermal condition from (*Z*) through 4-electron electrocyclic process. All thermolytic processes are symmetry-allowed.

3. Dimethyl furan-3, 4-dicarboxylate can be synthesised by the following steps :



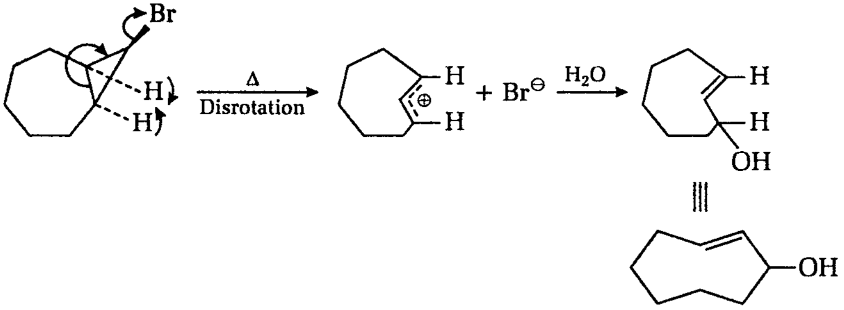
It is worthnoting that less-substituted double bond is preferentially reduced catalytically (H_2/Pd).

4. In the T.S. of solvolysis reaction, *p*-orbitals which come into existence by C—C cleavage of cyclopropane ring anchimerically assist solvolytic cleavage

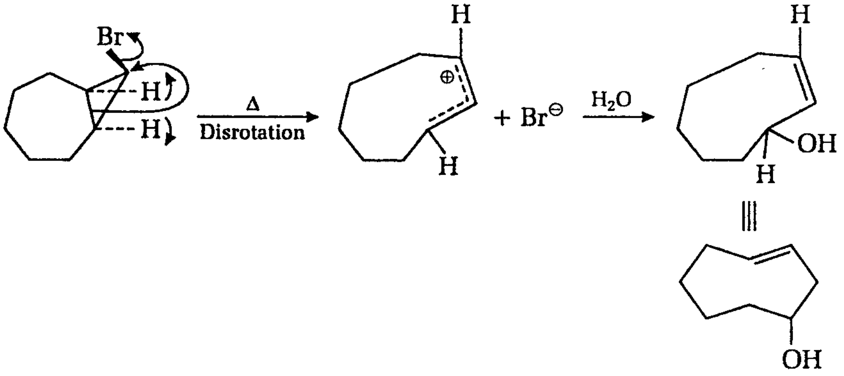
of C—Br bond stereospecifically through intramolecular S_{N^2} displacement on C-atom carrying Br atom (group). Such stereospecific reaction require C—C bond cleavage of cyclopropane and heterolysis of C—Br bond concurrently. Following this way (a) and (b) reactions should proceed through same intermediate carbonium ion and should afford the same product which is not the case here.

The ring-opening is two electron electrocyclic reaction. Two disrotatory opening are symmetry allowed under thermal conditions as illustrated below :

(a)

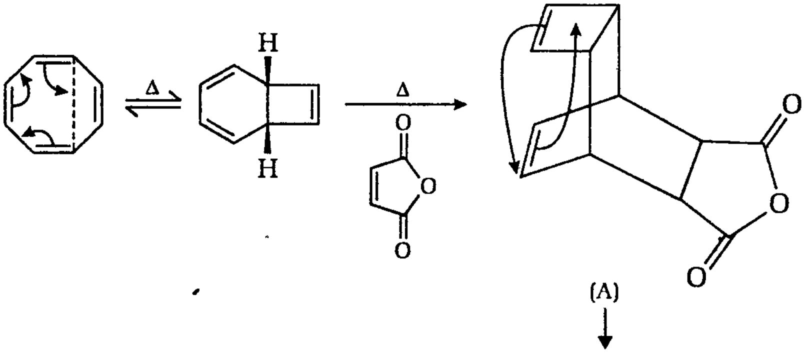


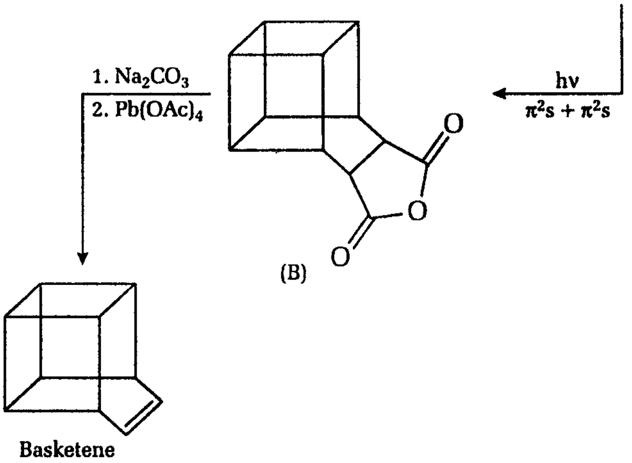
(b)



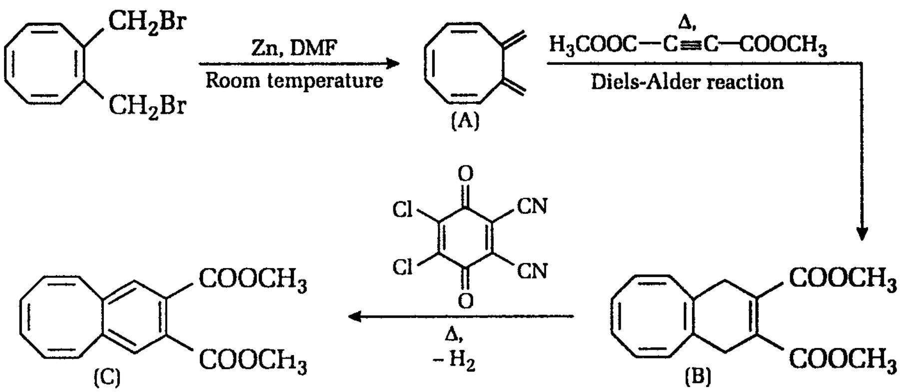
Out of these two process one forming *trans*-double bond is sterically preferred. Therefore, process (a) proceeds at faster rate than (b).

5. This conversion can be illustrated as given below :

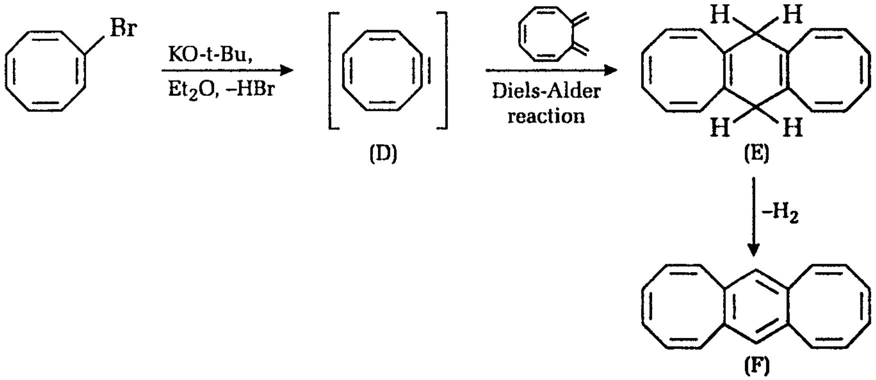




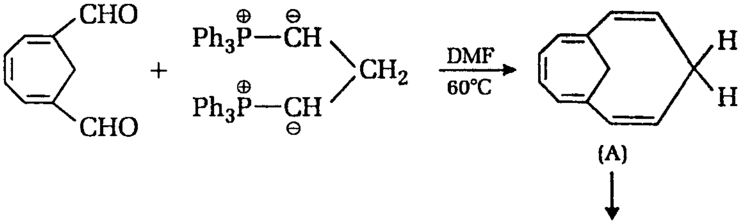
6. (a)

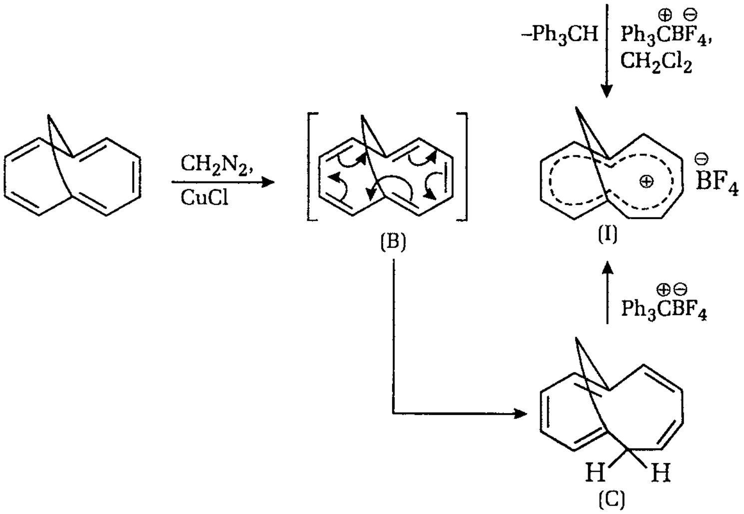


(b)



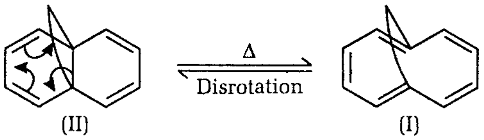
7. Structures of (A), (B), (C) and (I) in this preparation are illustrated below :



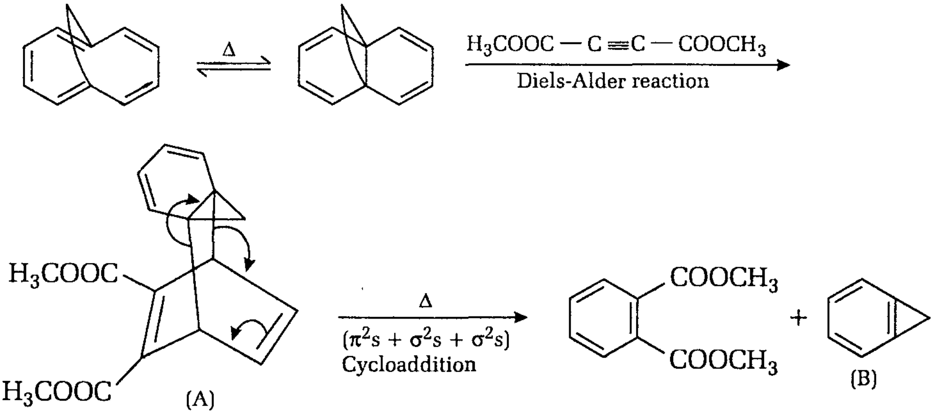


The interconversion $B \rightleftharpoons C$ is 10-electron electrocyclic reaction (thermal disrotation).

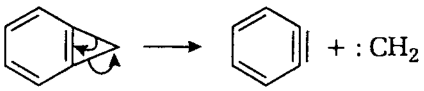
8. This is 6-electron electrocyclic reaction which proceeds by disrotatory motion under thermal conditions. Geometry of II presents no steric hinderance in disrotation.



9.

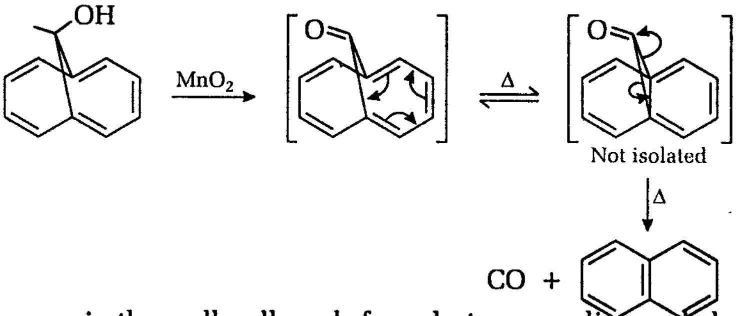


(B) is highly strained molecule. Reason for existence of (B) is that further reaction of (B) provides product which is thermodynamically less favourable than (B) as given below :



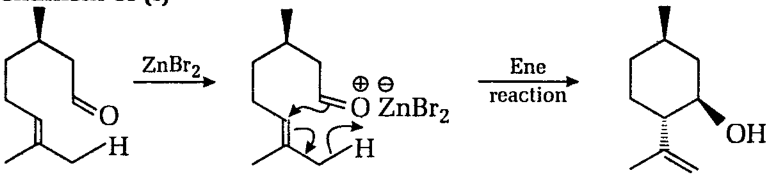
This is (2+0) cycloreversion which is probably endothermic.

10. MnO_2-oxidation of (*A*) may give another product naphthalene and carbon oxide through following mechanism :

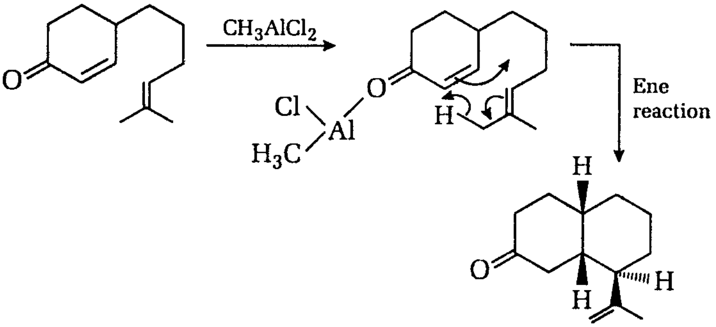


This process is thermally allowed, four-electron non-linear cheleotropic reaction. Thermodynamic stability of naphthalene and carbon monoxide is driving force for concerted decarbonylation process.

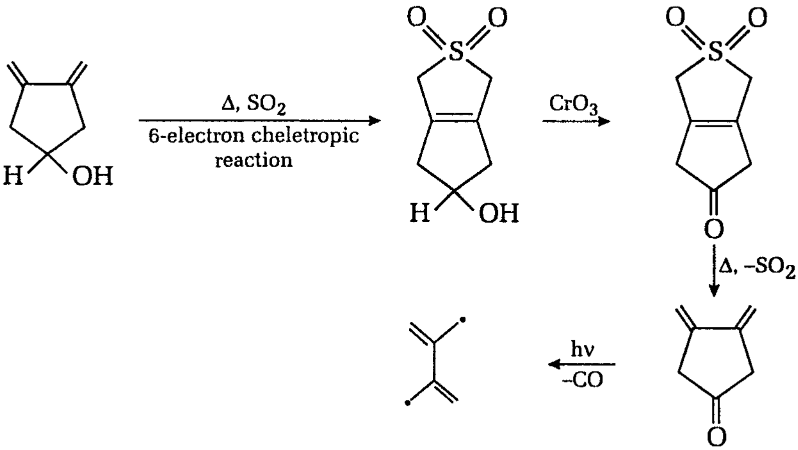
11. Mechanism of (i)



Mechanism of (ii)



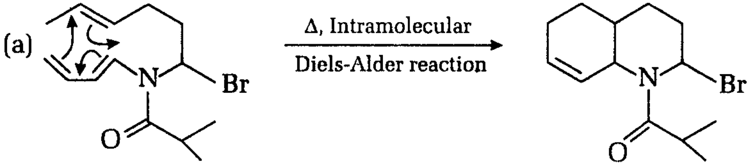
12.

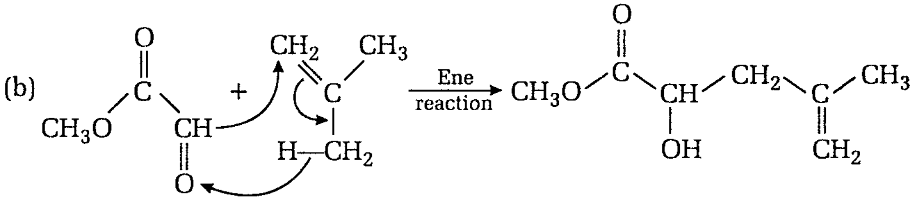


(B) (A)

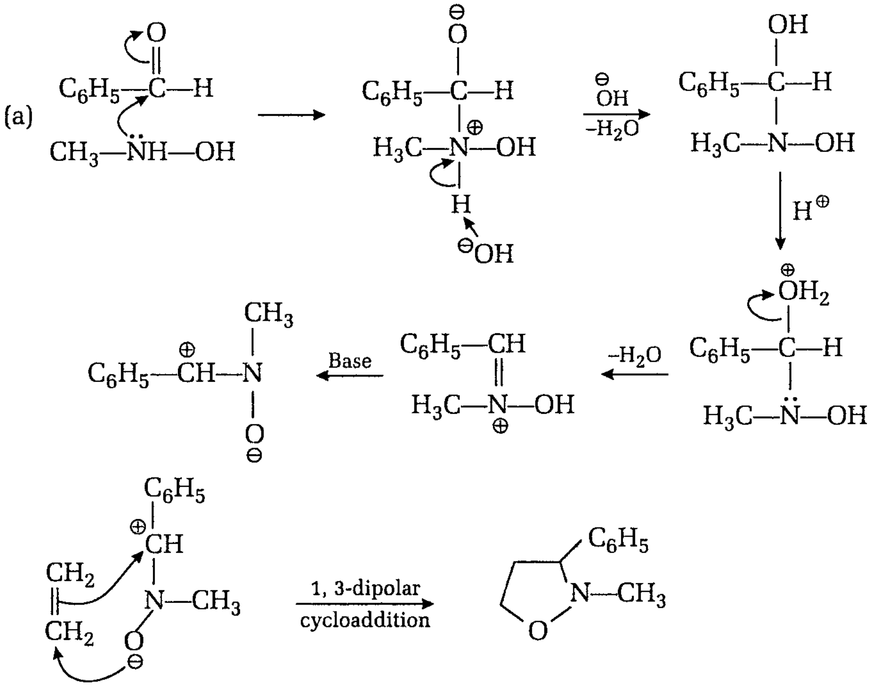
Tetramethyleneethane

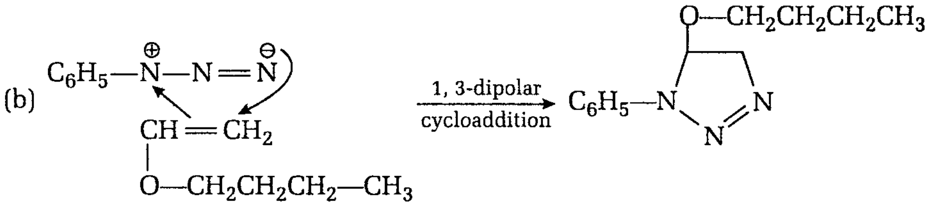
13. Mechanism of formation of products in (a) and (b) is as follows :

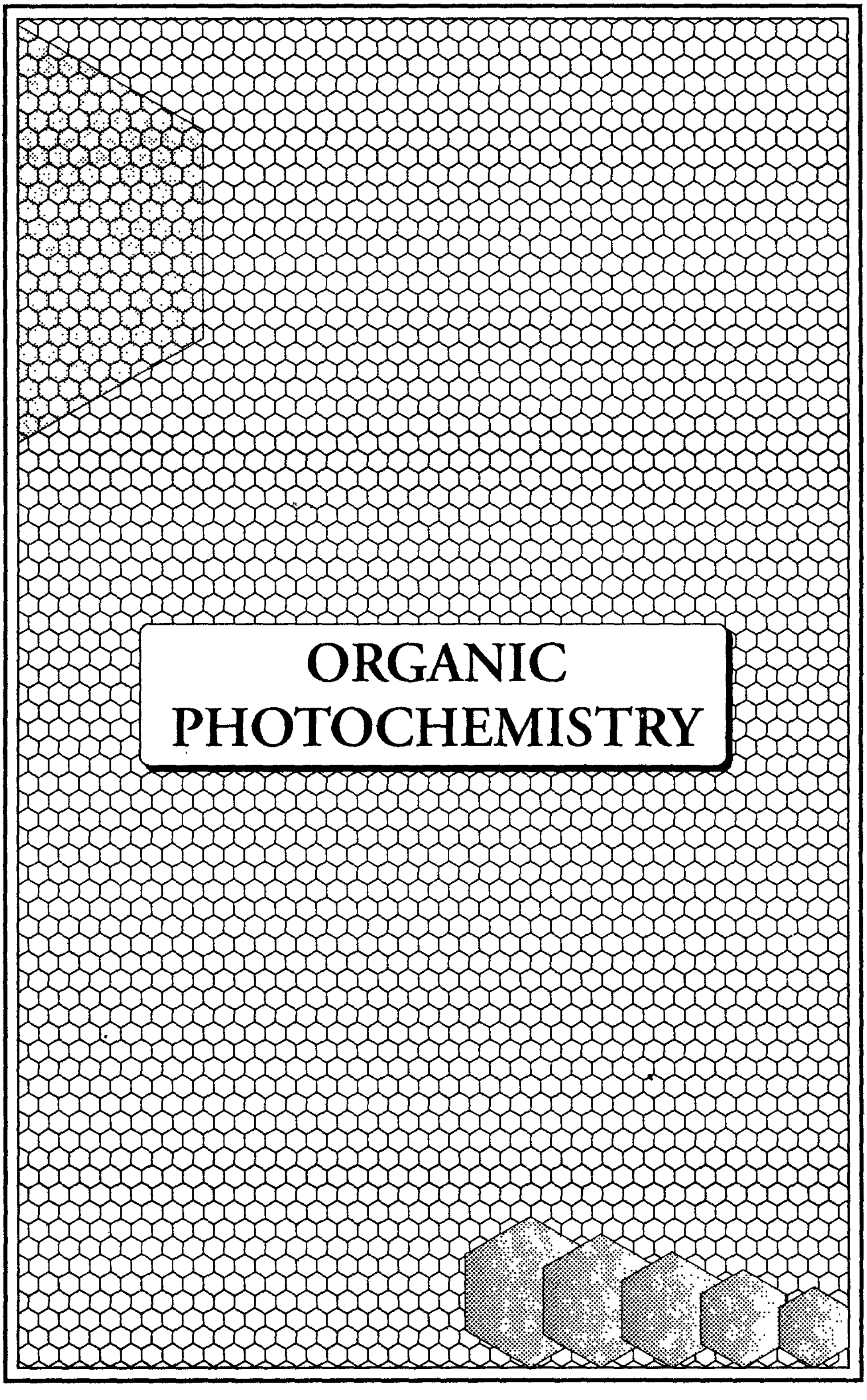




14. Product formed in reaction sequence in (a) and (b) and mechanism of their formation is discussed below :







ORGANIC PHOTOCHEMISTRY

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UNIT

1

INTRODUCTION

The evergreen branch of science—chemistry, deals with the different scientific aspects of chemical transformations. Almost all chemical/physical conversions need energy to get initiated. This required energy [or says Activation energy] can be supplied in two different ways. First, by increasing the temperature of reaction mixture [produces a continuous increase in energy]. Secondly, by irradiating the reaction mixture with radiations of suitable energy [produces discrete energy gain]. Plank's quantum hypothesis demonstrates that light is not continuous but it is made up of tinny energy particles, called quanta or photons. The energy associated with any radiation is directly proportion to the frequency of radiation and is expressed as,

$$E \propto \nu$$

$$E = h\nu \qquad \ldots(1)$$

where, E = the energy associated with radiation
ν = frequency of radiation
h = constant of proportionality and known as Plank's constant $\{6.62620 \times 10^{-34}$ Js$\}$.

$$\because \qquad \nu = \frac{c}{\lambda}$$

$$\therefore \qquad E = \frac{hc}{\lambda} \qquad \ldots(2)$$

where, c = velocity of light
λ = wavelength of radiation.

According to Bohr's quantum model of atom and molecular orbital theory, there are different energy levels in an atom/molecule. Hence, electrons present, could occupy only these discrete electronic energy levels, scientifically orbitals. So a definite energy is required for the excitation of a electron from one energy level to another higher energy level. The total energy of a molecule is the sum of its electronic energy, vibrational energy, rotational energy and transnational energy.

$$\boxed{E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}}}$$

The first three energies are quantised, *i.e.,* they can change only by discrete energy jump or fall, while transnational energy (Energy due to molecular movement) is not quantised and can change in a continuous manner.

To cause a chemical change, energy of radiation must be sufficient to make an electronic Transition from a molecular orbital of higher one. But each electronic state is associated with a number of vibrational and rotational energy levels. So not a specific radiation frequency but a region of electromagnetic radiation is taken into account. Morse diagram [Fig. 1.1] represent, it very beautifully.

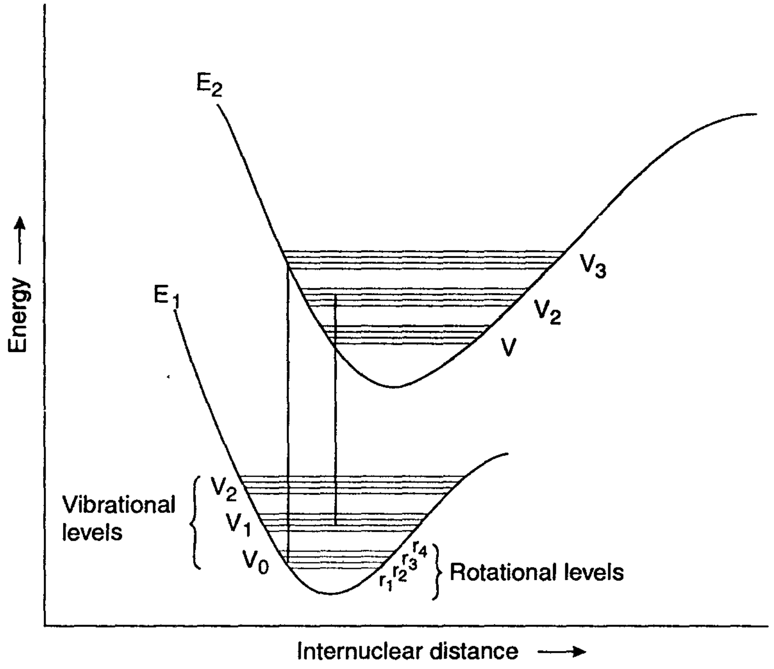


Fig. 1.1. Morse curves representing different energy states.

The electronic excitation is superimposed upon rotational and vibrational levels. Hence, during promotion, the electron moves from a vibrational and rotational level within one electronic mode to some other vibrational and rotational level of the higher electronic mode. So, there are a large number of transitions possible which are close together and responsible for change in electronic (*E*), vibrational (*v*) and rotational (*r*) energy levels. Hence, not just one wavelength but a large number of wavelengths which are close enough will be absorbed by same molecule [A region of electromagnetic spectrum be absorbed].

In view, to study photochemical changes, those electromagnetic radiations having wavelength from 200 nm to 800 nm are examined. Because this region contains energy [36–143 Kcal/mol] sufficient for electronic excitation from one molecular orbital to higher molecular orbital. Other radiations [higher or lower wavelength] do not make any contribution is photochemistry.

Thus, the branch of chemistry which deals with the study of chemical as well as physical changes initiated by light (radiation) is known as photochemistry. Here, the chemical change means the formation of new chemical species by the consumption of reacting ones. While physical changes means, those phenomena in which energy get released in different ways other than chemical change.

The actual starting of life an earth was with the evolution of Blue-Green Angle. Chemically, evolution of life was with a photochemical reaction—Photosynthesis, which is still ultimate source of food energy [Bio-organic food on earth].

$$6CO_2 + 12H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

In photosynthesis, the green pigment—Chlorophyll, present in the leaves of plants absorbs sun-light and this energy is used to convert carbondioxide and water into carbohydrate and releases oxygen.

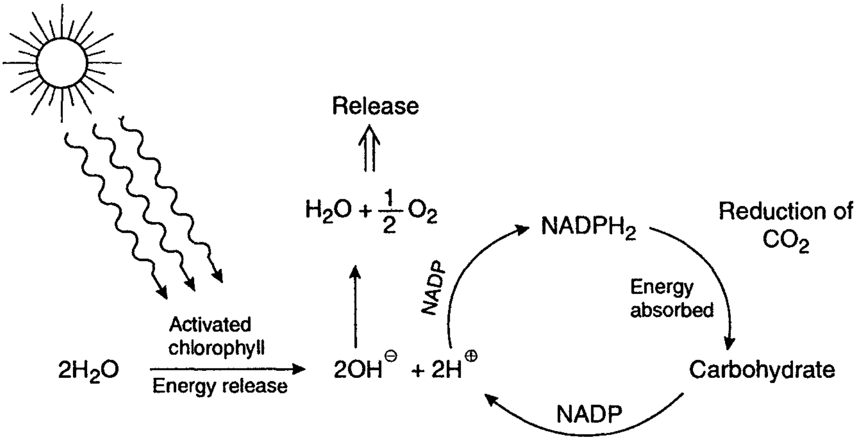


Fig. 1.2. **Photosynthesis.**

Photochemistry have a number of applications in the field of science and technology. A lot of synthetically important reactions which can't be carried out in dark, proceed photochemically. Another example of Bio-organic photochemical reactions is the synthesis of Vitamin D within the body. Vitamin D [calciferol] is formed in the presence of sunlight from Chole.

1.1 ACTIVATION ENERGY

Generally, energy is supplied to bring a chemical transformation. The reacting molecule first acquire enough energy to cross the energy barrier separating reactants and products. This required amount of energy is known as Activation energy (Ea).

In some cases activation energy may be so low that molecules have enough thermal energy at room temperature. Under these conditions a spontaneous reaction will occur. Additional energy is supplied for non-spontaneous reactions.

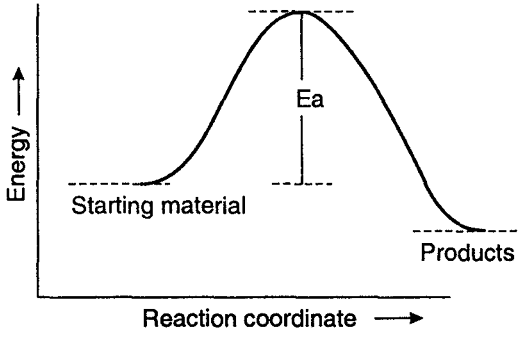


Fig. 1.3. **Activation energy curve.**

1.2 ENERGY INTAKE [THERMAL OR PHOTOCHEMICAL]

As the temperature of the system raised the molecules moves more rapidly, *i.e.*, translational energy increases. Some of these molecules moves faster and other slowly than the average ones. This additional movement facilitates more collision. At the same time molecules acquires additional rotational and vibrational energies also. When the energy absorbed by molecule, higher vibrational states [v_1, v_2 etc] get populated and reach excited state. In typical organic moles v_1 lies 2 to 10 Kcal/mol from v_0 vibrational state. At room temperature molecules have an thermal energy content of about 0.6 Kcal/mol. Many chemical reactions especially those that are intermolecular, involves these higher vibrational levels. This energy is sufficient to repture the bond [bond dissociation energy] [Fig. 1.4]. The bond dissociation energy varies widely and depends upon the structure of the molecule and nature of the atoms involved in the bond. About 101 Kcal/mol for C—H bond in methane and 83 Kcal/mol for C—C bond in ethane, is required bond dissociation energy.

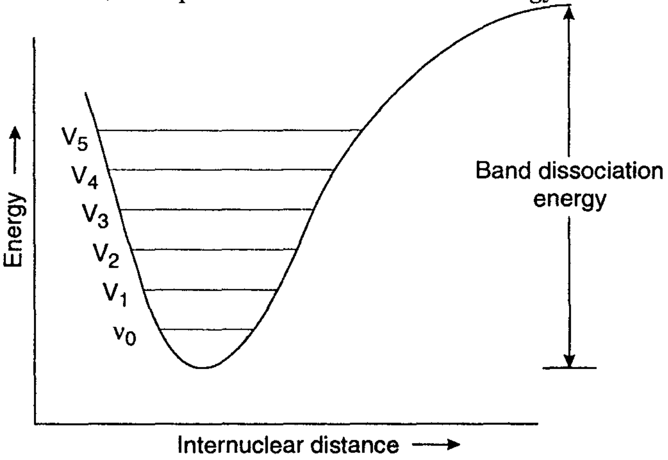


Fig. 1.4. Morse diagram representing bond dissociation energy and vibrational levels of the molecule.

On the other hand, absorption of light provides a large amount of energy to the molecules or to specific part of the molecule directly. Light of Infra-red region [> 8000 Å] having energy about 10 Kcal/mol which is sufficient for vibrational excitation. Light of shorter wavelength, visible region [4000 Å to 8000 Å], ultraviolet region [2000 Å to 4000 Å] and near ultraviolet region [100 Å to 2000 Å] of electromagnetic spectrum corresponds to energy about 36 to 143 kcal/mol. Light of UV-visible region have sufficient energy for electronic excitation of organic molecules. Fig. 1.5, morse curves represents different electronic states, lower curve represents electronic ground state [E_0] while, upper curve shows electronic excited state [E_1]. The transition involves excitation of an electron from a bonding molecules orbital to an antibonding molecule orbital.

Thermal and photochemical excitations provide two complementary methods for introducing energy into molecule. Thermal excitation introduces energy randomly into transnational, rotational and vibrational modes, producing

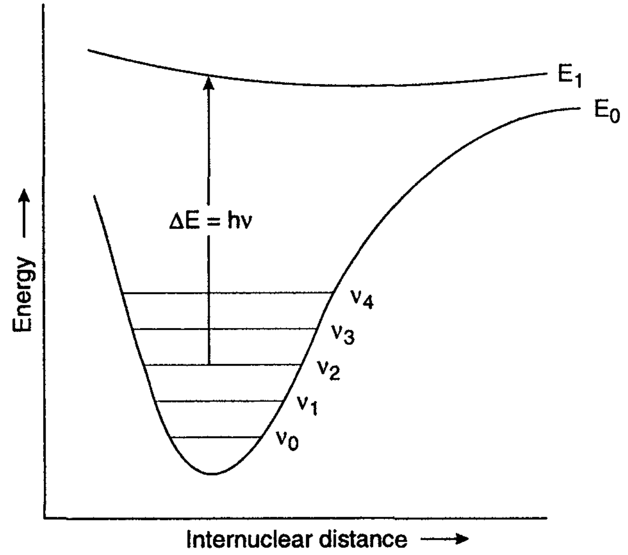


Fig. 1.5. Morse curve representing photochemical excitation.

an energy distribution in the system such that most molecules have about the same amount of energy. Absorption of electromagnetic radiation of UV-visible region, excites an individual molecule instantaneously to an excited electronic state. This promotion involves transition of an bonding electron to an antibonding electronic state. Thus, a large amount of energy is placed in a single molecule. That's why these two methods provides too different chemical sequences. "Now we can say photochemistry is the study of the chemistry of electronically excited molecules produced by the absorption of electromagnetic radiation".

1.3 BRIEF HISTORY OF PHOTOCHEMISTRY

Photochemistry probably begun with the origin of life. Indeed, photochemical reactions, such as photosynthesis have played a crucial role in the development of life. An average of about 418 kJ/cm^2 a day, radiation energy is continuously provided to earth by sun. Reports of organic photochemistry can be found in the earliest chemistry literature.* However, discovery and study of photochemical reactions were often result of an accident which could not be achieved by conventional synthetic methods. Until the development of quantum mechanics, interaction of light and matter not properly understood. As a result, during the primeval age the photochemistry [about 1850 to 1920] numerous and wonderous photochemical reactions were discovered. But useful application of these results lacking an unifying theory. Unfortunately, that time, the photochemical reaction mixture were often hopelessly complex and no method were available to control the reaction. The main causes of failure were :

1. Disability to trace impurities.
2. No control on experiments and
3. Effect of secondary reactions of the initially formed products makes the early photochemical literature difficult to interpret.

In early ninetees physical chemist starts a era in photochemistry, who studied the details of photoreactions in gas phase [Gas phase photolysis]. The availability of spectroscopic instruments and analytical techniques in mid nineteens till now and developments in other fields of chemistry, make photochemical studies easy and perfect. Because now

1. Difficulty in characterizing the complex products is decreased and
2. Gave promise of control of photochemistry [as a result of a more fundamental understanding of the nature of excited states].

Now it becomes increasingly clear that selectivity can be achieved in photochemical reactions. This is due to highly selective nature of light absorption which allows injection of energy into particular bonds of particular molecule. Under proper conditions, photochemistry may provide a short route for the synthesis of systems which are essentially unavailable by alternate synthetic methods. The development of spectroscopic techniques provides the way for direct study of transient intermediates. In this manner photochemistry gets today's face.

❑❑❑

UNIT

2

BASIC PRINCIPLES

Routes Available for Electronically Excited Species

The electronic excitation of organic molecules can happen after the absorption of light. But it always not produces chemical change. Because, after excitation, a number of physical phenomenons may occur which are in competition with chemical change. The ratio of product formed with number of quanta of light absorbed varies from fraction to several millions. Hence, it becomes very important for chemists to investigate these different routes available for photoexcited species and prediction to control these practical problems.

2.1 INTERACTION OF ELECTROMAGNETIC RADIATION WITH MATTER

Before studying interaction of electromagnetic radiation with matter, it is necessary to understand what electromagnetic radiation is.

Electromagnetic radiation shows both wave nature as well as particle nature.

According to Maxwell, **the electromagnetic waves are those waves in which there are sinusoidal variation of electric and magnetic field vectors at right angle to each other as well as at right angle to the direction of wave propagation.**

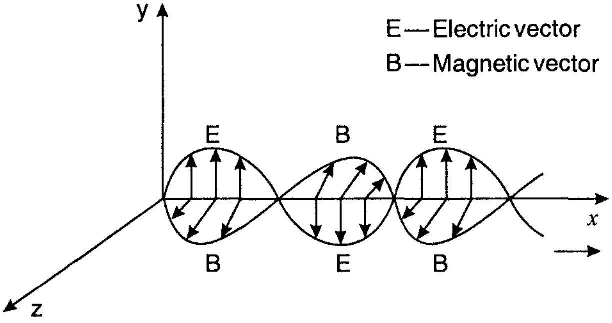


Fig. 2.1. Electromagnetic wave.

So, electromagnetic waves seems to be a stream, which progresses by interchanging electric and magnetic vector, to confirm flow of energy. The electromagnetic waves are produced by fluctuating magnetic field or by moving electric charge.

According to Plank, electromagnetic radiation is made of tiny energy packets, known as photons, which comes continuously from source of radiation.

Mathematically, the energy associated with the electromagnetic radiation is given by

$$E = h\nu$$

where, E = energy
h = Plank's constant
ν = frequency of radiation

Graphically, wave may be represented as follows.

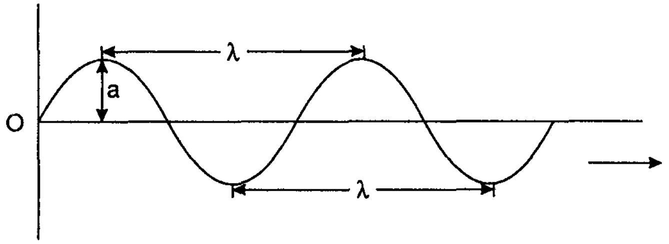


Fig. 2.2.

Different quantities associated

Wavelength : It is the difference between two adjacent trugs or crests. It is represented as λ and measured in nm (nanometer) or in Å [Angstrom].

Frequency : It is the number of waves passing through a point in one second. It is represented by ν and measured in Hertz [cycles/second].

$$\nu = \frac{c}{\lambda}$$

where, c is velocity of light.

Wave Number : It is the number of waves passing in one centimeter. It is represented by $\bar{\nu}$ and calculated in cm^{-1}.

$$\bar{\nu} = \frac{1}{\lambda}.$$

Amplitude : It is the height of through or crest. It is represented by a.

When a beam of radiation fall on the surface of matter [reacting species], it may get transmitted, reflected or absorbed. Transmission is the process in which electromagnetic radiation passes through the substance without any change in intensity. Reflection is the phenomenon in which radiation comes back without any change in intensity. Photochemistry begins with absorption of light. Absorption means, the light received after passing through, is of low intensity than that of incident light.

During the starting period of photochemistry, it was believed that photochemical transformation is caused by sun-light found near the earth surface. But the development of new techniques showed that the sunlight is composed of different components. The most valuable development arose is that both natural and man-made light produce identical chemical transformations. To undeastand of electromagnetic radiation we have to stud its spectrum [the arrangement of electromagnetic radiation is increasing wavelength or decreasing frequency]. The complete electromagnetic spectrum is shown in fig. 2.3.

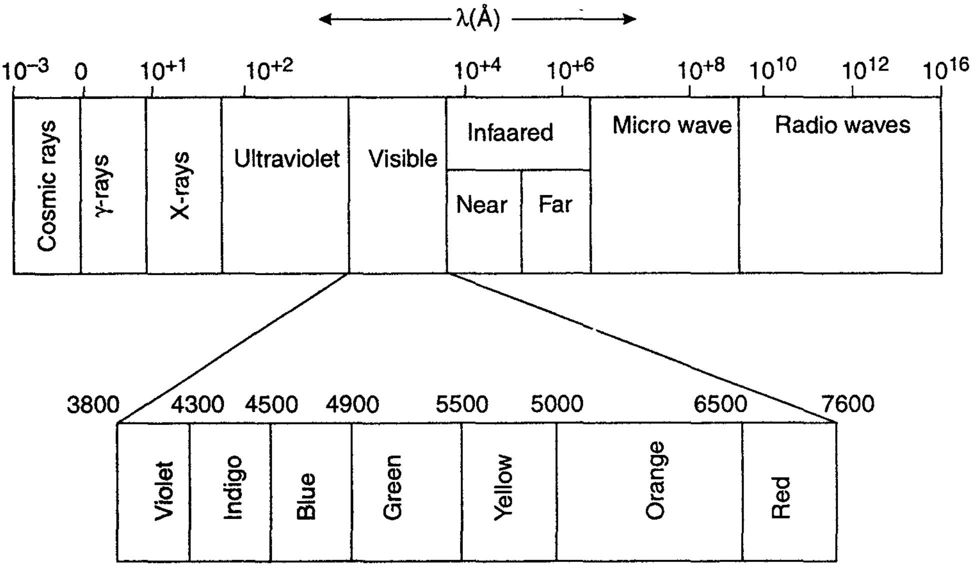


Fig. 2.3. Complete electromagnetic spectrum.

Only UV-visible region of electromagnetic spectrum [180 nm to 800 nm] are effective to produce chemical transformation because this region have sufficient energy for electronic promotion. Every organic molecule have different electronic energy levels in it, which are quantised. When light of sufficient energy falls on it, electrons from lower energy level [ground state] are promoted to higher energy levels. These electronically excited molecules may re-emit the radiation or produce a chemical change.

2.2 LAWS OF PHOTOCHEMISTRY

The study of photochemical reactions shows a number of variations like in absorption of specific frequency, specific chemical transformation and also specific photo-physical path to gain or utilise the gained radiation energy. These variations are following some rules. These rules are summerised in certain laws, termed as laws of photochemistry.

Absorption of specific frequency is due to the quantisation of electronic energy levels of molecules. Hence energy required for different transitions for different species are different. Also the portion of light used is not completely absorbed but only some fraction is utilized. These selections and utilizations are best demonstrated by Lambert-Beer's laws.

Lambert's Law : This law states that "When a beam of light is allowed to pass through a transparent medium, the rate of decrease in intensity with thickness is directly proportional to the intensity of light".

Mathmetically, $-\frac{dI}{dt} \propto I$

$$-\frac{dI}{dt} = kI \qquad \ldots(1)$$

where, I = Intensity of transmitted light
t = thickness of medium
k = Constant of proportionality

from eq. (1)

$$-\frac{dI}{I} = k\,dt \qquad \ldots(2)$$

On integration of eq. (2)

$$-I_n\ I = kt \qquad \ldots(3)$$

At $t = 0$, $I = I_0$

$\therefore$ $k = -I_n\ I_0$ put into eq. (3)

$$-I_n\ I = -I_n\ I_0 t$$

$$I_n \frac{I_0}{I} = kt \qquad \ldots(4)$$

or

$$I_t = I_0 e^{-kt} \qquad \ldots(5)$$

where, I_t is the intensity of transmitted light

I_0 is the intensity of incident light

k is the constant which depends on the wavelength and absorbing medium. $[K = k / 2.3026]$.

The ratio I/I_0 is termed as transmittance (T) and the ratio log I_0/I is absorbance (optical density) while I_0/I is termed as opacity.

It is very clear that the fraction absorbed by reacting molecule is independent of source intensity.

Beer's Law

It stats, "the decrease in intensity of incident monochromatic light is directly proportional to the number of reactant molecules (solution concentration)".

This law is based on the fact that intensity of transmitted light depends on the optical path length of the sample as well as on the concentration of solute. Then, the modified Lambert's law, mathematically is

$$\log \frac{I_0}{I} = act$$

or

$$\log \frac{I_0}{I} = \varepsilon t \qquad \ldots(6)$$

where, ε is the molar absorption coefficient and is a property of the individual compound {Helpful to measure absorptivity}.

Ultra-violet spectra are usually plotted as ε or log ε vs. wavelength. The log ε plots are particularly useful for exhibiting weak and strong absorption bands on the same scale. Fig. 2.4 shows the UV spectrum of a typical aromatic ketone {Benzophenone, Ph_2CO} and Fig. 2.5 shows UV spectrum of 1, 3-butadiene.

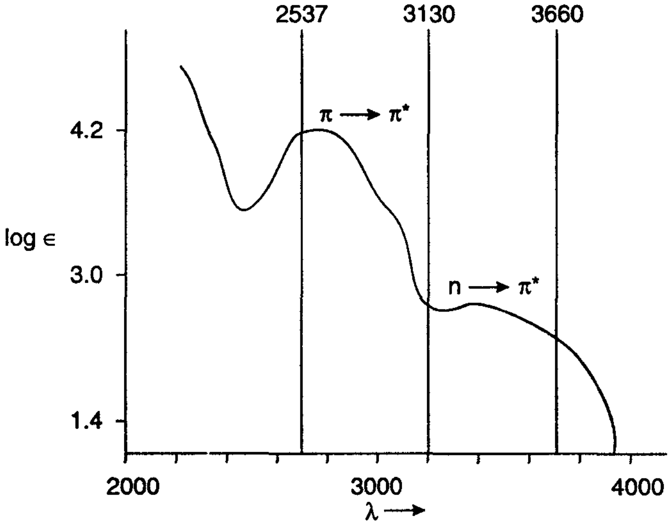


Fig. 2.4.

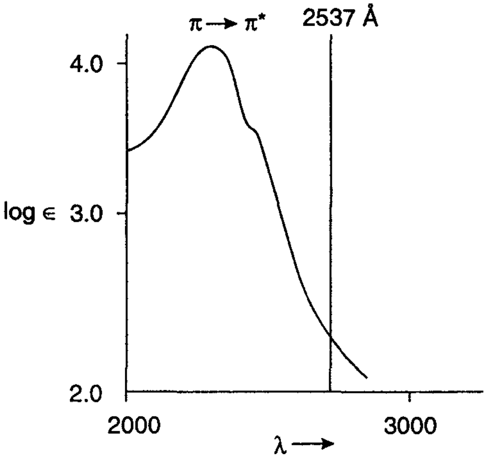


Fig. 2.5

There are few more laws which govern the interaction between electromagnetic radiation and matter which are also studied under the laws of photochemistry.

(I) Growths Draper Law : {Ist law of photochemistry} When light falls on any substance, only the fraction of incident light which is absorbed by reacting species can bring about a chemical change; reflected and transmitted light do not produce any such effect.

This law was found purely qualitative because when conditions are not favourable for molecules to react, in such cases the light absorbed in converted into heat or remitted as radiation of same or changed frequency.

(II) Law of Photochemical Equivalence : {IInd law of photochemistry}. This law was given by Stark in 1909 and in 1913 by Einstein. This states that, "Each molecules that takes part in a photochemical reaction absorbs one quantum of light, which induces the reaction".

2.3 FATE OF EXCITED MOLECULE

Polyatomic molecules have polydimensional surface which is too complex to be represented by Morse diagram. When such a molecule is irradiated by suitable electromagnetic radiation, it gets electronically excited and after it, a number of phenomenon may occurs which is best represented by Jablonski diagram.

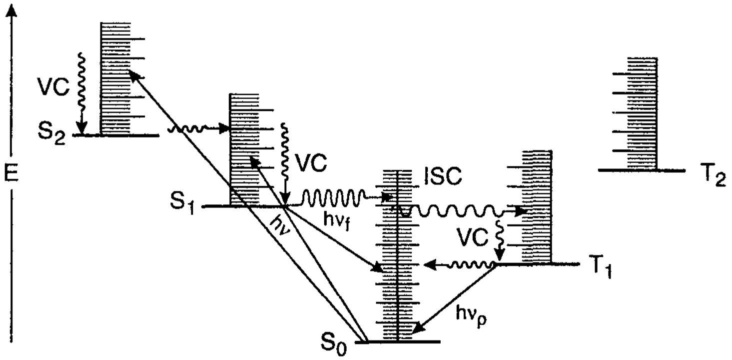


Fig. 2.6. Jablonski diagram showing electronic excitation and other phenomena.

where :

1. Radiative process : shown by straight line
2. Non-radiative process : shown by wave lines
3. VC : vibrational cascade
4. IC : Internal conversion
5. ISC : Intersystem crossing
6. $h\nu$: radiation
7. $h\nu_f$: fluorescence
8. $h\nu_p$: phosphorescence

Other than chemical reaction, the physical process which occur after electronic excitation of reactant are best represented in table 2.1.

Table 2.1 : Physical process undergone by excited molecule.

The superscript v indicates vibrationally excited states; excited states higher than S_1 and T_1 are omitted.

$S_0 + h\nu \rightarrow S_1^v$	Excitation
$S_1^v \rightsquigarrow S_1$ + heat	Vibrational relaxation
$S_1 \rightarrow S_0 + h\nu$	Fluorescence
$S_1 \rightsquigarrow S_0$ + heat	Internal conversion
$S_1 \rightsquigarrow T_1^v$	ISC
$T_1^v \rightsquigarrow T_1$	Vibrational relaxation
$T_1 \rightarrow S_0 + h\nu$	Phosphorescence

$T_1 \rightsquigarrow S_0 + \text{Heat}$	ISC
$S_1 + A(S_0) \rightarrow S_0 + A(S_1)$	Singlet-singlet transfer (photosensitisation)
$T_1 + A(S_0) \rightarrow S_0 + A(T_1)$	Triplet-triplet transfer (photosensitisation)

In order to study Jablanski's diagram, it is necessary to understand the concept of spin multiplicity. Ordinary organic molecules have an even number of electrons which are paired in ground state. Molecular states with paired electrons is called singlet state (S_n). After the absorption of light, the electronically excited molecules may have two electrons paired or unpaired. Paired state is defined as singlet excited state (S_n) and unpaired state by triplet state (T_n). These states are termed as spectroscopic states because a paired electrons gives a peak singlet while unpaired electrons gives splitted peak (triplet). The electronically excited species shows following major events, after the absorption of suitable energy radiation.

Energy Cascade : {Vibrational Cascade}

The loss of excess energy by electronically excited molecule to ground the vibratonal levels of the same electronic state, the energy is given in small increments to environment by collision with neighbouring molecules. The radiationless process is known by energy cascade.

In solution, the excess vibrational energy of S_2 electronic state will be rapidly disappeared by radiationless process, vibrational cascade to the solution.

Internal conversion : The process in which electronic excited states of molecule interchange from higher singlet to lower singlet excited state and higher triplet to lower triplet excited states, is a spin allowed process and termed as internal conversion. While transfer from singlet to triplet or triplet to singlet are known to be spin forbidden process.

$$\left.\begin{array}{l} S_n \rightarrow S'_n \\ T_n \rightarrow T'_n \end{array}\right\} \text{ spin allowed transition}$$

$$\left.\begin{array}{l} S_n \rightarrow T'_n \\ T_n \rightarrow S'_n \end{array}\right\} \text{ spin forbidden transitions}$$

{where $n > n'$}

When a spin allowed transition occurs with loss of energy to its environment in form of radiation or radiationless cascade is known as Internal Conversion (IC).

$$S(\nu_n) \longrightarrow S(\nu_0)$$

Internal conversion of electronically excited states requires very short time, about 10^{-11} S. The life time of upper excited singlet state is generally less than 10^{-11} S. The thermally equilibrated low lying singlet excited states $S_1(\nu_n)$ has relatively long life-time (10^{-8} S). The life time of this state is limited by four important processes.

(i) Fluorescence
(ii) Chemical reaction
(iii) Radiationless decay to ground state
(iv) Intersystem crossing

Fluorescence : It is the emission of radiation of longer wavelength after a time-leg from the absorption of radiation. This emission of radiation is accompanied by the deactivation of an electronically excited species to the same multiplicity, *e.g.*, $S_1 \rightarrow S_0, T_2 \rightarrow T_1$ etc. [spin-allowed]. Let, molecules from the S_1 state can drop to any vibrational level of So state with giving up all its energy at once in the form of radiation with in $10^{-9}S$. The pathway is not very common because it is relatively slow except shown by small molecules, *e.g.*, diatomic and rigid molecules. For most other compounds, fluorescence is very weak and not detectable. For compounds that do fluorescence, the fluorescence spectra are usually the approximate mirror image of the absorption spectra. This comes about because the fluosescencing molecule drops from the lowest vibrational level of S_1 state to various vibration at levels of S_0 and from the lowest vibrational level of S_0 to various levels of S_1.

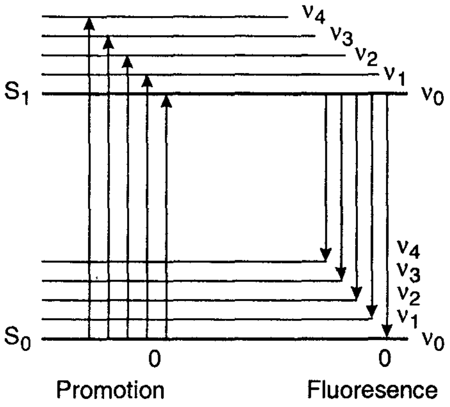


Fig. 2.7. Possible excitations of fluoresence.

The peak only common is one called 0-0 pears, that results due to the transition between lowest transition levels of S_1 and S_0.

$$S_0(\nu_0) \longrightarrow S_1(\nu_0) \quad \text{promotion}$$

$$S_1(\nu_0) \longrightarrow S_0(\nu_0) \quad \text{fluorescence}$$

The light emitted by illuminating system, is studied under three categories. When light emitted have same wavelength, fluorescence is termed as resonance fluorescence. If the fluorescence is sensitised by additional matter is termed as sensitised fluorescence. And if remission of radiation occur after sometime, it termed as slow fluorescence. There are a number of compounds emitting fluorescence like flourine, mercury, uranium, acetone, anthracene, Iodine vapours etc.

Chemical Reaction

Those excited states are very important, having long life-time. Because life-time of an excited state is directly proportional to the probability of occurance of a chemical reaction other then dissociation. Long lived excited states S_1 are one of the major reactive excited states in photochemical process. The life time of singlet excited state is about $10^{-8}S$.

Radiationless decay to ground state : Radiationless decay is already discussed in "energy cascade" and it occur in the form of electronic cascade or vibrational cascade. This decay makes the conversion of excitation energy into thermal or kinetic energy to its environment.

$$S_1(\nu_n) \longrightarrow S_1(\nu_0)$$

$$S_0(\nu_n) \longrightarrow S_0(\nu_0)$$

$$S_1 \longrightarrow T_1$$
$$T_1 \longrightarrow S_0$$
$$S_2 \longrightarrow S_1$$

Intersystem Crossing : The transfer of electronically excited state from singlet excited state to triplet excited state and triplet excited state to singlet state, is termed as ISC [Intersystem crossing]. ISC is a spin forbidden process. In some molecules it occurs with 100% efficiency, whereas in other it does not occur to any measurable extent. It depends on the energy difference between the excited singlet and triplet state Fig. 2.8.

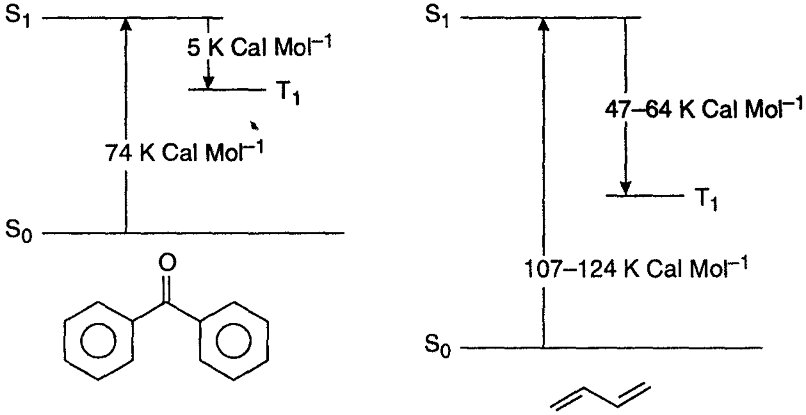


Fig. 2.8. Energetic representation of ISC.

In benzophenone it occurs with 100% efficiency, while in 1, 3-butadiene the ISC efficiency approaches zero. The efficiency of ISC depends upon a number of factors, but it mainly depends on the long-lived states and most stable geometry of the molecule. ISC is the conversion of one state to another of different multiplicity with loss of energy and provides the most favorable route to the triplet state. The potential and kinetic energy of both singlet and triplet states are the same at the point of ISC point as shown in the figure. Clearly ISC is most efficient when the singlet and triplet excited state energies are comparable energy to each other. The triplet so produced will be high in vibration energy and vibration cascade will rapidly occur. The reverse ISC process $T_1 \rightarrow S_1$, is highly unlike, since the most stable form of the triplet is lower in energy than the singlet excited state, but this case has also been reported in some compounds. [Molecular oxygen]. The ease and efficiency of ISC varies from compound to compound, being dependent on the structural environment of the chromosphere. In general, the longer lived an excited singlet, the more liable to undergo ISC. Carbonyl compounds give a high triplet state population by this route. The produced triplet state can undergo any of the following processes.

(i) Phosphorscence
(ii) Chemical reaction
(iii) Radiationless decay to S_0.

Phosphorescence

The molecules with relatively stable triplet excited state (T_1) may return to a singlet ground state (S_0) by giving up heat (ISC) or radiation of UV or visible region. The process of emission of radiation is termed as phosphorescence. The phosphorescence is a very slow process and requires approximately 10^{-3} to 10 seconds to occur. The triplet excited state generally have much longer life-time than singlet excited state.

When both fluorescence and phosphorescence occurs in same molecule, phosphorescence is found of lower frequency than the frequency of fluorescence. This is due to energy difference between $T_1 \rightarrow S_0$ and $S_1 \rightarrow S_0$ respectively. The phosphorescence and fluorescence best represented by Morse diagram Fig. 2.9.

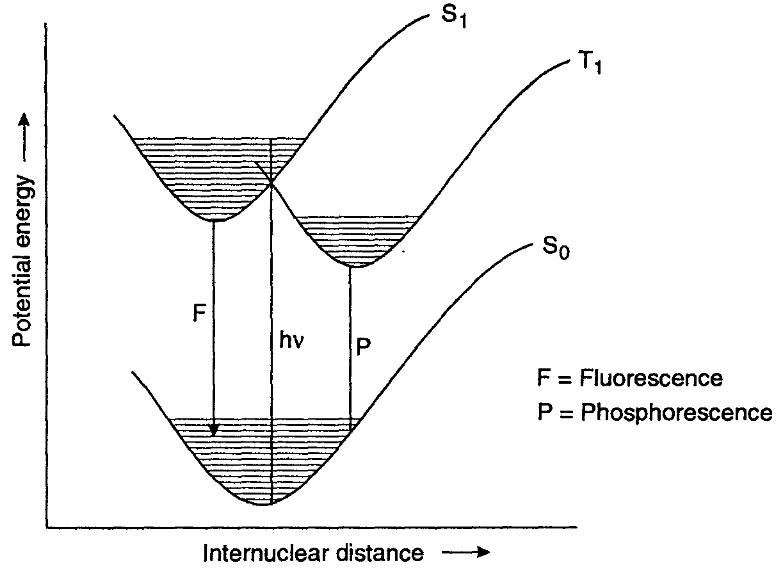
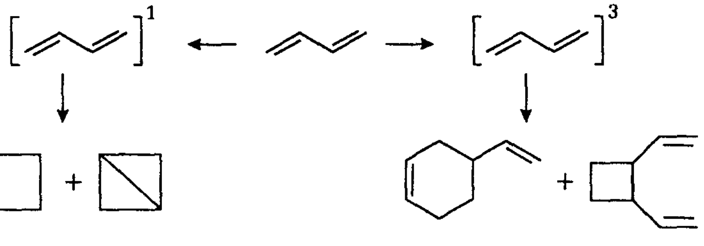


Fig. 2.9.

Chemical Reaction

Low lying triplet states have generally life-time greater then 10^{-6}S. But certain molecules have been reported which have life-time of triplet excited state greater than 10^{-6}S. Due to longer life-time, most chemical reactions occur from this triplet excited state.



Chemical reactions especially inter molecular reactions are favoured by long life-time of triplet excited states

Radiationless Decay to So

The another spin-forbidden ISC comes into existence when a triplet excited species looses its energy to its environment and comes back to ground state (S_0). This is accompanied by the negligible difference in energy of two points.

$$T_1(v_0) \longrightarrow S_0(v_n)$$

And this higher vibration ground state undergoes vibrational cascade to $S_0(v_0)$.

$$S_0(v_n) \longrightarrow S_0(v_0)$$

2.4 TYPES OF EXCITATIONS

According to molecular orbital theory, every molecule posses low energy bonding molecular orbitals, non-bonding molecular orbtals and antibonding high energy molecular orbitals. When molecule is excited by absorption of radiation (UV or visible light), its valence electrons are promoted from a bonding orbital to an antibonding molecular orbital. The energy of various molecular orbitals is in given order. Fig. 2.10.

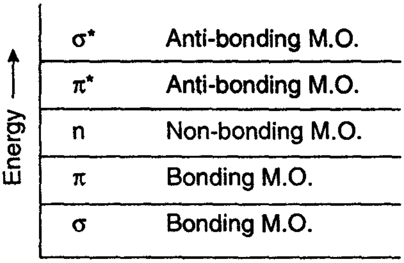


Fig. 2.10. Various electronic energy levels.

Only following four transitions [excitations] of electrons from low energy molecular orbitals to high energy molecular orbitals are allowed. Fig. 2.11.

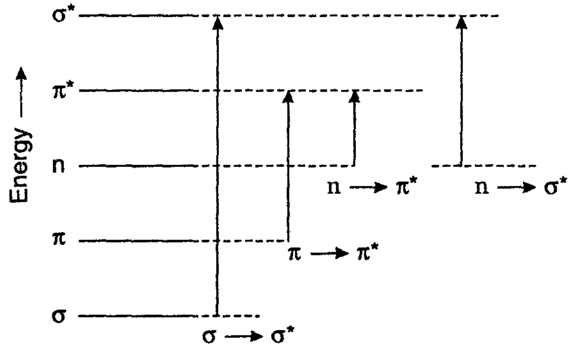


Fig. 2.11. Allowed electronic transitions.

Energy required for various transition obey the following order.

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

$\sigma \rightarrow \sigma^*$ Transitions

The antibonding molecular orbital associated with the excitation of σ electrons is called σ * [sigma asterike] (Fig. 2.10) and transition of electrons from σ to σ * is termed as $\sigma \rightarrow \sigma^*$ transition. This transition requires high energy and high energy radiations of vacuum ultra violet region (> 150 nm) are used for this purpose. Organic compounds with all valencies satisfied show this transition, *e.g.*, saturated hydrocarbons—methane, ethane, propane etc.

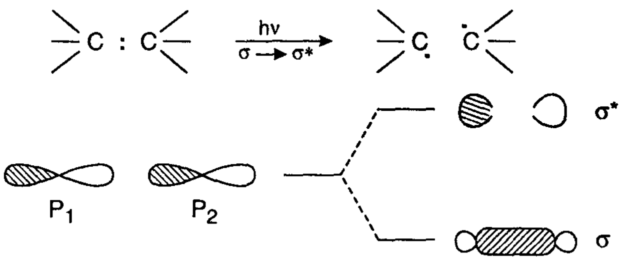
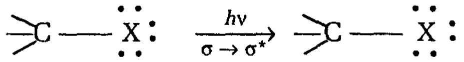


Fig. 2.12. σ and σ* molecular orbital.

n → σ * Transitions

The transition of electrons from a non-bonding orbital to σ * (antibonding) orbital, is reported in saturated compounds containing one Hetero atom with unshared pair of electrons [lone pair of electrons], known as non-bonding electrons. For example, Alcohols, ethers, ketones, aldehydes, saturated halides, amines etc.



$$\gt C — \underset{\bullet\bullet}{\overset{\bullet\bullet}{X}}: \xrightarrow[\sigma \to \sigma^*]{h\nu} \gt C — \underset{\bullet\bullet}{\overset{\bullet\bullet}{X}}:$$

This transition requires less energy than σ — σ * transition and is caused by radiations of wavelength below 200 nm. For example, water absorbs at 167 nm, methyl alcohol at 174 nm and methyl chloride at 169 nm.

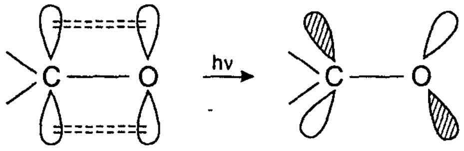
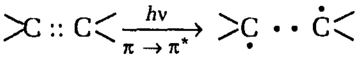


Fig. 2.13.

π → π * Transition

The transition from π (bonding orbital) to π * (antibonding orbital) occurs on the unsaturated centres of molecule. The organic compounds containing double or triple bonds shows this excitation.



$$\gt C :: C \lt \xrightarrow[\pi \to \pi^*]{h\nu} \gt \underset{\bullet}{C} \cdot\cdot \dot{C} \lt$$

This transition requires lesser energy than the previous transitions. The absorption of radiation-wavelength is fluctuate and depends on the molecule. For ethylene π → π * transition occurs at 171 nm (700 kJ mol^{-1}) and for butadiene at 214 nm (560 kJ mol^{-1}). This transition occurs at wavelength around 200 nm.

This transition occurs by the promotion of an electron from highest occupied molecular orbital [HOMO] to the lowest unoccupied molecular orbital [LUMO].

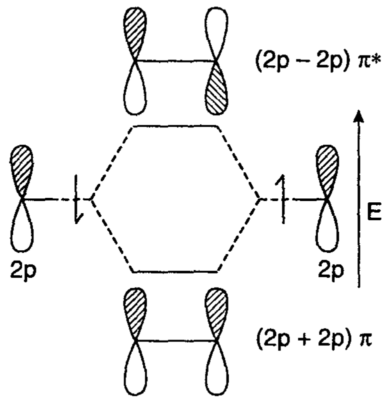


Fig. 2.14. Molecular orbital representation of ethylene.

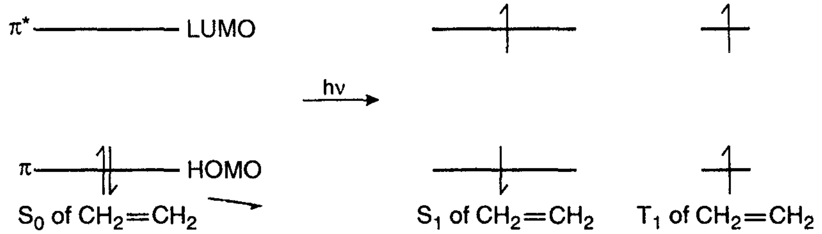


Fig. 2.15. π – π* excitation of ethylene.

n → π * Transition

The transition of electron from non-bonding orbital (*n*) to antibonding (π*) orbital is reported when an electron of unshared electron pair on hetero atom get excited to π * orbital. *n* → π * transition requires least energy out of all the transitions. Saturated aldehydes [$>C{=}\ddot{\underset{..}{O}}$] shows both π → π * and *n* → π * transitions at 180 and 290 nm respectively.

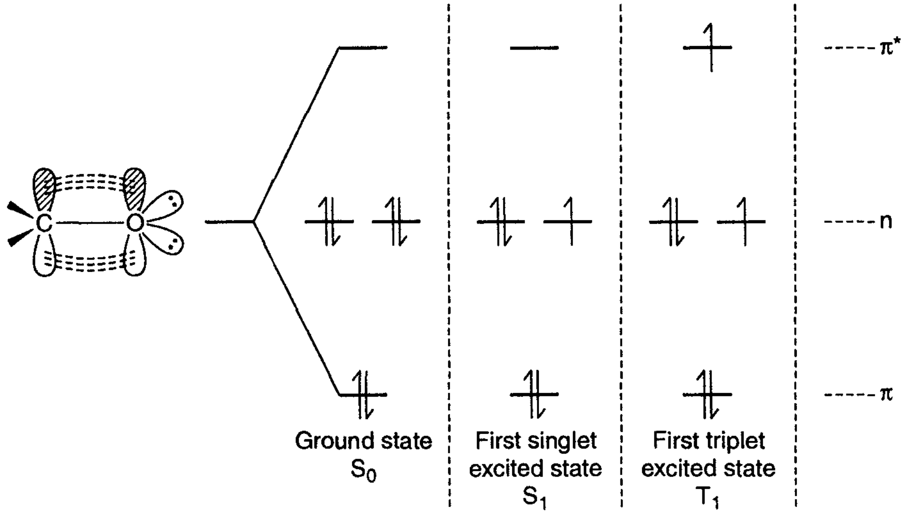


Fig. 2.16. *n* → π* excitation of carbonyl group.

2.5 TRANSFER OF EXCITATION ENERGY : [SENSITISATION AND QUENCHING]

There is one more way to produce electronically excited molecules by photochemical means. This method involves transfer of excitation energy from electronically excited molecule to ground stated molecule of other species. "The excitation of ground state molecule by the energy transfer from another species is termed as sensitisation while the deactivation of excited species is termed as quenching". The sensitisation mostly produce triplet excited species. The chemical changes produced by singlet and triplet excited states are quite different. Singlet excitation energy can be transferred but the probability is limited, because life-time of singlet excited species is quite small ($\sim 10^{-8}$ *S*) as compared to life-time of triplet excited state ($\sim 10^{-6}$ to 1*S*).

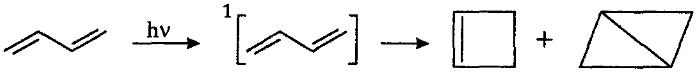
Imagine a donor-acceptor system, such as

$$\begin{aligned} D+h\nu &\longrightarrow {}^1D \\ {}^1D &\xrightarrow{\text{ISC}} {}^3D \\ {}^3D+A &\longrightarrow D+{}^3A \\ {}^3A &\longrightarrow \text{product} \qquad \text{(sensitisation)} \\ {}^3D &\longrightarrow \text{products} \qquad \text{(quenching)} \end{aligned}$$

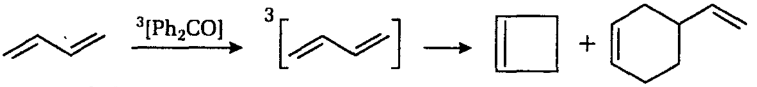
$$\left.\begin{array}{l} D:\text{donor} \\ A:\text{Acceptor} \end{array}\right\} \text{of photochemical excitation energy}$$

Only the donor molecule absorbs the incident light, and the triplet excited state energy of donor is at least 3 kcal/mol greater than that of triplet excitation energy of Acceptor [$E_T = E_{(T_1)} - E_{(S_0)}$]. Light absorption by donor produces singlet excited donor ${}^1D$, which undergoes intersystem crossing to give triplet excited donor ${}^3D$. Triplet excited donor then colloids with the ground stated acceptor, producing triplet excited Acceptor ${}^3A$ and ground state donor D. If the ${}^3A$ gives the product of interest, this is called sensitisation mechanism. If the product of interest derived from ${}^3D$, A is termed as quenching and this mechanism is termed as quenching mechanism.

Let us discuss some specific examples showing photochemical sensitisation. Direct irradiation of 1, 3-butadiene in solution gives cyclobutene and bicyclobutane with minor amount of dimers.



Intersystem crossing efficiency approaches zero in 1, 3-butadiene and triplet derived products are not formed. Triplet excited 1, 3-butadiene is produced by photosensitisation, in which triplet excited benzophenone is used as sensitiser. Triplet excited 1, 3-butadiene produces only dimers.



The possibility of intersystem crossing in 1, 3-butadiene is about to nil, while in benzophenone it is approximately 100%. This is due to the small energy

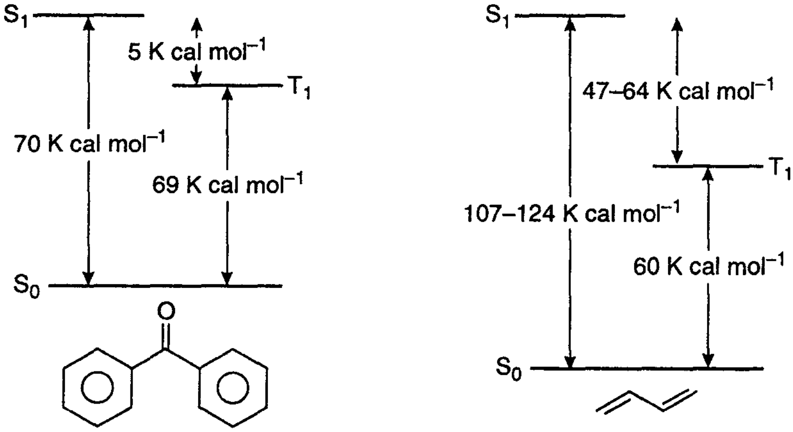
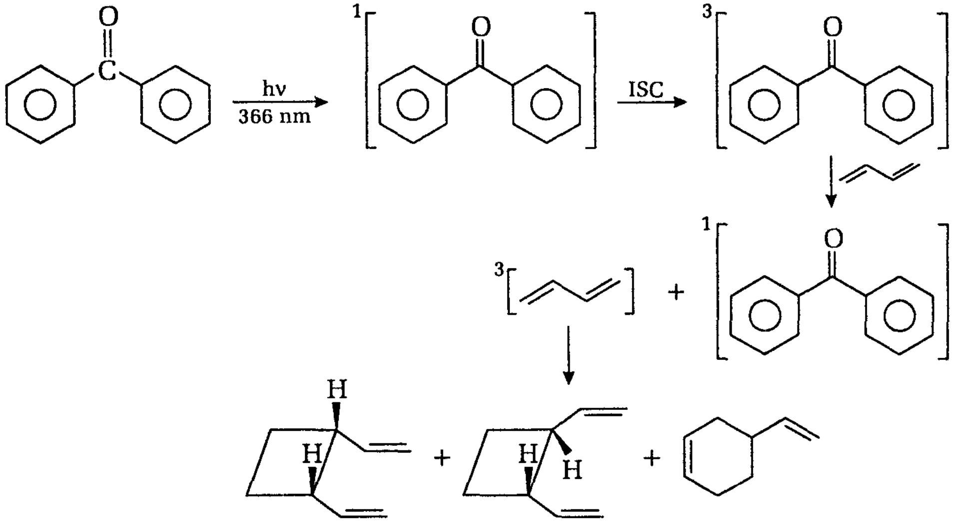


Fig. 2.17.

difference between singlet excitation energy and triplet excitation energy (Fig. 2.17).

Benzophenone is used as sensitiser for 1, 3-butadiene because triplet energy of benzophenone (69 k cal mol^{-1}) is slightly greater than the triplet energy of 1, 3-butadiene (60 k cal mol^{-1}). Now overall reaction mechanism is as follows.



In any transfer of electronic energy between an excited species and a ground state species, the overall spin angular momentum does not change. Thus, energy transfer is subjected to the Wigner spin conservation rule. In photosensitisation, there are following allowed spin possibilities.

$$D_{S_0}(\uparrow\downarrow) \xrightarrow{h\nu} D_{S_1}(\uparrow\downarrow) \xrightarrow{\text{ISC}} D_{T_1}(\uparrow\uparrow)$$

(a) $D_{S_1}(\uparrow\downarrow)+A_{S_0}(\uparrow\downarrow) \longrightarrow D_{S_0}(\uparrow\downarrow)+A_{S_1}(\uparrow\downarrow)$

(b) $D_{T_1}(\uparrow\uparrow)+A_{S_0}(\uparrow\downarrow) \longrightarrow D_{S_0}(\uparrow\downarrow)+A_{T_1}(\uparrow\uparrow)$

(c) $D_{T_1}(\uparrow\uparrow)+A_{T_0}(\downarrow\downarrow) \longrightarrow D_{S_0}(\uparrow\downarrow)+A_{S_1}(\uparrow\downarrow)$

The most important type of photosensitisation is governed by Wigner's rule, *i.e.*, a triplet excited state produces another triplet and a singlet excited state produces another singlet

$D_{T_1} + A_{S_0} \longrightarrow A_{T_1} + D_{S_0}$ (triplet-triplet transfer)

$D_{S_1} + A_{S_0} \longrightarrow A_{S_1} + D_{S_0}$ (singlet-singlet transfer)

Singlet-singlet transfer can take place over selectively long distance (~40 Å), but triplet-triplet transfer normally requires a collision between the two molecules. Both type of photosensitisation can be useful for creating the excited states, which are difficult to produce by direct irradiation. Photosensitation from photochemistry point of view is very important because we produce desired chemical change by selective excitation. Photosensitisation can also be accompanied by electron transfer.

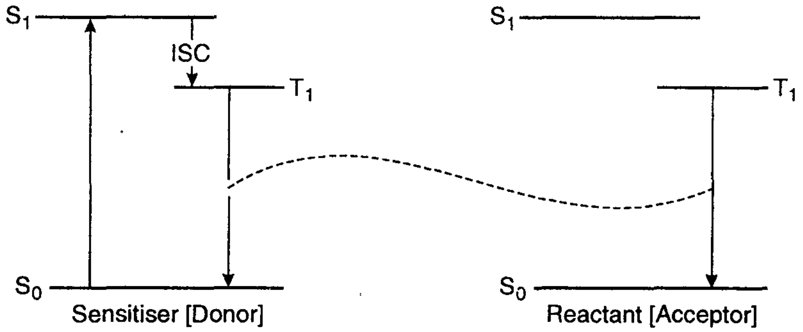
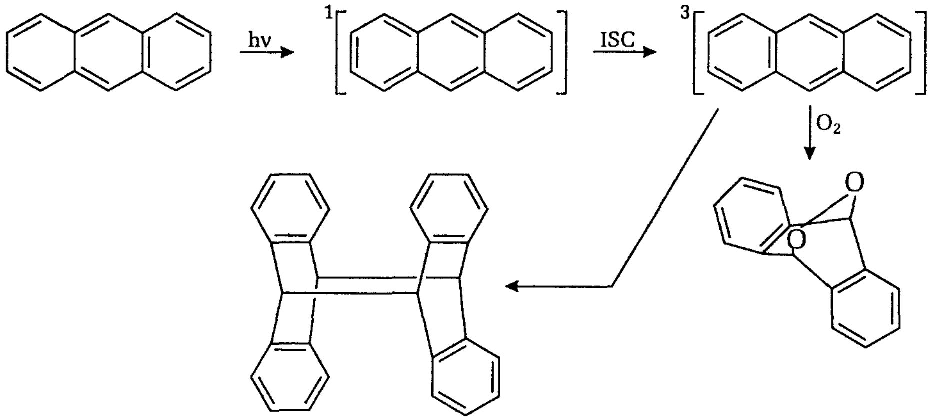
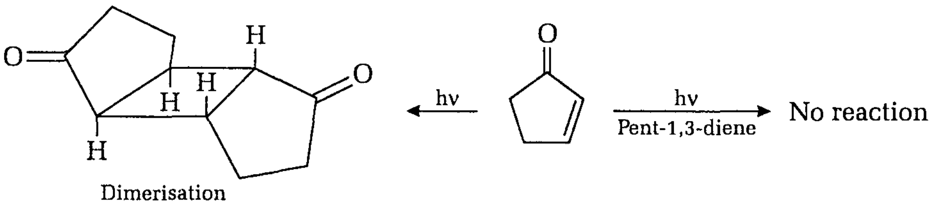


Fig. 2.18. Mechanism of photosensitisation by electron transfer.

The process of sensitisation allows to populate one excited state, which it is very difficult by selective irradiation. While the reverse process-quenching of an excited species by a ground state molecule, removes an excited species before reaction will occur. The most common quencher is molecular oxygen. A ground state triplet colloision of oxygen with a triplet excited species can results into quenching of the triplet and formation of excited singlet oxygen. The process of quenching by molecular oxygen can be best explained by following reactions.

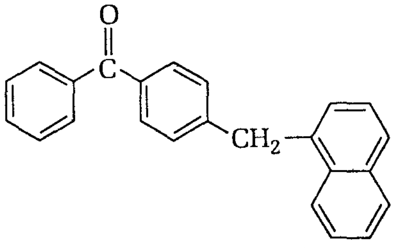


Another very important example is, cyclopantenone, It dimerises on irradiation, but if the same reaction is carried out in presence of pent-1, 3-diene, the reaction is inhibited. Pent-1, 3-diene act as quencher.



Intramolecular Energy Transfer

There are certain complex molecules, like substituted aromatic ketones or aldehydes which shows electronic excitation of one part of the molecule and transfer of this excitation energy from one part to the another part, in the same molecule. This phenomenon is known as Intramolecular energy transfer.



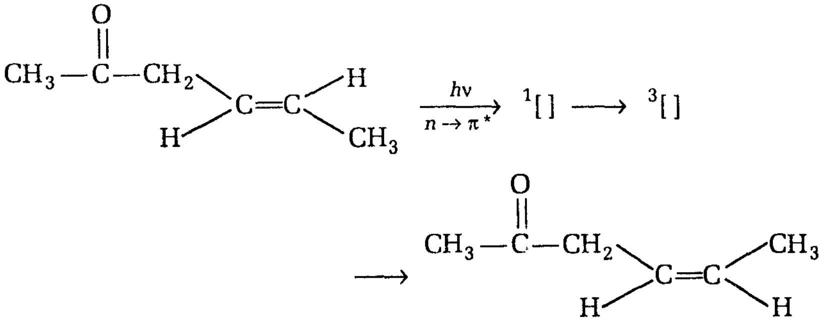
4-(1-napthyl methyl)-benzophenone

During irradiation of the above mentioned compound with radiation of wavelength 366 nm, absorbed by benzophenone, the benzophenone moiety get excited and goes to triplet excited state by ISC. This triplet excited energy shows efficient transfer from benzophenone moiety to naphthalene moiety. This is supported by emission spectra. Here benzophenone act as sensitiser to populate the triplet state of naphthalene and the data for the excited singlet and triplet states of naphthalene and benzophenone are given in table 2.1. These data demonstrate conditions satisfactorily for sensitisation. Since the energy and geometry of singlet and triplet states of the given molecule differs, the photochemical reactions of molecules from these states are entirely different.

Table : 2.1

	λ_{max}	E_{S_1} (kJ mol^{-1})	E_{T_1} (kJ mol^{-1})	ϕ_{ISC}
Naphthalene	320	385	255	0.7
Benzophenone	367	314	289	1.0

cis-trans isomerisation of 4-Hexen-2-one on irradiation, has been observed. This photochange takes place by energy, transfer from carboxyl group [$>C=O$] to unsaturation [$C=C$]



Importance of Energy Transfer

To achieve desired chemical transformation, energy transfer play a vital role. There are a number of molecules which do not absorb light at convenient wavelength range and if some absorbs the ISC is quite insufficient. Therefore to populate the molecules triplet excited states, photosensitisers are used.

2.6 QUANTUM YIELD/QUANTUM EFFICIENCY

The law of photochemical equivalence is restricted to primary photochemical process, *i.e.*, each reacting species excited by the absorption of one radiation get chemical transformation and formed products produce no further reaction. In such cases, these will be 1 : 1 relationship between the number of quantas absorbed and the number of reacting molecules. But in practice, most of photochemical reactions undergoes secondary photochemical reactions, *i.e.*, photochemically activated species or product molecule initiates a series of chemical transformations; while in some cases, photochemically activated species undergoes deactivation, they lose their energy in the form of heat or radiation. Under such conditions, there will be no more 1 : 1 relationship between the number of quanta absorbed and the product molecules. The deviation from photochemical equivalence (1 : 1 relationship) is described by the idea of quantum yield or quantum efficiency (ϕ). It is defined as

"It is the number of molecules undergoing chemical transformation per quantum of suitable radiation absorbed."

Mathematically,

$$\phi = \frac{\text{No. of molecules reacting in given time}}{\text{No. of quanta absorbed in same time}}$$

or $$= \frac{\text{No. of moles reacting in given time}}{\text{No. of einstein absorbed in same time}}$$

or $$= \frac{\text{Rate of chemical reaction}}{\text{No. of einsteins absorbed}} \qquad \ldots(1)$$

1 Einstein = 1 mole of quanta of radiation

Experimental Determination of Quantum Yield

Quantum yield of a photochemical reaction gives valuable information about the mechanism of photochemical reaction. In order to determine quantum yield of photochemical reaction, it is essential to measure

(i) No. of moles reacting and
(ii) No. of Einstein absorbed

Experimental set up for the determination of quantum yield of a photochemical reaction is as follows.

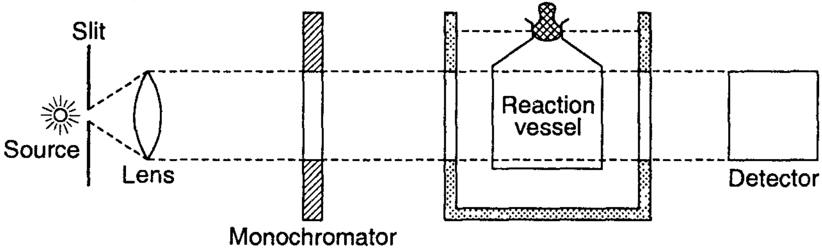


Fig. 2.19. Experimental setup for determination of quantum yield.

(a) Light source : For UV-visible region of electromagnetic radiation-sun light, arc lamp [sodium arc lamp], mercury vapour lamp, discharge tube, etc are used. And used according to wavelength range needed for examined photochemical reaction.

(b) Monochromator : Monochromator works as a filter for radiation source. When light for source is passed through the lens and allowed to pass through it, it will absorb all of undesired wavelengths and transmit light of definite wavelength. Manochromators are generally made of gelatin or coloured glass or transparent plates with metal films of suitable thickness.

(c) Reaction cell : It is of suitable size, made generally of glass or quartz with optical place windows for free exit and entrance of light radiation. Reaction cells contains reaction mixture and its material is inert towards chosen wavelength range.

(d) Detector : It is used for determining the intensity of light coming wheather from the reaction mixture placed or not. The difference of these two measured intensities gives the absorbed light. There are a number of detectors available commercially, based on the wavelength range. A detail description of detectors is given under the heading—Actinometry. [An actinometer is a chemical or physical device that measures the total amount of incident radiation].

Procedure for determining quantum yield of a photochemical reactor : The set-up of the apparatus has been discussed above. The choice of light source, filter, reactor cell and detector depends upon the wavelength range used for the photochemical reaction.

First keep the reaction vessel empty and allow the light to pass through it. Determine the light intensity. [In case of solution, follow procedure by filling reaction cell with solvent].

Now, fill reaction vessel with reaction mixture. Allow the light to pass through it for a known time and record the intensity of received light. The difference between the two readings will give the amount of energy absorbed by the reaction system under examination. Analyze the contents of reaction mixture.

Now, apply the following equation and put values, to get quantum efficiency.

$$\phi = \frac{\text{No. of moles reacting in given time}}{\text{No. of einsteins absorbed in same time}}$$

The quantum yields of photochemical reactions are important because they inform us of the paths by which the electronically excited molecules disposes off its energy. The primary quantum yield of a photochemical transformation may be different from overall or measured quantum yield. Quantum yield varies from factor to several millions.

Reason for low quantum yield :

(i) Deactivation of photoexcited species before chemical transformation.
(ii) Recombination of fragmented intermediates.
(iii) Inter or intramolecular energy transfer.

Reason for high quantum yield :

(i) The photo fragmented radicals by primary process initiate chain reaction.
(ii) The formed product initiates another reaction [secondary process] or number of thermal reactions.

Table 2.2 : Quantum yield of some photoreactions

Reaction	Wavelength (nm)	ϕ
$Cl_2 + O_2 \rightarrow Cl_2O_2$	4200	1.0
$H_2 + O_2 \rightarrow H_2O_2$	1710–1720	1.0
$2NO_2 \rightarrow 2NO + O_2$	3660	1.5
$2HBr \rightarrow H_2 + Br_2$	2070–2530	2.0
$2HI \rightarrow H_2 + I_2$	2070–2820	2.0
$Cl_2 + CO \rightarrow COCl_2$	4000–4360	10^3
$Cl_2 + H_2 \rightarrow 2HCl$	4000–4360	10^4
$2NH_3 \rightarrow N_2 + 3H_2$	2100	0.25
$2CH_3I \rightarrow C_2H_6 + I_2$	2020–2100	0.01
$2CH_3Br \rightarrow C_2H_6 + Br_2$	2530	0.004

2.7 ACTINOMETRY

There is a direct relation between the rate of a photochemical reaction and rate of light-quantas absorbed, and their ratio is known as quantum efficiency. To determine quantum yield of a particular reaction, it is necessary to know incident light flux I_0. There are a number of techniques available for the measurement of I_0. The equipment used for this measurement is known as actinometer and phenomenon Actinometry. Actinometry provides determination, measurement and standardisation of the light source. For perfect calibration, a standard lamp (light-source) of known colour-temperature is used to standardise the detector which may be :

(i) A thermopile or a bolometer
(ii) A photocell or a barrier layer photocell
(iii) A photomultiplier.

Thermopile

Thermopile is made up of thermocouples which are connected in series and generate an e.m.f. on heating (Fig. 2.20). While bolometers are thin blackened strips which changes resistance on absorption of radiation. Thermopile and

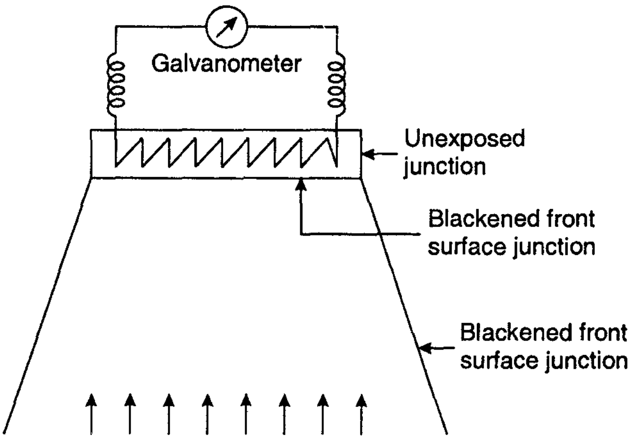


Fig. 2.20. Thermopile.

Bolometer both are not able to discriminate between the quality of radiation, but their results are integrated with the total energy absorbed.

Photocell

A photocell consists of a photosensitive cathode and a collector anode, enclosed in a evacuated bulb. Quanta of electromagnetic radiation having energy greater than the threshold value of metal composing photocathode, causes ejection of electrons from the surface of photosensitive cathode. These ejected electrons are collected by and make current to flow through the circuit. The intensity of photocurrent thus generated will be linearly proportional to the incident light intensity. The photosensitivity of the cathode depends on wavelength. Different photosensitive materials are used for different regions of spectrum. It is therefore necessary to calibrate the photocell against standard photocell or other secondary standards to make correct wavelength sensitivity. Amplification may be employed if thought necessary (Fig. 2.21).

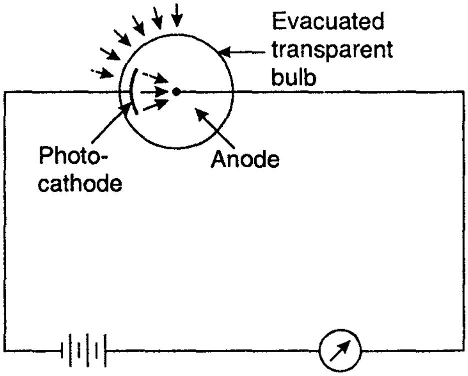


Fig. 2.21. Vacuum tube photocell.

There are second kind of photocells which are also used for same purpose, are Barrier layer photocells. It works on a totally different principle. It is a semiconductor device, in which impinging photons, promote the electrons from valence band to conduction band, by making energy available to cross the energy gap. A photovoltage is generated which can be measured by a voltmeter. Such photovoltic devices have a large surface area and are easy to operate. They are commonly used in many simple colourimeters and fluorimeters, and as light meters for cameras (Fig. 2.22).

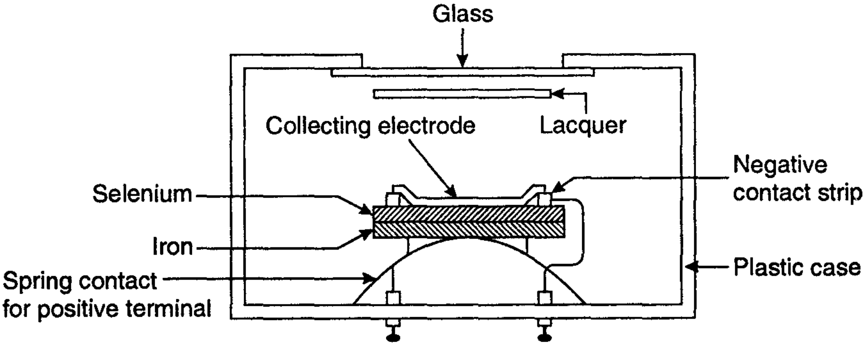


Fig. 2.22. Barrier-layer photocell.

Photomultipliers

Photomultiplier is a vacuum tube photocell, with a sealed in set of dynodes. Each successive dynode is kept at a potential difference of 100 V. So, the photoelectrons ejected from cathode surface are accelerated at each step. The secondary electron ejected from last dynode are multiplied so that a $10^6 - 10^7$ fold amplification of electron-flux is achieved. This allows simple devices such as microammeter to measure weak light intensities. Background thermal emission can be minimised by coding the photomultiplier.

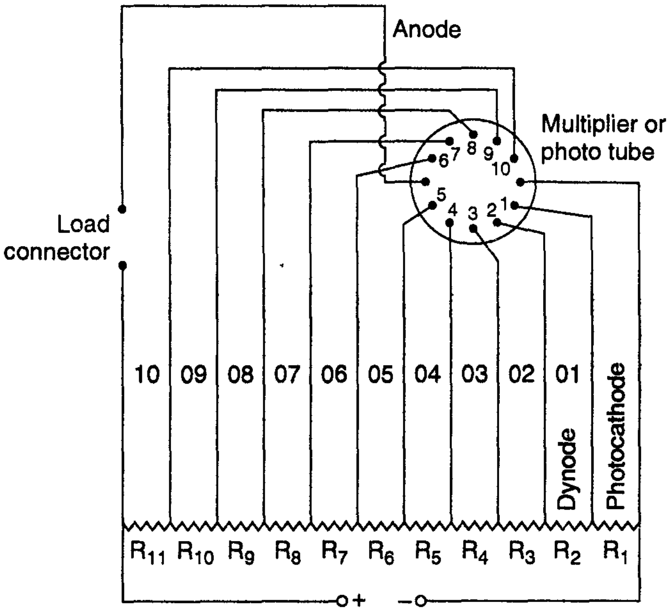


Fig. 2.23. Photomultipliers.

Types of Actinometers

Following actinometers are available commercially for the measurement of light intensity flux in photochemical measuring technique.

(a) Ferrioxalate Actinometer

(b) Uranyloxalate Actinometer

(c) Malachite Green Leucocyanide Actinometer

(d) Reineck's salt Actinometer

Ferrioxalate Actinometer

Photo decomposition of potassiumferrioxalate was developed into an actinometer by Parker and Hatchard. It is one of the most accurate and widely used actinometer. It operates between 250 nm to 577 nm wavelength range. The mechanism inbehind is, irradiation of ferrioxalate which results into the reduction of Fe^{3+} to Fe^{2+}, which is estimated colorimetrically by using *o*-phenanthroline, as complexing agent. The quantum yield for the formation of Fe^{++} is same through the wavelength range 250 to 577 nm. The optical density of ferrioxalate solution at 510 nm, of the deep red colour produced is compared with standard. It shows negligible variation in quantum yield with temperature, solution composition and light intensity. The recommended actinometric solutions are used :

Wavelength range	Solution
250–400 nm	0.006 M $K_3Fe(Ox)_3$ in 0.1 N H_2SO_4
400–577 nm	0.15 M $K_3Fe(Ox)_3$ in 0.1 N H_2SO_4

and quantum yield varies from 1.1 to 1.2.

Uranyloxalate Actinometer

It is now out of use due to low quantum yield (~ 0.5) and other drawbacks. The actinometer works in wavelength range from 208 to 435 nm. The UO_2^{2+} ion acts as a photosensitiser for oxalate decomposition. The light absorption remains constant by required long exposure to final accurate oxalate titration.

Malachite Green Leucocyanide Actinometer

This actinometer is very efficient between wavelength range 200 nm to 300 nm and show strong absorption in its wavelength range. On irradiation, the Malachite Green Leucocyanide (MGL) get ionised into MG^+ and Leucocyanide. The MG^+ shows strong absorption at 662 nm. The quantum yield for decomposition of MGL is 0.91 throughout the wavelength range.

Reineck's Salt Actinometer

The actinometer working very efficiently within the wavelength range from 316 nm to 735 nm [used in visible region]. The Reineck's salt is commercially available as ammonium salt $[(\overset{\oplus}{N}H_4)_3Cr(NH_3)_2\ (NCS)]$. It should be converted into potassium salt before use. The Ligand-field band extend from 400–735 nm. On irradiation, the salt releases thiocyanate. The quantum yield is calculated by production of thiocyanate in moles per Einstein of light. The quantum yield is about 0.27–0.30 for visible range of light.

Chemical Actinometry

A convenient method for standardisation of light source in the laboratory is the use of a photochemical reaction whose quantum yield in already determined by standard light source. During irradiation absorption must be constant, throughout the exposure. Hence the reaction must be photosensitised or have such sensitivity that the small photochange as product can be detected.

Quantum yield of a reaction

$$\phi = \frac{\text{Rate of reaction}}{\text{Rate of absorption of light}}$$

$$= \frac{\text{No. of molecules decomposed/formed}}{\text{No. of quanta absorbed in same time}}$$

$$= \frac{-dc/dt \text{ or } +dx/dt}{I_0 \times \text{fraction of light absorbed}}$$

The fractional absorption can be measured by separate experiments. By knowing the quantum yield and reaction rate, incident light intensity I_0 can be calculated in terms of Einstein S^{-1} cm^{-3} falling on reaction cell. To avoid geometrical errors due to difference in absorptivity of the actinometric solution, the same cell is used for the actinometry, and under same reaction conditions of equal optical density. There are a number of photochemical reactions which are found suitable for actinometery. They are useful in their specific wavelength range.

□□□

UNIT

3

DETERMINATION OF REACTION MECHANISM

The photochemical reaction mechanism is not identical with the thermal reaction mechanism because in thermal reactions, the absorption of energy is in continuous manner while in photochemical reactions, energy is supplied in a single instalment. The methods used for the determination of photochemical reaction mechanism are largely the same, used for organic reaction mechanism determination. Like product identification, isotope tracing, the detection and trapping of intermediates and study stereochemistry and kinetics. However in photochemical reaction mechanism determination some more factors are also taken into account.

(i) There are a number of products obtained.

(ii) When measuring photochemical kinetics, there are more variables. So, we can study the effect of the intensity or the wavelength of light on the rate of reaction.

(iii) Flash photolysis is used for the detection of intermediates by spectra, because by this technique we can detect extremely short-lived intermediates.

(iv) With these methods, there are two additional techniques :

   (a) The use of emission (fluorescence and phosphorescence) as well as absorption spectroscopy. From their spectra, the presence as well as the energy and life-time of singlet and triplet excited states can often be calculated.

   (b) The study of quantum yield : the fraction of absorbed light that produce a particular chemical change. A primary quantum yield is the fraction of molecules that undergoes the particular process. Thus, if 10% of all the molecules that are excited to S_1 state cross over to the T_1 state. The primary quantum yield for this process is only 0.1. However primary quantum yield is difficult to measure. A product quantum yield (ϕ) for a product P that is formed from a photo reaction of an initially excited molecule can be expressed as

$$\phi = \frac{\text{number of molecules of } P \text{ formed}}{\text{number of quanta of light absorbed}}$$

Product quantum yield is too easier to measure. The number of quanta absorbed can be determined by an instrument called actinometer, which is actually a standard photochemical system whose quantum yield is known. An example of the information that can be learned from quantum yields is as follows.

If the quantum yield of a product is finite and invariant with change in experimental conditions, it is likely that the product is formed, in a primary rate-determining process.

If the product quantum yields are found to be well over 1 (like 1000). Such a finding indicates a chain reactions.

3.1 CLASSIFICATION : [THERMODYNAMIC PATHWAYS]

Photochemical reactions are the same as other chemical reactions, like addition, cleavage, or rearrangements of molecules. The actual difference is the way to supply energy. Here we discuss the classification of photochemical reactions on the basis of potential energy as a function of reaction coordinates. On this basis photochemical reaction is of following three types :

(i) Adiabatic reaction
(ii) Diabatic reaction and
(iii) Intermediate reaction

Adiabatic Reactions

When the photochemical change occurs on the same continuous potential surface (a), the photochemical reaction so occur is known as adiabatic reaction (fig. 3.1.)

In an adiabatic reaction products will be in electronically excited state. According this criteria, the reactants and products both will be in electronically excited states which will be distinguished by luminescence and/or other photochemical properties.

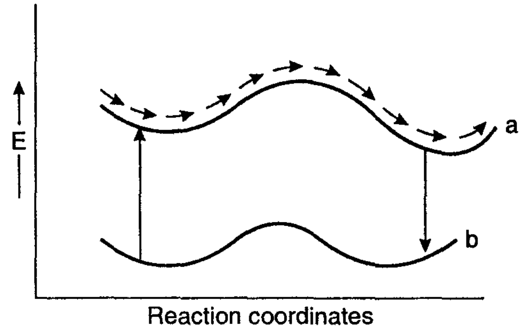


Fig. 3.1. Adiabatic reaction.

Example : $\underset{\text{Vapour state Iodine}}{I_2 + h\nu} \xrightarrow{\text{Photodissociation}} I^* + I$

Diabatic Reactions

When during the photochemical change, the crossover of potential energy surface is seen, the process is termed by diabatic reaction (Fig. 3.2.).

A number of photochemical changes in condensed phase produce product molecules in the ground state. This is accompained by radiationless transition from higher energy surface (a) to lower energy surface (b) of the system before the reaction completed.

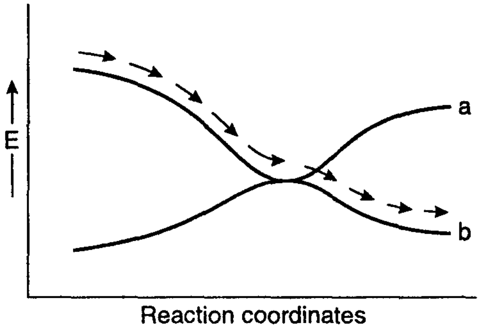


Fig. 3.2. Diabatic reaction.

Intermediate Reaction

Those photochemical reactions in which fraction of reacting species may be deactivated long enough to attain the products is known to intermediate case of adiabatic and diabatic reactions.

The cross over is governed by

(i) Conservation of energy and momentum.

(ii) Symmetry allowedness and applicable radiationless cascade.

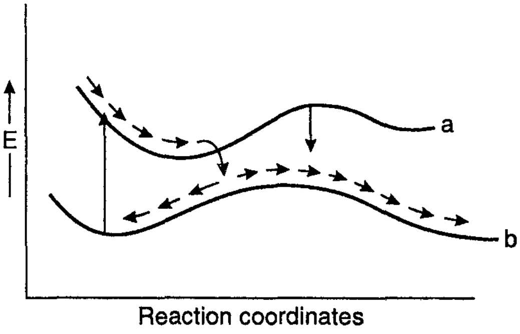


Fig. 3.3. Intermediate case.

The following rules may be influenced by local forces at the point of interaction.

1. Electronic configuration
2. Vibrational interaction
3. Magnetic interaction such as spin-spin coupling, spin-orbit coupling or Hyperfine splitting.

3.2 RATE CONSTANTS AND THEIR RELATION WITH THE LIFE-TIME OF REACTIVE EXCITED STATES

The rate of chemical reaction (thermal or photochemical) is, the velocity by which reaction proceeds. All the photochemical reactions go through excited intermediate states. The life-time of reactive excited states effects the rate of a reaction directly because this is the time which is provided for the chemical transformation. Mostly photoexcited species undergo chemical change but there are equal chances of photophysical deactivation also. Hence, there is difference in the number of molecules get excited and molecules converted into product. Thus, it is very important to make a relation between rate constant of photochemical reaction and life-time of reactive **energy state** of reactant.

The photochemical reaction may be unimolecular such as photo dissociation and photo isomerisation, or bimolecular or polymolecular. The polymolecular photoreactions occurs between one photoexcited molecule with other molecules.

Unimolecular photochemical reaction

$$A^* \xrightarrow{K} \text{Product}$$

$$\text{Rate} = \mathrm{K}[A^*]$$

Bimolecular photochemical reaction.

$$A^* + B \xrightarrow{K} \text{Product}$$

$$\text{Rate} = \mathrm{K}[A^*]\,[B]$$

where K is rate constant.

The photochemistry is the study of chemistry of excited states. There are two types of excited states, singlet excited state and triplet excited state, having life-time very short about 10^{-9} S to 10^{-7} S and 10^{-6} to 1S respectively. The efficiency of a photochemical reaction is expressed in terms of quantum efficiency (ϕ) of the reaction. Quantum efficiency or quantum yield is the ratio of rate of reaction and rate of absorption of radiation.

$$\phi_R = \frac{\text{Rate of reaction}}{\text{Rate of Absorption of Radiation}}$$

$$= \frac{\text{Moles of product formed or moles of reactants consumed S}^{-1}\text{ cm}^{-3}}{\text{Einstein of radiation absorbed S}^{-1}\text{ cm}^{-3}}$$

Let we consider a unimolecular photochemical reaction from electronically excited species A_i^*.

$$A_i^* \longrightarrow \text{Product}$$

The A_i^* is not initially photoexcited state but may be reached by subsequently photo physical process. The initially excited state A_1^* of reacting species is formed by absorption of radiation. The excited species may deactivate or get Inter system crossing to triplet from singlet excited state (A_i^*). This triplet excited reacting species either undergo chemical change or deactivate to ground state.

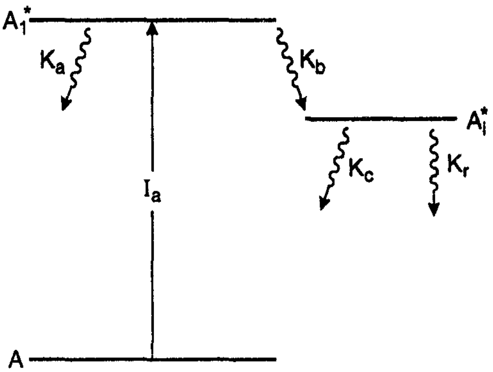


Fig. 3.4.

where :

I_a : Rate of absorption of radiation or rate of formation of A_1^*.
K_a : Sum of rate constants for deactivating A_1^*.
K_b : Rate constant for crossing over to A_i^*.
K_c : Sum of rate constants for deactivating A_i^* except photoreaction.
K_r : Rate constant for the formation of product.

The concentration of reactive species in short lived excited states is given by the ratio of rate constant of photo excitation and rate constants of simultaneous decay.

$$[A_1^*] = \frac{I_a}{K_a + K_b} \qquad \text{...(1)}$$

$$[A_i^*] = \frac{K_b\,[A_1^*]}{K_c + K_r} \qquad \text{...(2)}$$

Rate of unimolecular reaction can be represented as

$$\text{Rate} = K_r[A_i^*] = \frac{K_r K_b\,[A_1^*]}{K_c + K_r} \qquad \{\text{from (2)}\}$$

$$= \frac{K_r K_b I_a}{(K_c + K_a)\,(K_a + K_b)} \qquad \{\text{from (1)}\} \qquad \text{...(3)}$$

Quantum yield is the ratio of rate of photoreaction and rate of radiation absorption.

$$\phi_R = \frac{K_r K_b I_a / (K_c + K_r)(K_a + K_b)}{I_a} \qquad \text{\{from (3)\}}$$

$$\phi_R = \frac{K_r K_b}{(K_c + K_r)(K_a + K_b)}$$

$$\phi_R = K_r(\tau_{A_i^*})(K_b \tau_{A_j^*}) \qquad \ldots(4)$$

where $\tau_{A_i^*} = \frac{1}{K_c + K_r}$, is the life-time of reactive species in A_i^* excited state.

$\tau_{jA^*} = \frac{1}{K_c + K_r}$, is the life-time of reactive species in A_J^* excited state.

If the reactive species goes through a number of excited states to reach reactive state, then quantum efficiency of reaction is expressed as shown below :

$$\phi_R = (K_R \times \tau_{A_i^*})(\pi k_J \tau_J) \qquad \ldots(5)$$

where,

K_r : Rate constant of the reaction.

$\tau_{A_i^*}$: Life time of reactive state A_i^*.

$\pi k_J \tau_J$: Product of rate constants of excited states and life time of these excited states.

The rate constant is expressed as

$$K_R = \frac{\phi_R}{\tau_{A_i^*} \pi K_J \tau_J} \qquad \ldots(6)$$

The determination of specific reactivity or life-time of a given excited state is governed by knowledge of several quantities, K_a, K_b, K_c, K_r, I_a etc., which represents radiative decay process, radiation less decay, physical quenching, chemical reaction and radiation absorption. These are out of direct interest but we must assign them. The following cases can be happened.

1. The reaction can occur from initially excited (singlet or triplet) states by direct absorption of radiation.

$$K_R = \phi_R / \tau_{A_1^*} \qquad \ldots(7)$$

2. If quantum efficiency is unity, it makes, reaction rate directly related with life-time of the excited state.

$$K_R = \frac{1}{\tau_{A_1^*}} \qquad \ldots(8)$$

3. If the quantum efficiency is not unity then reaction can proceed from primary excited state. Rate of such reactions is determined by rates of radiationless processes and quantum yield of the formation of reactive excited state.
4. Bimolecular photochemical reactions occurs between photoexcited molecule A_i^* with B. The knowledge of concentration of B is required for the determination of rate of reaction.

$$\phi_R = \frac{K_R[A_i^*]\,[B]}{I_a}$$

$$= \frac{K_R K_b\,[B]}{(K_c + K_r[B])\,(K_a + K_b)} \qquad \ldots(9)$$

The reactivity of the given excited-state can be obtained by measuring life-time of reactive excited state at two different concentrations of B.

$$K_R = \left\{\frac{1}{\tau_2} - \frac{1}{\tau_1}\right\} \Big/ [B_2]-[B_1] \qquad \ldots(10)$$

The life time of reactive excited state is closely related with the rate of photo reaction given by this reactive state. A short lived state of high reactivity may be less efficient towards product formation than a long lived state of lower reactivity. The initially excited state shows following phenomenons.

	Rate
$A + h\nu \longrightarrow {}^1A^*$	I_a
${}^1A^* \longrightarrow A$	$K_{IC}[{}^1A^*]$
${}^1A^* \longrightarrow {}^3A^*$	$K_{ISC}[{}^1A^*]$
$\boxed{{}^1A^* + B \longrightarrow \text{Product}}$	${}^1K_R[{}^1A^*]\,[B]$
${}^3A^* \longrightarrow A$	$K'_{ISC}[{}^1A^*]$
${}^3A^* + B \longrightarrow \text{Product}$	${}^3K_R[{}^3A^*]\,[B]$

The quantum efficiency of secondary photochemical processes varies from fractional value to several millions. This is due to the fact that initially excited molecule starts a chain of excitation (like photo degradation of ozone by chloro-floro hydrocarbons). Those reactions which are monophotonic occur from singlet excited state

$$\phi_R + \phi_f + \phi_{IC} + \phi_{ISC} \cong 1.0$$

The low quantum yield is caused by recombination of products due to solvent cage effect and several other factors are responsible for low quantum yield.

3.3 DETERMINATION OF RATE CONSTANTS OF PHOTOCHEMICAL REACTION

We have already studied the relation between life-time and the rate of reactive intermediates. Consider the scheme for a bimolecular reaction.

$$A^* + B \xrightarrow{K_r} P$$

Assume that the reaction occurs from triplet excited state only and step (4) is replaced by fluorescence emission step

	Rate
$A + h\nu \longrightarrow {}^1A^*$	I_a
${}^1A^* \longrightarrow A$	$K_{IC}[{}^1A^*]$

$$^1A^* \longrightarrow {}^3A^* \qquad K_{\text{ISC}}[^1A^*]$$

$$\boxed{^1A^*+B \longrightarrow \text{Product}} \qquad {}^1K_R[^1A^*]\,[B] \qquad ...(4)$$

Fluorescence emission.

$$^3A^* \longrightarrow A \qquad K'_{\text{ISC}}[^3A^*]$$

$$^3A^*+B \longrightarrow \text{Product} \qquad {}^3K_R[^3A^*]\,[B]$$

The rate of reaction expressed in terms of quantum yield (ϕ) of disappearance of the reactant or the appearance of the product.

$$\phi_R^{\circ} = -\frac{I}{I_a}\frac{d[x]}{dt} = \frac{K_{\text{ISC}}}{K_{\text{IC}}+K_{\text{ISC}}+K_f}\;\frac{K_R[B]}{K_{\text{ISC}}^T+K_R[B]}$$

$$= \phi_{\text{ISC}}\frac{K_R[B]}{K_{\text{ISC}}^T+K_R[B]}$$

$$\frac{1}{\phi_R^{\circ}} = \frac{1}{\phi_{\text{ISC}}} + \frac{1}{\phi_{\text{ISC}}}\frac{K_{\text{ISC}}^T}{K_R[B]} \qquad ...(16)$$

In above equations, a plot of $\frac{1}{\phi^R}$ Vs $\frac{1}{[B]}$ should be linear. From the intercept ϕ_{ISC} can be obtained and the slope/intercept ratio is K_{ISC}^T/K_R. The rate constant for the reaction K_R can be calculated by comparison method.

The reaction is carried out in presence of a third substance which quenches the reaction chemically or physically, by competing for the reaction intermediate. In this case, if the triplet state of the photochemically excited reactant is the intermediate, and if the quenching step is.

$$^3A+\theta \longrightarrow A+\theta \qquad K_\theta[^3A]\,[\theta]$$

Therefore quantum of yield of the reaction becomes

$$^3\phi_R = \phi_{\text{ISC}}\frac{K_R[B]}{K_{\text{ISC}}^T+K_R[B]+K_\theta[\theta]}$$

The ratio of quantum yield in presence and in absence of quencher is

$$\frac{\phi_R^{\circ}}{\phi_R} = \frac{K_{\text{ISC}}^T+K_R[B]+K_\theta[\theta]}{K_{\text{ISC}}^T+K_R[B]}$$

$$= 1+\frac{K_\theta[\theta]}{K_{\text{ISC}}^T+K_R[B]}$$

$$= 1+K_\theta[\theta] \qquad ...(17)$$

At constant $[B]$, a curve plotted between $\frac{\phi_R^{\circ}}{\phi_R}$ against $[\theta]$, it is linear and slop is equal to K_θ.

If the experiment is repeated for a set reactant concentrations $[B]$, a set of straight lines of unit intercept will be obtained. The slop K_θ will be a function of $[B]$.

$$K_\theta = \frac{K_\theta}{K_{ISC}^T + K_R[B]} = K_\theta \tau$$

where τ = lifetime of ^3A [in absence of quencher]

If K_θ is considered as diffusion-controlled, then τ can be measured

$$\frac{1}{K_\theta} = \frac{K_{ISC}^T}{K_\theta} + \frac{K_R[B]}{K_\theta} \qquad ...(18)$$

K_{ISC}^T and K_R can be calculated from the slope and intercept of the linear plot between $\frac{1}{K_\theta}$ Vs $[B]$.

3.4 EFFECT OF LIGHT INTENSITY ON THE RATE OF PHOTOCHEMICAL REACTIONS

Intensity of light at a point is defined as the number of photons passing through the point per second. Therefore intensity is directly proportional to the number of photons. Primary photochemical reactions are Monophotonic photochemical reactions where each absorbed quanta excites one molecule which then reacts. That's why the rate of primary photoreactions is usually directly proportional to the light intensity [Rate $\propto I$]. But in case of secondary photochemical reactions [which are initiated by species formed by primary photochemical reactions], the proportionality depends on the :

(i) Chain termination : If the chain intermediates are terminated by unimolecular reactions, as with vessel walls or with other molecules to give relatively stable products, the rate is proportional to intensity [Rate $\propto I$].

(ii) Recombination : If excited reactants or radicals recombined bimolecularly, rate of reaction is directly proportional to square root of light intensity. [Rate $\propto \sqrt{I}$].

(iii) In case of biphotonic photochemical reactions, either two quantas are simultaneously absorbed by one molecule or more commonly reaction occurs by the interaction of two excited molecules. Rate of such biphotonic reactions becomes directly proportional to the square of light intensity. [Rate $\propto I^2$].

Still there is no definite relation between the rate of photochemical reaction and light intensity because there are a number of process which are possible after the absorption of photon [Rate of excited molecule].

3.5 TYPES OF PHOTOCHEMICAL REACTIONS

The most weakly bound electrons of a molecule define the chemical behaviour of the molecule. The chemistry of a molecule in the excited state differs from the ground state molecule because of difference in energy. Irradiation produces an excited electronic state that alters the reactivity of molecule in a number of ways which decide the nature of photochemical reaction path.

(i) Photodissociation : In the excited state, the nuclei are more weakly bound than in the ground state. Therefore the molecule may get easily dissociated.

(ii) Photoaddition : The excited electron may interact with any other odd or unpaired electron of attacking agent and form a bond.

(iii) Photoxidation : The excited electron is in a more weakly bound orbit than other. This is, it often extending over a large space and, therefore is more likely to be removed by an electrophilic reagent.

(iv) Photo-redox reaction : Inorganic molecules or compounds shows variable valencies in the system. A electron transfer process is setup in intermolecular or intermolecular system. This makes oxidation and reduction simultaneously.

(v) Photo-isomerisation : According to Frank Candon principle, a number of vibrational and rotational modes are associated with each electronic state. The vibrationally or rotationally excited species undergo rearrangement by twisting or intramolecular shifting. This process is known as isomerisation.

3.6 PHOTODISSOCIATION

The direct irradiation of molecule sets up the molecule in vibrationally excited state. When the energy of photon is sufficient to overcome bond dissociation energy, the fragmentation will occur at the excited bond. The photodissociative mechanisms are best represented with the help of potential energy curves for diatomic molecules [like Cl_2 and HI].

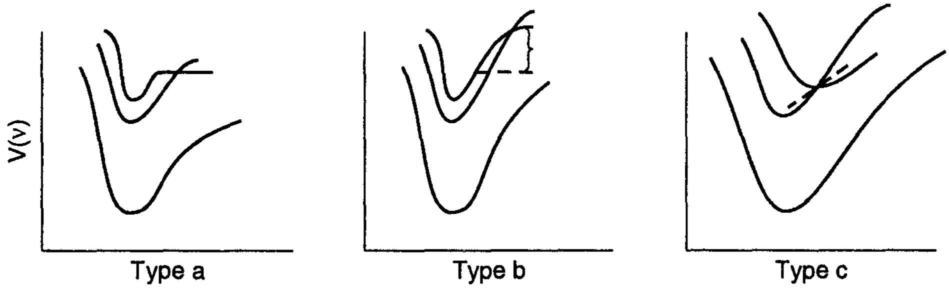


Fig. : Potential energy curve representation of band dissociation of diatomic molecule.

The photofragmentation occurs with unit quantum efficiency. The process of dissociation of a molecule from photochemically excited species is termed as photolysis.

In case of photolysis, at least one fragment is in excited state. Any excess energy will appear as kinetic energy of the fragments. The excess potential and kinetic energies may increase the chemical activity of the photofragments. The energy states of the product particles can be predicted with the help of symmetry correlation rules :

(a) The symmetry of the products must correlate with the reactants.

(b) In setting up the reactant-product symmetry correlation, it is not possible to leave a lower energy state of a given symmetry uncorrelated.

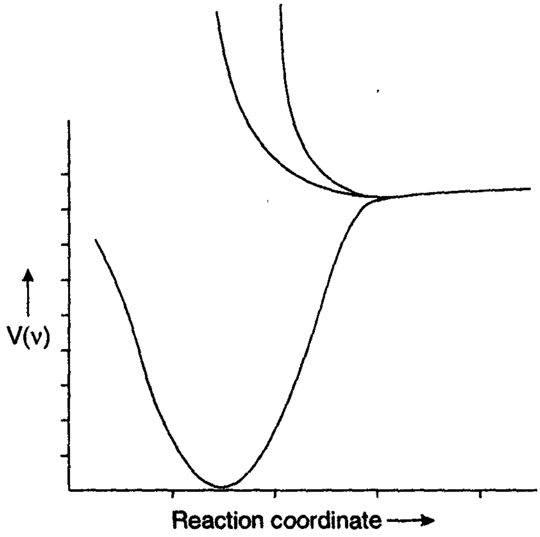
(c) The energy states of the same symmetry do not cross. Thus reactant-product must lie on the same potential energy surface. [adiabatic reaction].

The most important process of photodissociation is gas phase photolysis.

3.7 GAS PHASE PHOTOLYSIS

The gas or vapour phase photolysis of halogens and their acids are studied intentially. They absorbs light of near UV and visible region. On irradiation the electron present in non-bonding orbital of halogen atom of R—X are promoted to antibonding σ-orbital of R—X molecule [where R = X or H].

The mechanistic studies of HI molecule on irradiation show that the absorption bond of HI molecule on irradiation shows that the absorption bond of HI begins to dssociate at 360 nm and is completely continuous to 218 nm. Evidently, the molecule are excited to the repulsive part of the upper electronic state resulting in dissociation with unit quantum efficiency.



Irradiation of Gaseous Mixture of H_2 and Cl_2

On irradiation chlorine molecule in gas phase, fragmentation occurs into two homogenous chlorine radicals. These chlorine radicals take one Hydrogen from H_2-gas and leave a Hydrogen radical. In this way a chain reaction get initiated and propagated.

Initiation :

$$Cl_2 \xrightarrow[(478\ nm)]{h\nu} 2\ {}^{\bullet}Cl$$

Propagation :

$${}^{\bullet}Cl_2 + H{-}H \longrightarrow HCl + {}^{\bullet}H$$

$${}^{\bullet}H + Cl{-}Cl \longrightarrow HCl + {}^{\bullet}Cl$$

Experimental conditions decides the termination point of the chain reaction is, if the atoms are removed by wall effects or by inhibiting molecules such as O_2 present in the system. Rate is directly proportion to light intensity. But when highly purified gases in large vessel, the reaction chain produces 10^5 product molecules ($\phi_{HCl} \approx 10^5$).

The chain termination by bimolecular recombination is operated by introducing third molecule which absorbs excess energy. (Rate $\propto \sqrt{I}$).

Termination :

$$^{\bullet}Cl + {}^{\bullet}Cl + M \longrightarrow Cl_2 + M$$

$$^{\bullet}Cl + {}^{\bullet}H + M \longrightarrow HCl + M$$

Reaction between Br_2 and H_2

Because of low reactivity of Bromine atom, the reaction between H_2 and Br_2 needs little high temperature. Generally, the chain termination is caused by the recombination of Bromine radicals, (Rate $\propto \sqrt{I}$). The quantum yield expression for HBr formation can be from steady state approximation.

$$\phi_{HBr} = \frac{d[HBr]}{dt} / \text{Rate of light absorption}$$

$$= \frac{K[H_2]}{\sqrt{I_{ab}}\left\{1 + \frac{K'[HBr]}{K''[Br]}\right\}}$$

I_{ab} = Intensity of Absorbed light

Reaction between I_2 and H_2

Because of the poor reactivity of Iodine, no photoreaction occur between I_2 and H_2. As the reaction of I_2 and H_2 is endothermic, so no reaction possible. The ϕ for photodecomposition of HI.

$$\phi_{HI} = 2$$

$$HI + h\nu \longrightarrow H^{\bullet} + I^{\bullet}$$

$$^{\bullet}H + HI \longrightarrow H_2 + I^{\bullet}$$

$$I^{\bullet} + I^{\bullet} \longrightarrow I_2$$

These results emphasize the importance of energy change involved in bond breaking and bond making in the reactions. The abstraction of H by Cl is thermoneutral ($\Delta H \cong 4.2$ kJ mol^{-1}), but the next step of abstraction of chlorine by Hydrogen radical from chlorine atom is highly exothermic. [$\Delta H \approx -189$ kJ mol^{-1}] Thus the radicals are formed with excess energy. Those radicals having enough energy to propagate chain reaction are termed as hot radicals. The reaction $Br_2 + H_2$ is less exothermic and therefore produces small chains. Whereas $I_2 + H_2$ reaction is endothermic ($\Delta H \cong +38$ kJ mol^{-1}) and no chain reaction is possible.

The photodissociation of I_2 molecule generates one ground-stated Iodine atom and one excited Iodine atom

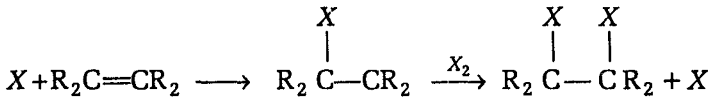
$$I_2 \xrightarrow[\text{[>499 nm]}]{h\nu} I + I^*$$

The excited I* has enough energy to abstract Hydrogen atom from hydrocarbon in gas phase.

$$I^* + CH_3CH_2CH_3 \longrightarrow HI + CH_3CH_2CH_2$$
$$\longrightarrow HI + CH_3CHCH_3$$

In presence of unsaturated hydrocarbons, chain reaction can be generated by halogen radical. This process is termed as photo halogenation.

$$X_2 \xrightarrow{h\nu} 2X$$



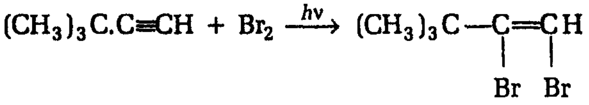
$$X + R_2C{=}CR_2 \longrightarrow R_2\overset{X}{C}{-}CR_2 \xrightarrow{X_2} R_2\overset{X}{C}{-}\overset{X}{C}R_2 + X$$

The reactivity of halogens towards such addition reactions is in the following order.

$$Cl > Br > I$$

Usually chloro- and bromo- compounds are produced by this method.

$$CH_2{=}CHCl + Cl_2 \xrightarrow{h\nu} CH_2Cl.CHCl_2$$



$$(CH_3)_3C.C{\equiv}CH + Br_2 \xrightarrow{h\nu} (CH_3)_3C{-}\underset{Br}{C}{=}\underset{Br}{C}H$$

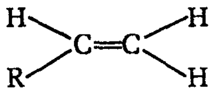
The photodissociation of hydrogen bromide with olefins and actylenes is used to synthesize alkyl and alkenyl bromide.

$$CH_3CH{=}CH_2 + HBr \xrightarrow{h\nu} CH_3CH_2CH_2Br$$

$$CH{\equiv}CH + HBr \xrightarrow{h\nu} CH_2{=}CHBr$$

The vapour phase photolysis of Hydrocarbons occur in vacuum UV region (120–200 nm), The fragmentation process results in the elimination of hydrogen.

$$RCH_2R \xrightarrow{h\nu} RCR + H_2$$



$$\xrightarrow{h\nu} RC{\equiv}CH + H_2$$
$$\longrightarrow RCH{=}C{:} + H_2$$
$$\longrightarrow RC{=}CH_2 + H$$
$$\longrightarrow RCH{=}CH + H$$
$$\longrightarrow CH{=}CH_2 + R$$

Azoalkenes on photolysis in vapour phase yield alkyl radicals and nitrogen.

$$CH_3N{=}NCH_3 \xrightarrow{h\nu} 2CH_3 + N_2$$

Amides and amines on gas phase photolysis produces a variety of products like as

$$RCONH_2 \xrightarrow{h\nu} RCO + \ddot{N}H_2$$

$$RCONH_2 \xrightarrow{h\nu} \dot{R} + \dot{C}ONH_2$$

$$RCH_2NH_2 \xrightarrow{h\nu} RCH_2\dot{N}H + \dot{H}$$

$$\xrightarrow{h\nu} R\dot{C}HNH_2 + \dot{H}$$

$$\xrightarrow{h\nu} \dot{R} + \dot{C}H_2NH_2$$

Chemical Laser

The reaction system in which partial liberation of heat of reaction can generate excited atoms or molecules are capable of laser action. This laser in known as chemical laser. The laser is chemically pumped, with out any external source of radiation.

The two well known examples, are gas phase photolysis of CF_3I and $F_2 + H_2$.

The reaction of Hydrogen and fluorine is very much exothermic and can produce energy rich Hydrogen fluoride molecules.

$$F_2 \xrightarrow{h\nu} 2F^{\cdot}$$

$$\dot{F} + H_2 \longrightarrow HF + {}^{\cdot}H \qquad \Delta H = -139.9\ \text{kJ mol}^{-1}$$

The heat of chemical reaction is distributed in various vibrational-rotational modes to give vibrationally excited HF molecules in large number. Emission from these hot molecules can be observed in IR region at wavelength $= 3.7 \times 10^{-6}$ m.

Another system in which laser action was observed is the photolysis of CH_3I, emitting at wavelength 1.315×10^{-6} m.

$$CF_3I \xrightarrow{h\nu} {}^{\cdot}CF_3 + I^{\cdot}$$

The laser action originates from electronically excited Iodine radical also. This type of Laser is termed as photodissociation laser. There is no vibrational or rotational mode involved.

❑❑❑

UNIT

4

ELECTROCYCLIC REACTIONS

The photochemistry of alkenes attract a great deal of attention and it startes a new era in organic synthesis. Electronically excited olefinic bond gives a number of reactions like isomerisation, dimerisation, intermolecular addition and many more. The energy of triplet excited state T_1 of an alkene is lower than that of excited singlet state S_1. However intermolecular system crossing [ISC] is inefficient and in order to examine reactions of the triplet excited state, population of this state must be achieved by sensitisation.

Photochemistry of alkenes may be studied under two categories-(1) Intramolecular photoreactions and (2) Intermolecular photoreactions of Alkenes. The second is mainly the study of intermolecular addition. The photolysis products from an intermolecular reaction of an alkene depend on the nature of alkene, the number of sites of unsaturation in the molecule and their structural relationship to one another. While the intramolecular reactions of Alkenes is governed by life-time of excited states mainly.

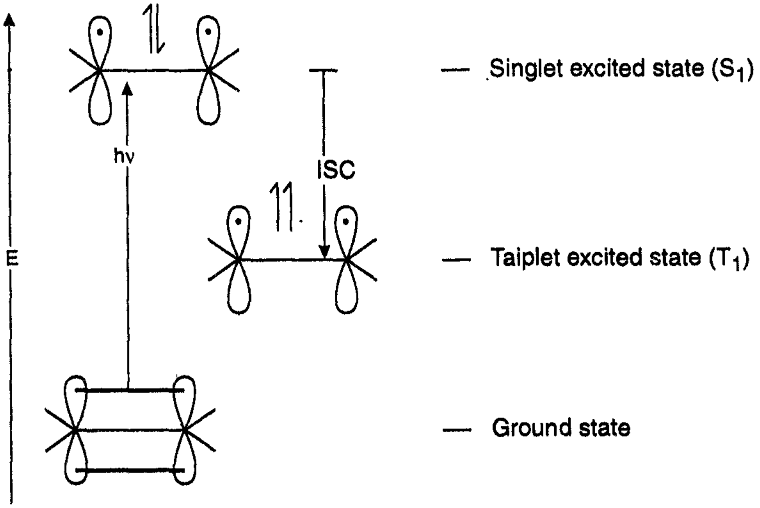


Fig. 4.1. Different electronic states of alkene.

Intramolecular Reactions of Olefinic Bonds

On irradiation of olefinic bond with a light of suitable frequency, the unsaturated hydrocarbon get electronically excited. Beyond physical phenomena, excited olefinic bond produces following chemical changes :

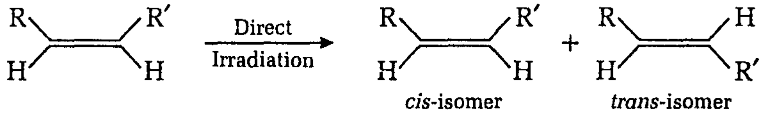
(i) Geometrical Isomerisation

(ii) Cyclisation and
(iii) Rearrangement

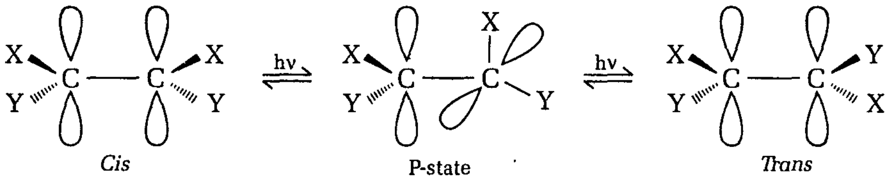
The intramolecular reactions of alkenes falls under a general heading "rearrangement". Above mentioned chemical transformations are nothing but only subdivisions of molecular rearrangements.

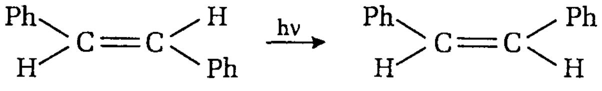
4.1 GEOMETRICAL ISOMERISATION

The *cis-trans* or $(E)-(Z)$ isomerisation is equally reported in both thermal ground state reactions as well as excited state reactions. Photochemical excitation give rise to geometrical isomerisation.



In the ground state isomerisation or thermally induced isomerisation, the reaction is considered to proceed through a unplanned transition state-common to both *cis*- and *trans*- isomers. This transition state gives greater population of *trans*- isomer which is thermodynamically more stable. The same situation arises in photochemical isomerisation where population of S_1 and T_1 states is followed by vibrational cascade which is associated with a twisting of the molecule about the C—C σ-bond of the alkene. The energy minimum to both the S_1 and T_1 excited states corresponds to a structure in which a rotation of 90° has occurred and where the adjacent *p*-orbitals are orthogonal. The structure is frequently termed as *p*-state and geometry corresponds to the energy maximum in ground state.





Trans - Stilbene
λ_{max} - 295 nm
$\varepsilon_{t\ max}$ - 27000

Cis - Stilbene
λ_{max} - 280 nm
$\varepsilon_{c\ max}$ - 13500

Irradiation of a pure *cis*- or *trans*- isomer or a *cis*- *trans* mixture will lead to an equilibrium between these two geometrical isomers, which on further irradiation does not change. This equilibrium state is termed as photostationary state.

$$\underset{\text{Stilbene}}{\text{Ph—HC═CH—PH}} \xrightarrow{h\nu} \underset{93\%}{\textit{cis}\text{-Stilbene}} + \underset{7\%}{\textit{trans}\text{-stilbene}}$$

The ratio of *cis*- and *trans*- isomers in photostationary state will depends on the absorption maximum (λ_{max}) and molar excitation coefficient (ε_{max}) of the isomer. *Trans-* isomer will absorbs more light than *cis-* isomer because *trans-* isomer have longer wavelength absorption and higher value of molar excitation coefficient. The quantity of light absorbed by an isomer at any wavelength depends on the molar excitation coefficient. On continuous photolysis a photostationary state will be achieved at which the rate of conversion of *trans-* to cis- is equal to the rate of conversion of *cis* to *trans*. At photostationary point the cis- isomer will be in greater concentration than the *trans*-isomer.

Formation of Perpendicular State [*p*-state] : (Common Intermediate)

The direct irradiation of geometrical isomer gives rise to vertical excited state, *i.e.*, from *cis* S_0 to *cis* S_1 and *trans* S_0 to *Trans* S_1. After passing life time of particular excited state, the decay should be as shown in fig. 4.2. But evidence shows that the decay favours the path shown in fig. 4.3 from the excited states.

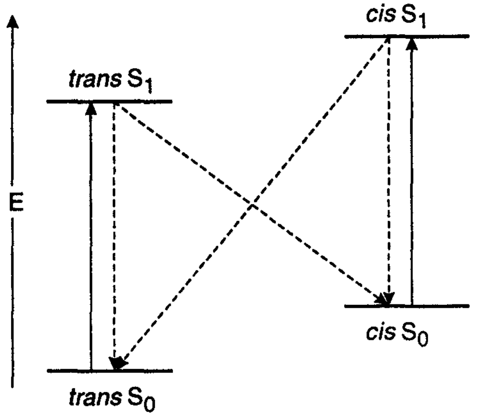


Fig. 4.2. Excitation and decay of geometrical isomers [direct decay]

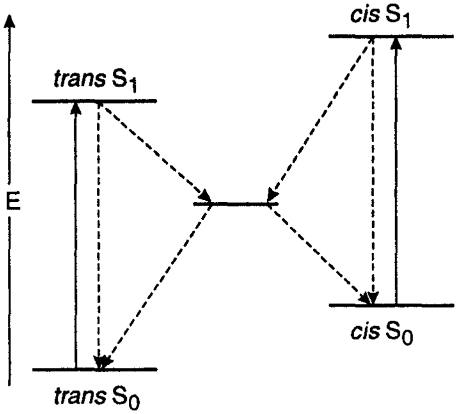
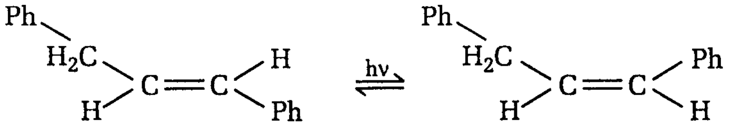
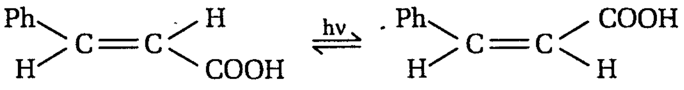


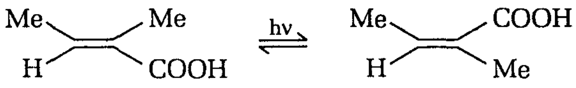
Fig. 4.3. Excitation and decay of geometrical isomers [through *p*-state intermediate]

The isomerisation of alkenes takes places via an excited state shown in fig. 4.3, in which two sp^2 hybridised carbon atoms are twisted at 90° with respect to the other. The intermediate state formed is referred to as the perpendicular state. The geometry is believed to be of lowest energy geometry for both *cis-* and *trans-* excited states.

Some examples of Geometrical photo isomerisation of alkenes are given below :

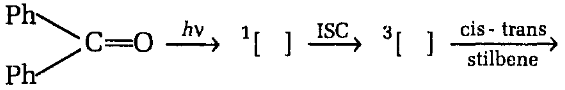






Sensitised Geometrical Isomerism

There is another way to produce geometrical isomerisation, initiated by light. In this method a photosensitiser is used to deliver energy required for cross over from one geometrical isomer to another. Under these conditions, the composition of stationery state depends on the triplet energy of the sensitiser. If the used sensitiser having triplet energy greater than 60 k cal/mol, the *cis- trans* ratio of photostationary state is approximately one. But when triplet energy of sensitiser is approximately 52 k cal/mol, the *cis- trans* ratio get much higher.



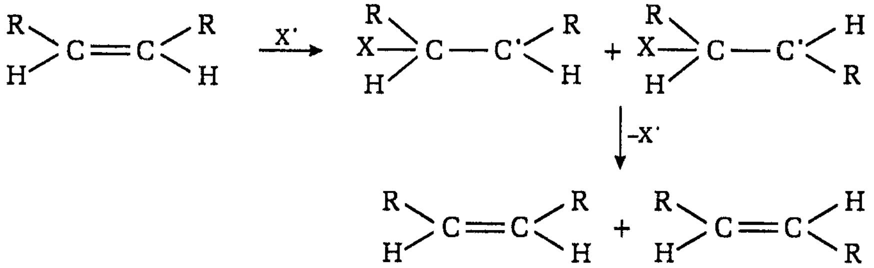
$$Ph_2C{=}O \xrightarrow{h\nu} {}^1[\ \ ] \xrightarrow{ISC} {}^3[\ \ ] \xrightarrow[\text{stilbene}]{\text{cis - trans}}$$

$$\underset{(E\ =\ 52\ \text{k cal / mole})}{{}^3[PhCH{=}CHPh]} + Ph_2CO \longrightarrow \textit{cis}\text{- stilbene } 93\% + \textit{trans}\text{- stilbene } 7\%$$

The triplet excitation energy of benzophenone is approximately 69 k cal/mol and makes the *cis-* isomer in dominance, from this fact it is concluded the energy required for excitation of *trans-* isomer is less than that for *cis-* isomer. Also the sensitiser having triplet energy in the range of 52–58 k cal/mol, selectively excites the *trans-* isomer. Since the rate of *trans* to *cis* conversion increased, the photostationary state is enriched with *cis-* isomer.

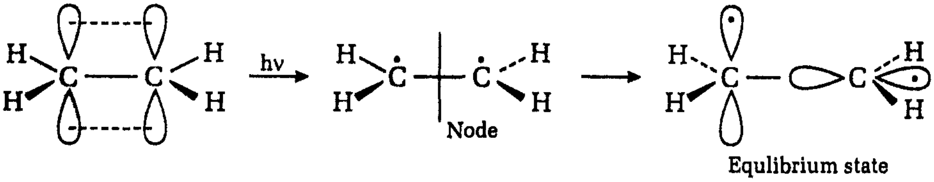
Presence of Halogens also support geometrical isomerisation, but with a totally different mechanism. Absorption of radiation makes the decomposition of halogen molecule into free radicals which get attached to the olefinic bond and produce isomerisation.

$$X_2 \xrightarrow{hv} 2X^{\cdot}$$



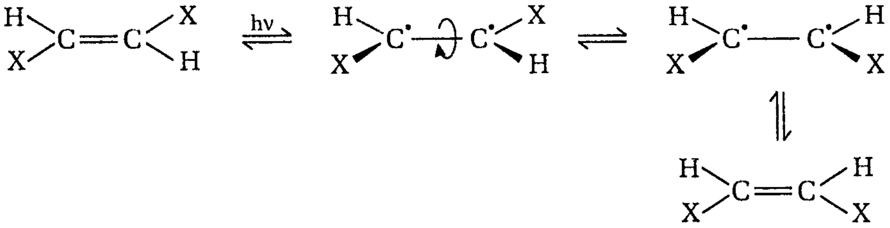
Free- Radical Mechanism

The excitation of olefinic bond makes the excitation of electrons from (bonding) π orbital to π * (antibonding) orbital, then the carbon-carbon double bond act as single bond and free rotation becomes possible around carbon-carbon bond. The possibility of free rotation facilitates the *cis- trans* isomerisation. Starting from any given configuration the corresponding isomer after rotation can



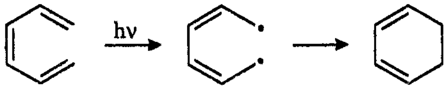
be produced on photoexcitation with suitable wavelength. A photostationary equilibrium is established differing from the thermo- dynamic equilibrium.

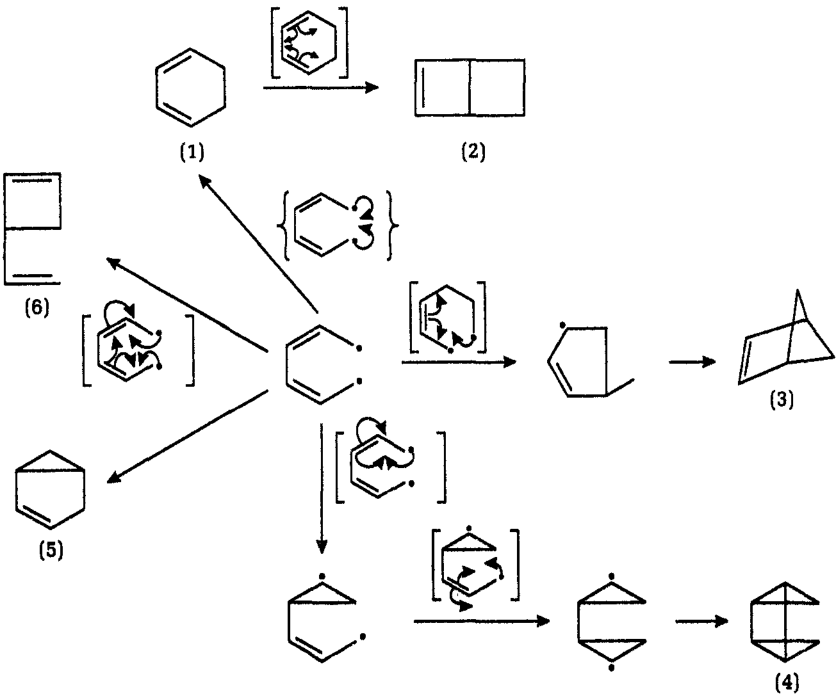
Frank-Condon π → π * excitation of ethylene and subsequent relaxation cause isomerization.



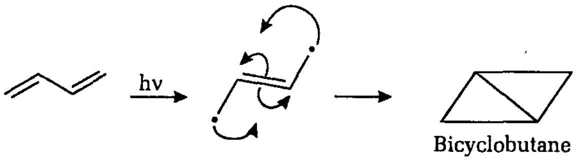
4.2 CYCLISATION REACTIONS : VALENCE ISOMERISATION

The electronically excited conjugated polyenes behaves as radical on irradiation, which leads to a number of products by the recombination of radicals and also lead to cyclisation. For example- cyclisation of hex-1, 3, 5-triene.

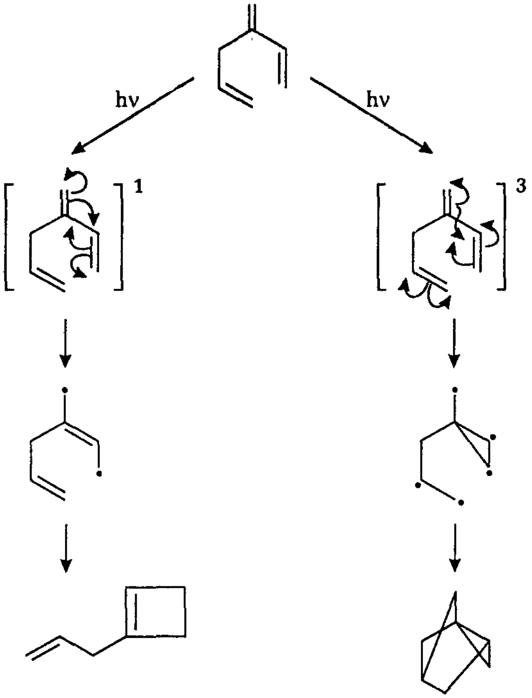




In case of butadiene, the photochemical cyclisation reaction produces two products—cyclobutene and bicyclobutane. The product obtained depends on geometry of butadiene.



In some case, the photolysis products of dienes and trienes depends on the excited state in which photochemical cyclisation occurs (singlet or triplet). To populate triplet state, suitable triplet sensitizer are used if required. The 3-Methylene-1, 5-hexadiene gives a cyclobutadiene derivative through singlet excited state and tricyclic ring compound from triplet excited state. This difference of photochemical process is because of life-time of the excited states. Higher the life-time of reacting intermediate more will be possibility to form more stable radicals.



4.3 PHOTOCHEMICAL REARRANGEMENTS OF ALKENES

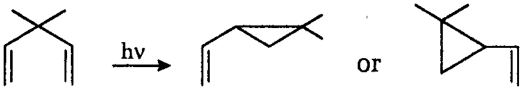
Rearrangement reactions are those in which an atom or a group transfer from one position to another in same molecule. Photochemical initiation of polyenes gives rearranged products. Out of these only following two photochemical rearrangement are of synthetic importance.

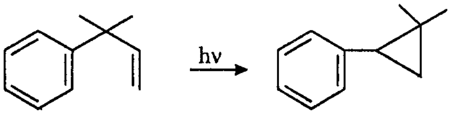
(i) Rearrangement of 1, 4- diene.

(ii) Rearrangement of 1, 5- diene.

4.4 REARRANGEMENT OF 1, 4- DIENE (DI-π METHANE REARRANGEMENT

The most common photochemical reaction of 1, 4- diene is the di-π methane rearrangement or Zimmerman rearrangement, in which a 1, 4- diene carrying alkyl or aryl substituent at carbon-3, can be photochemically converted into vinyl cyclopropane.

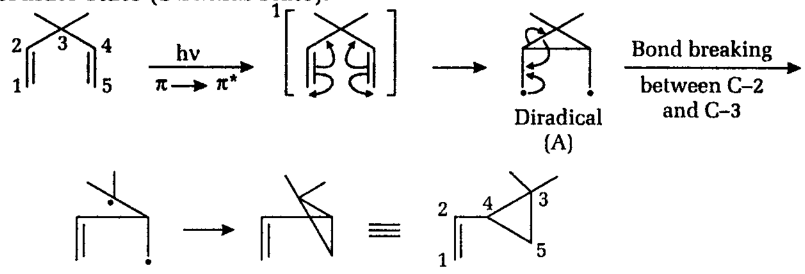




The photo-induced rearrangement is shown by the singlet excited state of 1, 4- diene derivative. The reaction is stereospecific at all the chain centres, with a retention at carbon-1 and carbon-5 and inversion at carbon-3. The reaction proceed in a concerted mechanism.

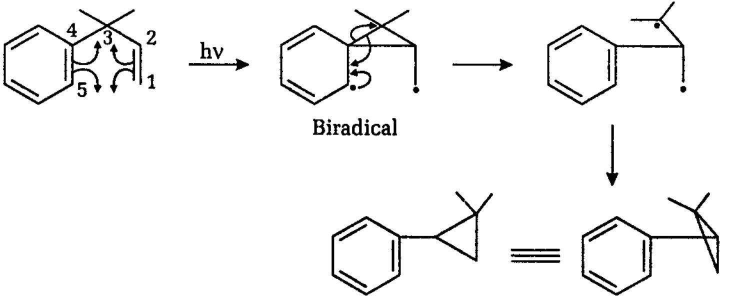
Mechanism

The reaction proceed via a biradial pathway. The biradial is formed by the irradiation. The substituent present on the C-3 will act as stabilizer for excited intermediate state (biradial state).

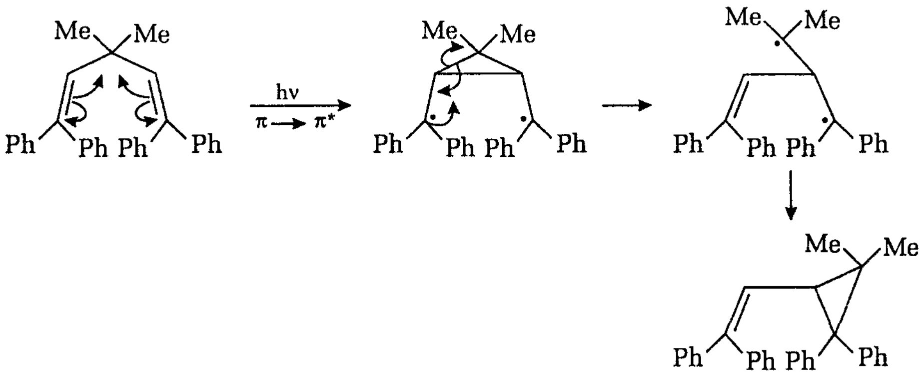


The rearrangement is accompanied by the retention of configuration at $C-1$ $C-5$, and inversion at $C-3$.

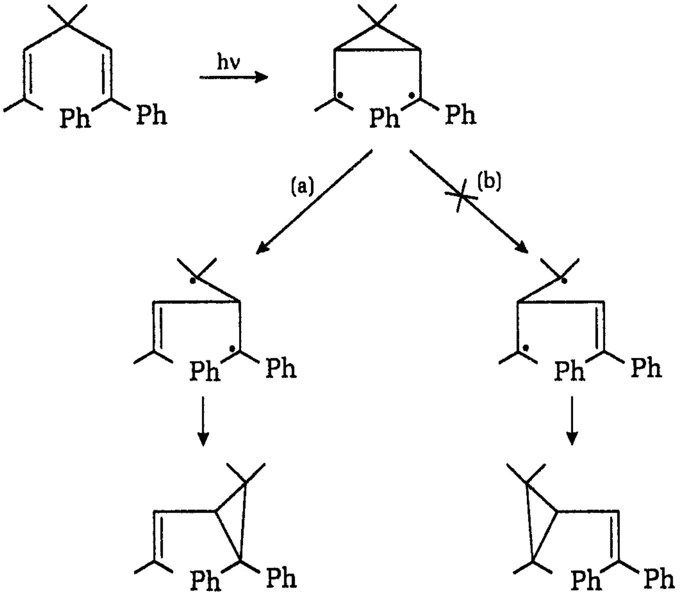
The same mechanism is followed in case of aromatic derived 1, 4-dienes.



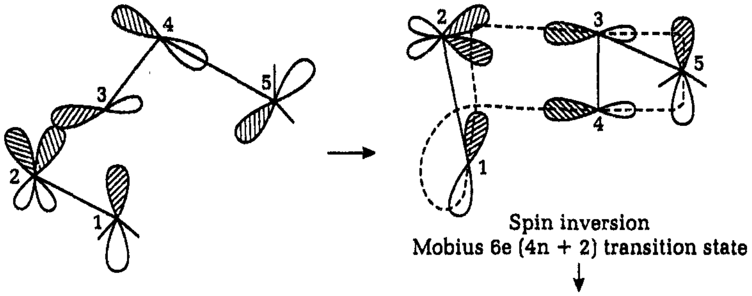
For unsymmetrical 1, 4-dienes, the rearrangement is regioselective. The direct photolysis of 3, 3-dimethyl-1, 1, 5, 5-tetraphenyl penta-1, 4-diene has been found to give the vinyl cyclopropane as the sole of primary photo product.



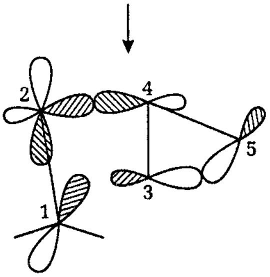
But the different substituent at $C-1$ and $C-5$ has shown, two routes (a) and (b). However the reaction proceeds via the path (a) only and gives 1, 1-dimethyl-2, 2-diphenyl-3 (2, 2-dimethyl) vinyl cyclopropane. This regiospecific process results from cleavage of the three membered ring of diradical towards the isopropyl radical [path (a)] rather than the more stable diphenyl methyl radical [path (b)].



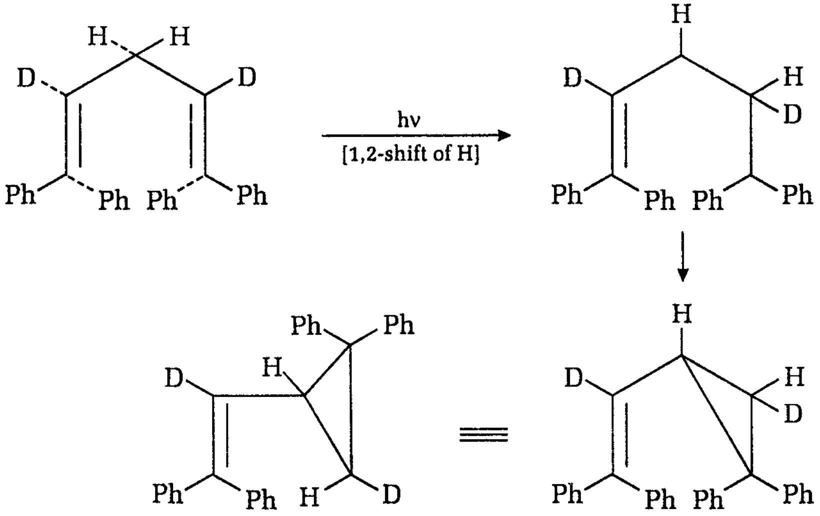
Zimmerman has chosen to describe the di-π-methane rearrangement as in Mobius array which corresponds to a delocalised transition structure for an allowed photochemical reaction, but not for ground state reaction.



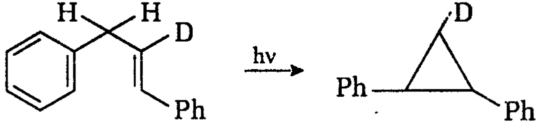
Spin inversion
Mobius 6e (4n + 2) transition state



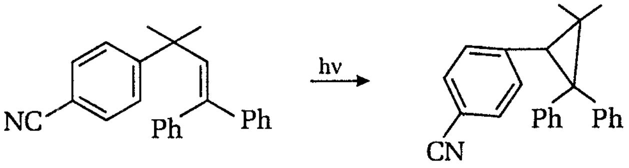
In the absence of gem dimethyl substituent at $C-3$, a di-π-methane rearranged product still formed from 1, 4-diene, but through a 1, 2-shift in contrast to previous mechanism. However, this is confirmed by deuterium labeling.

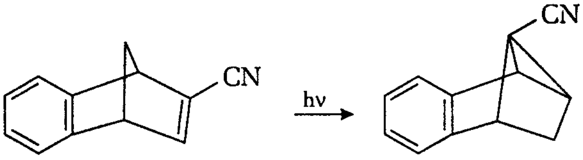


The direct irradiation of 1, 3-diphenylpropene gives *cis*-1, 2-diphenyl cyclopropane. The absence of deuterium migration in labelled substrates establishes the route of the normal di-π-methane rearrangement.

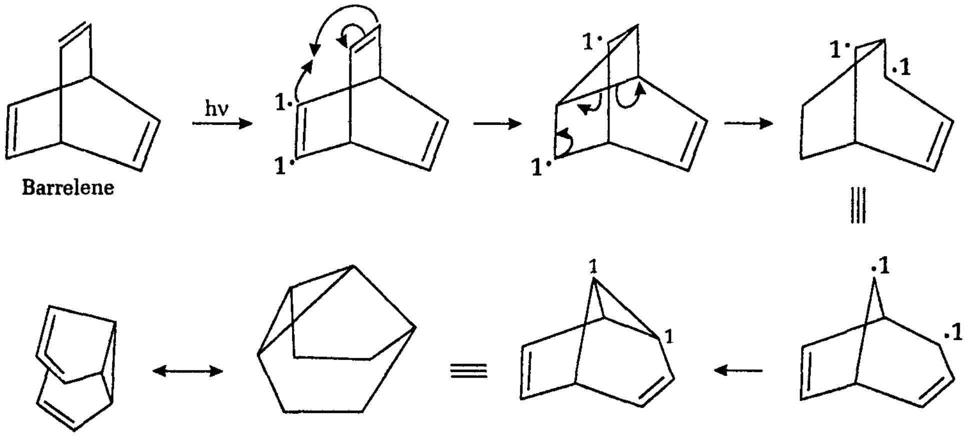


Some more examples :

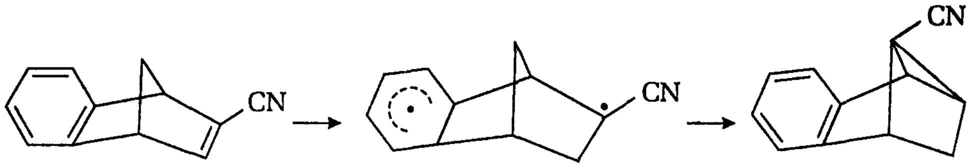




The di-π-methane rearrangement proceeds by a singlet mechanism, for acyclic and monocyclic systems, while triplet sensitised reactions of the dienes usually results in geometrical isomerisation.



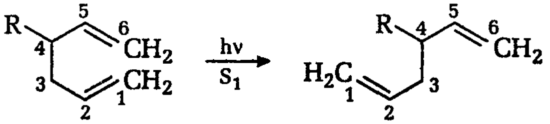
Benzobicyclo [2.2.1] heptene yields di-π-methane product on sensitised irradiation, with a vinylcyanide, the cyano group dictates the triplet pathway, so the bridging yields the cyano substituted radical.



4.5 REARRANGEMENT OF 1, 5-DIENE

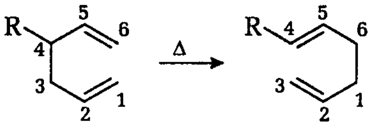
The excited singlet and triplet state reactions of 1, 5-dienes are in marked contrast to each other, as well as with the ground state reactions.

(i)



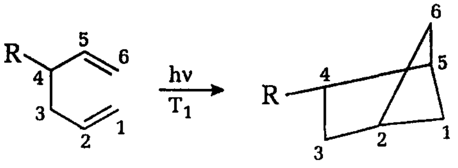
[1,3]-sigmatropic reaction

(ii)



Cope rearrangement
[3,3]-sigmatropic reaction

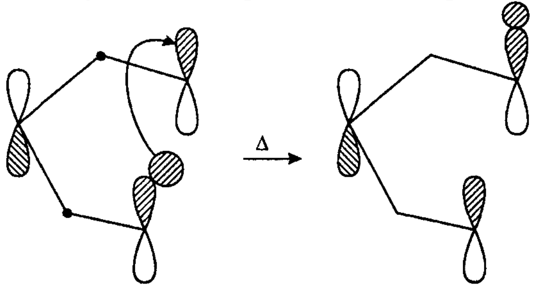
(iii)



1, 5 : 2, 6-Cross cycloaddition

Of all the above mentioned reactions, (i) and (ii) reactions are known as sigmatropic reactions. "A sigmatropic reaction involves the migration of σ bond adjacent to one more π-electron systems, to a new position in the uncatalysed intramolecular reaction". The (ii) reaction is a thermal reaction and known as cope-rearrangement.

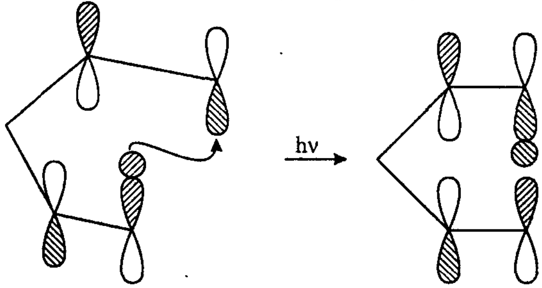
The group being transferred by the π-bond, migration may be associated with the same face of the π-system throughout. This case of migration may be referred to as suprafacial sigmatropic shift. The suprafacial sigmatropic shift is performed by thermally induced degenerate [1, 5] suprafacial shift.



Suprafacial

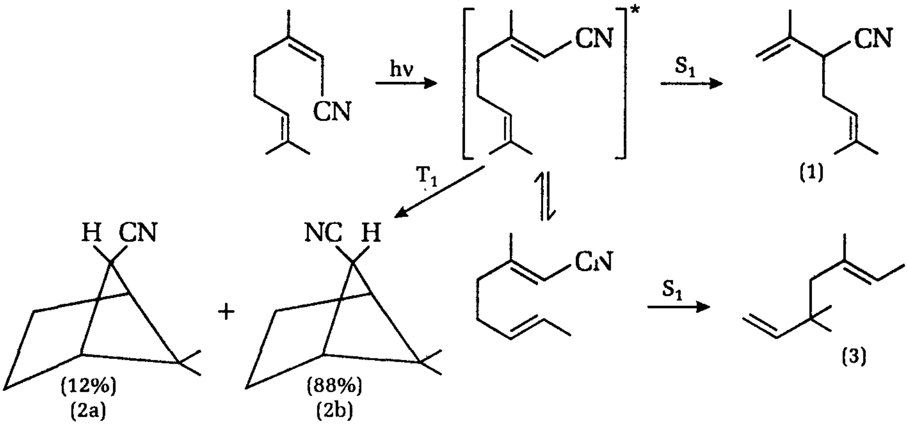
Sigmatropic [1,5] shift
[Thermally allowed]

If the group being transferred through one face of π-system to the opposite face of the π-system, the process is referred as antrafacial sigmatropic shift. The antrafacial sigmatropic [1, 5] shift of Hydrogen is photochemically allowed.



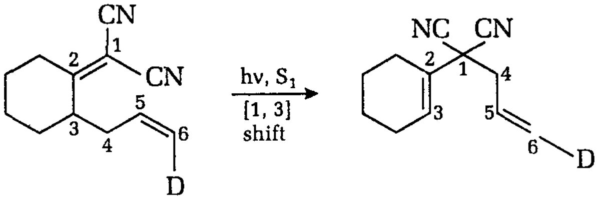
Antrafacial sigmatropic [1,5]-shift {photochemically allowed}

The different Antarafacial and suprafacial sigmatropic shifts of H-atom or other groups which are photochemically allowed have been studied under photochemical rearrangements of 1, 5-diene.



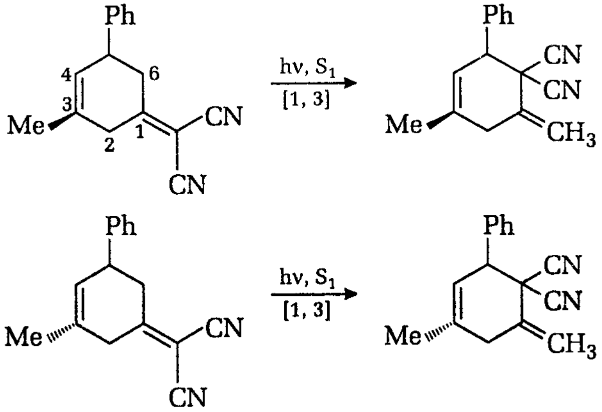
Several rearrangements of 1, 5-dienes have already been discussed above they demonstrate that the reaction path depends on nature of the photochemically excited states [S_1 or T_1]. The unsensitised (S_1) photochemical reaction lead to the two possible [1, 3] sigmatropic shifts to produce (1) and (3), while photolysis is presence of triplet sensitiser results in cross cycloaddition to give (2a) and (2b).

Deuterium labelling experiments have demonstrated the validity of [1, 3] sigmatropic rearrangement, as shown below.



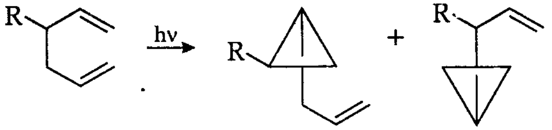
The photochemical reaction leads to a product with the deuterium still attached to a double bonded carbon. This result is consistent only with a [1, 3] shift of $C-4$ from $C-3$ to $C-1$. A further [1, 3] shift of $C-1$ and $C-6$ does not occur because the light absorbing dicyanoethene moiety is no longer present.

The photolysis of *cis-* and *trans-* isomers of 3-methyl-5-phenyl dicyanomethylene cyclohexene gives rise to a [1, 3] benzylic shift, leading to *cis-* and *trans-* 6, 6-dicyano-3-methyl-5-phenylmethylene cyclohexanes, respectively.

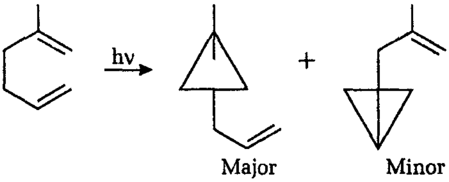


Each reaction is stereospecific with retention of configuration to the migrating benzylic centre.

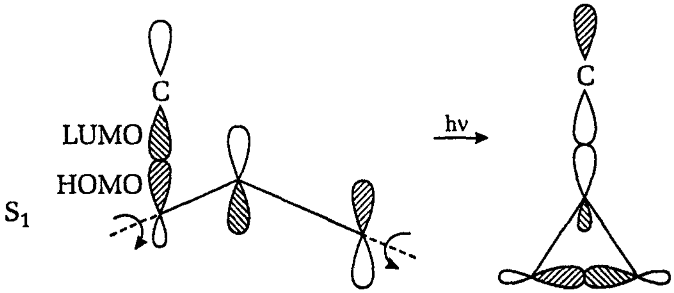
A different type of sigmatropic reaction has been observed for a variety of acyclic alkyl substituted 1, 5-dienes. The reaction occur on direct irradiation and in competition with the [1, 3] sigmatropic shift, discussed earlier. The product of this rearrangement is an allyl cyclopropane and it arise by a [1, 2] sigmatropic shift.



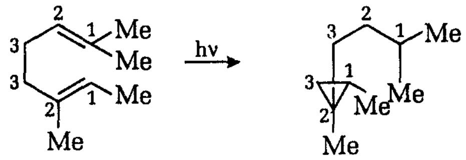
Studies on a number of substituted 1, 5-dienes support the thought; it has been shown that formation of a three membered ring is regioselective and occurs preferentially across the more substituted allyl moiety.



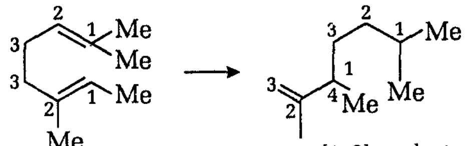
Application of symmetry arguments to the [1, 2] shift shows, it to be allowed in the excited states; the migration proceeds with inversion of configuration at the migrating centre and requires disrotatory closure across the allyl system to give cyclopropane.



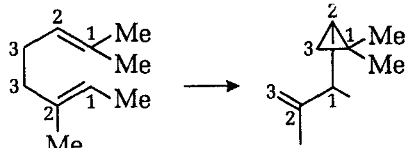
An alternative course for the reaction would give product via an allowed [3, 2] sigmatropic shift, but such products are rarely observed. The [1, 2] shift is effected when a medium pressure mercury arc is used as the light source. If direct irradiation at 254 nm is employed the sole reaction is observed, but studies show that neither π → π * singlet or triplet states are involved in these allyl migrations.



[1, 2] product



[1, 3] product



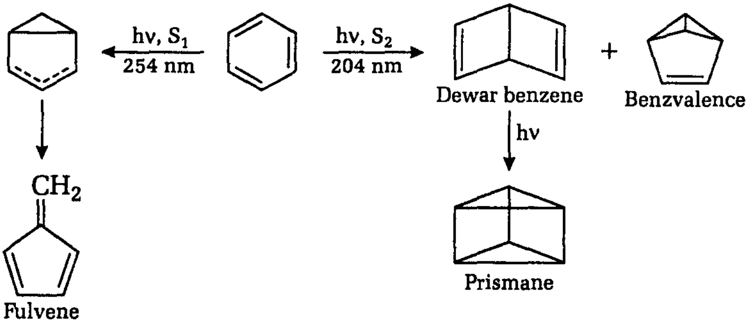
[3, 2] product

UNIT

5

PHOTOCHEMISTRY OF AROMATIC COMPOUNDS

Aromatic compounds are thermally very stable but they undergo many photochemical transformations. The photochemical transformation of benzene and its derivatives provides a lot of surprising changes. The solution phase photolysis of benzene with short wavelength, *i.e.*, irradiation of benzene at 204 nm causes $S_0 \rightarrow S_2$ excitation and observation shows that bonding between the para position is favoured. Dewar benzene is formed. When irradiated at 254 nm the meta position favoured for to give benzvalene and fulvene.

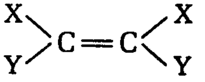


The following transformations and excitations make the different routes for a kind of photochemical reactions. These surprising photochemical changes of aromatic compounds are synthetically very important. Therefore, there is a need of systematic study, which may be under following categories :

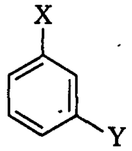
1. Isomerisation 2. Addition and 3. Substitution

5.1 PHOTOCHEMICAL ISOMERISATION OF AROMATIC COMPOUNDS

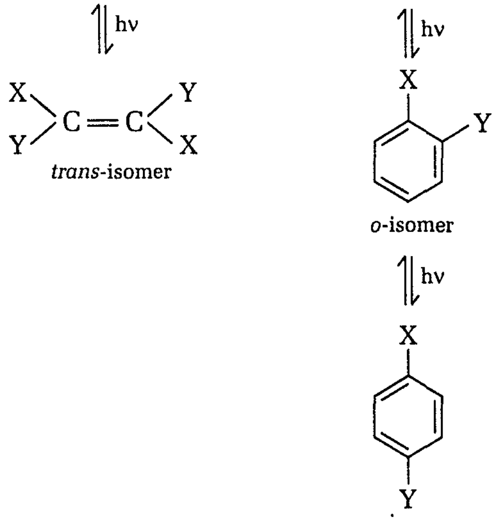
Photochemistry of aromatic compounds provides a number of new photochemical pathways for these reactions which are not thermally feasible. The photoisomerisation of aromatic compounds differ from olefinic non-aromatic compounds. For example, an unsaturation provides two geometrical isomers (*cis* and *trans*), while disubstituted benzene gives three isomers (*o*-, *m*- and *p*-).



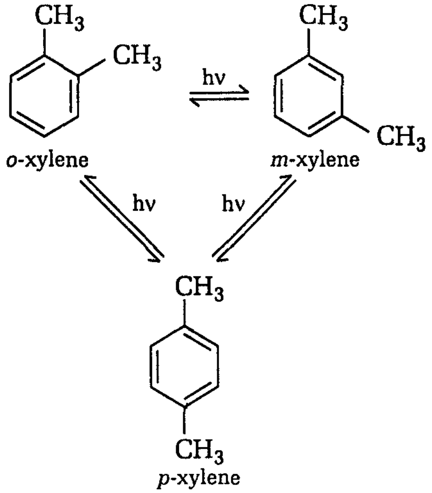
Cis-isomer



m-isomer



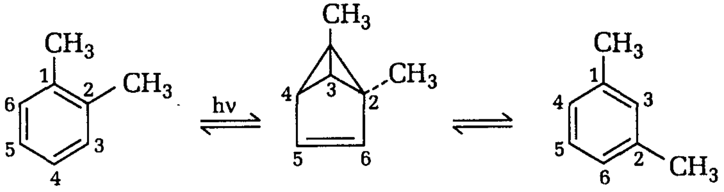
Monocyclic aromatic compounds undergo remarkable photochemical rearrangements on irradiation, and provides photochemical isomerisation. For example; an aromatic compound *o*-xylene an irradiation gives a mixture of *o*-, *m*- and *p*-xylenes.



Mechanism

Mechanisms of the following photochemical isomerisations can be described as : conversion of *o*-xylene into *m*-xylene and *m*-xylene into *p*-xylene, is accompained by 1, 2-alkyl shift. Similarly conversion of *o*-xylene into *p*-xylene and vice-versa is accompained by the 1, 3-alkyl group shift.

1,2-alkyl shift takes place through benzvalene as well as prismane intermediates and obey following pathway.



1,2-shift of CH_3 group by benzvalene intermediate is as given above.

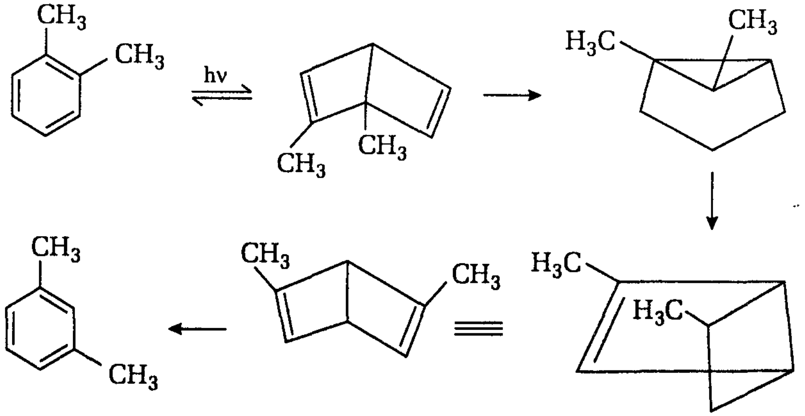


Fig. 5.1. 1,2-shift of CH_3 group through Dewar intermediate.

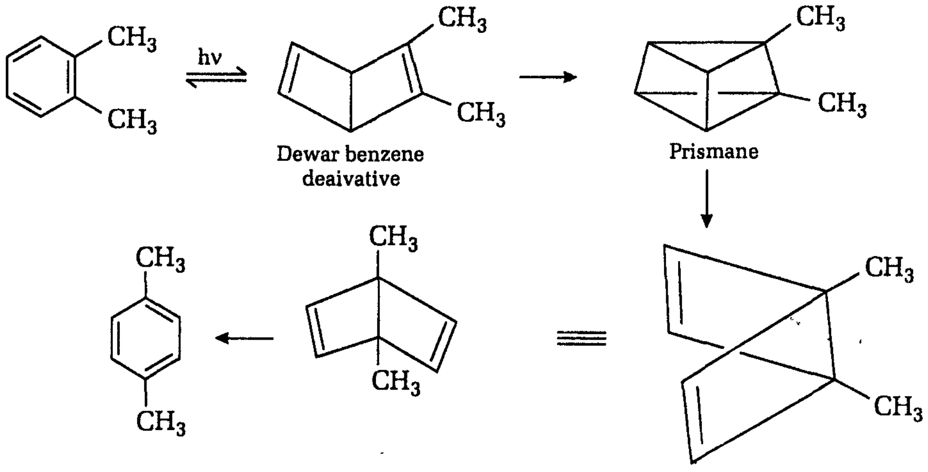
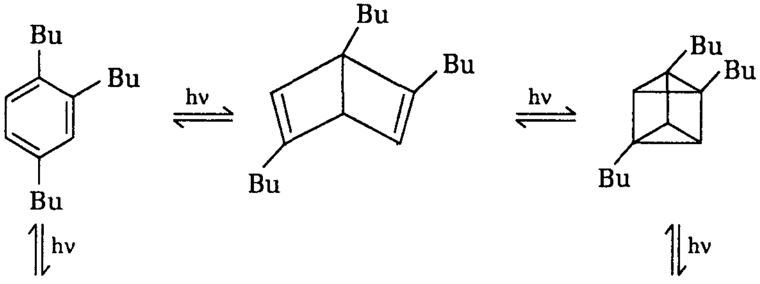
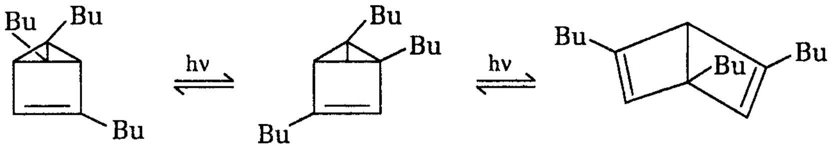


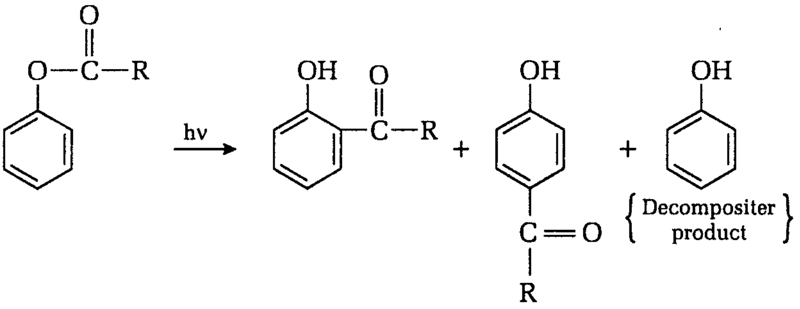
Fig. 5.2. 1,3-shift of CH_3 group through prismane intermediate.

The Photochemical synthesis of alkyl substituted benzene takes advantage of various pathways to provide one or more of the valence bond isomers or a positional isomer of the starting material as illustrated for 1,2,4-tributyl benzene, shown below. The formation of the 1,3,5-isomer results from cycloreversion of the prismane depicted or arises via the benzvalene to yield the least sterically congested product. By an analogus sequence *o*-xylene can gives *m*- and *p*-isomer.





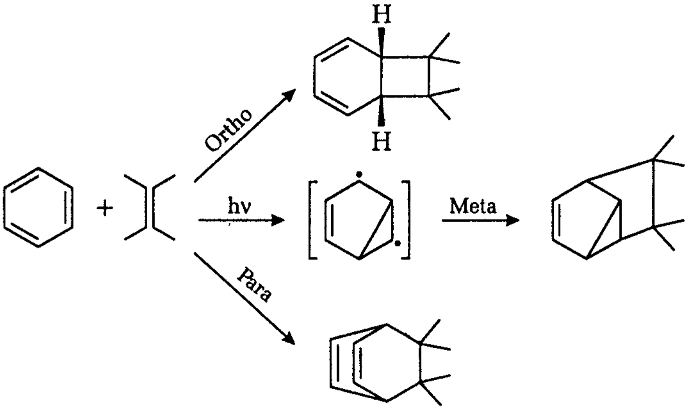
Variety of aromatic compounds, arylesters, aryl ethers, anilides etc. undergoes photochemical rearrangements. In these rearrangements acyl or aryl groups migrates from one position to other in the benzene ring. For example, photo-Fries rearrangement. This is an intramolecular photochemical rearrangement which involves —COR group migration to orthoposition.



5.2 PHOTOCHEMICAL ADDITION REACTIONS SHOWN BY AROMATIC COMPOUNDS

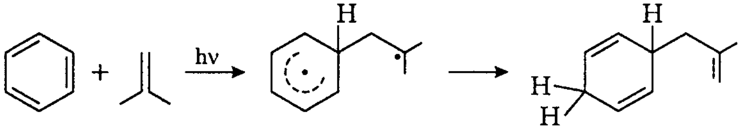
Addition reactions given by aromatic compounds are studied in two categories. First consists, addition reactions by benzene and its derivatives, while second category contains other aromatic compounds.

The photochemistry of benzene is in contrast to ground state chemistry and provides a full exploitation in synthetic applications, which is thermally not possible. The addition of an alkenes, dienes, alkynes, amines, alcohols or carboxylic acids to benzene, can occur across the *ortho-*, *meta-*, and *para-*positions to give three distinct products. The addition of alkene gives *ortho-*, *meta-* and *para-*cycloadditions. All the addition are streospecific with respect to alkene component.

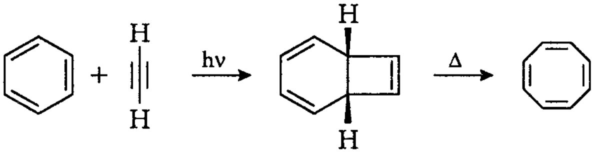


All of these three additions [*o*-, *m*- and *p*-] can occurs from the singlet excited state of aromatic compound. The excitation can be caused by excitation of aromatic chromosphere, *i.e.*, initial excitation of alkene addend or charge transfer complex formed between addends.

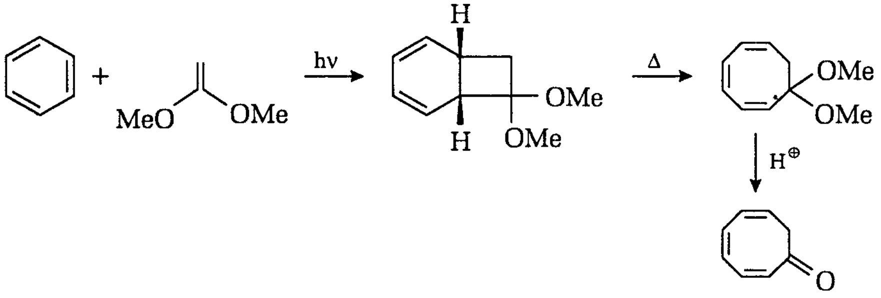
The reaction of benzene and alkenes like an isopropyldiene ($Me_2C{=}C$) moiety produces an non-cyclic "ene-type" of reaction product with effective *p*-substituent. The reaction is a non-concerted process and is considered to proceed either via a biradical or from an equivalent polarised complex. The reaction involves charge transfer by donation of an electron from alkene to excited benzene.



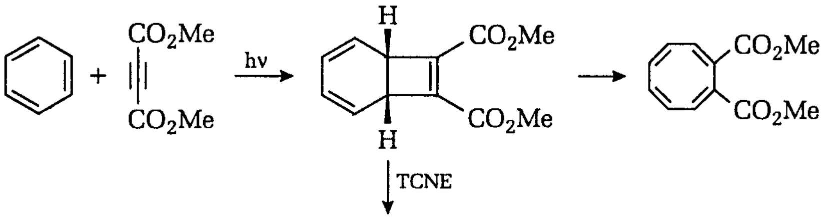
The primary product of a cycloaddition is often unstable in employed conditions. For example, the photochemical addition of ethyne to benzene gives an ortho-adduct, which undergoes thermal disrotatory electrocyclic ring opening of cyclohexadiene to give a cyclooctateraene.

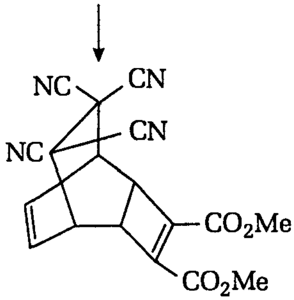


The reaction of benzene with substituted ethylene, gives an ortho-cycloadduct product which undergoes same disrotatory electrocyclic ring opening to give cyclooctatrienone.

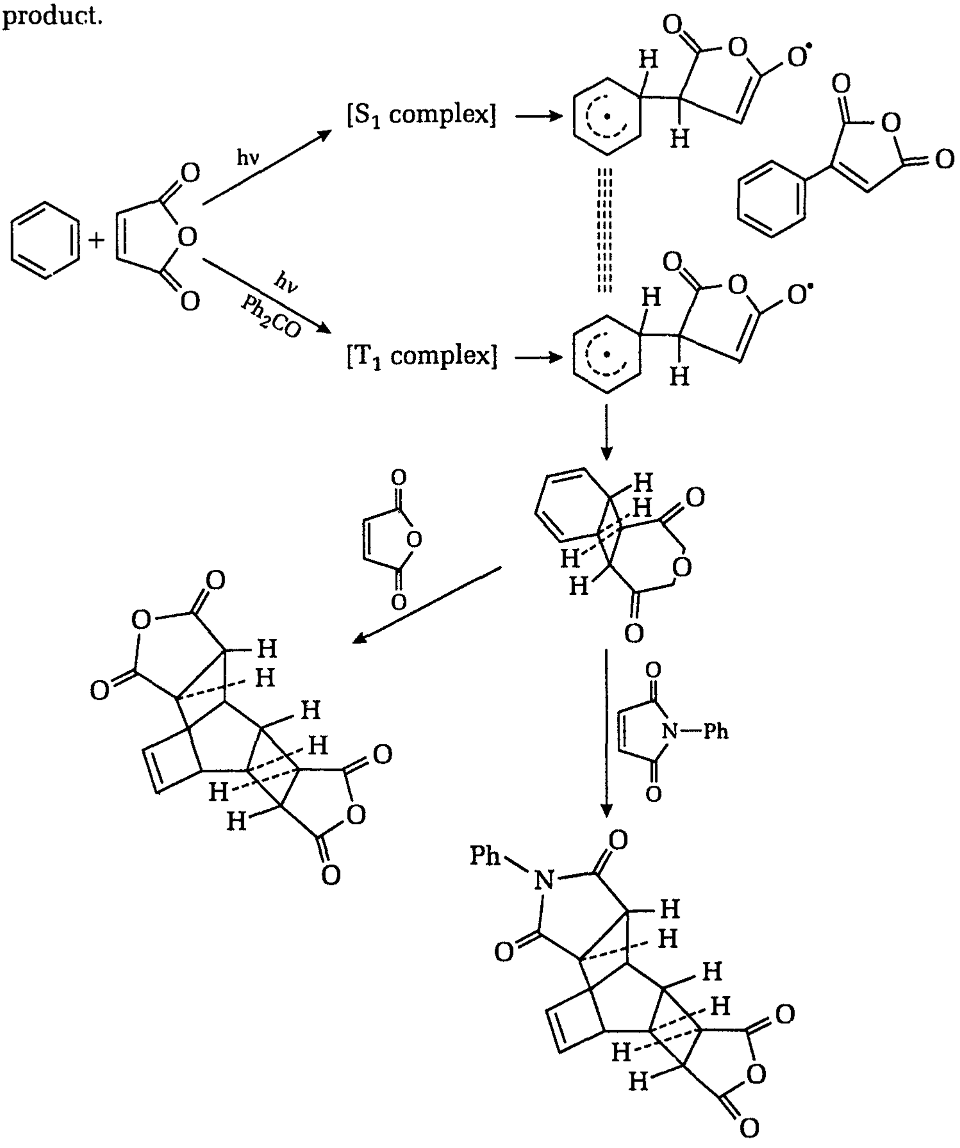


If the ethyne derivative is dimethylethynecarboxylate, the initial product can be trapped before ring opening if tetracyanoethene is added to the reaction mixture.

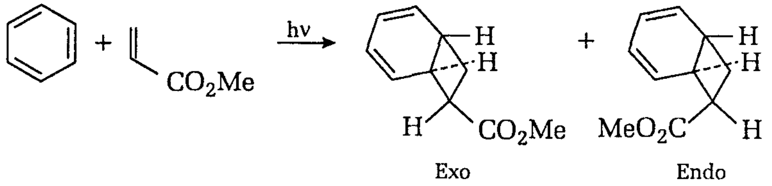




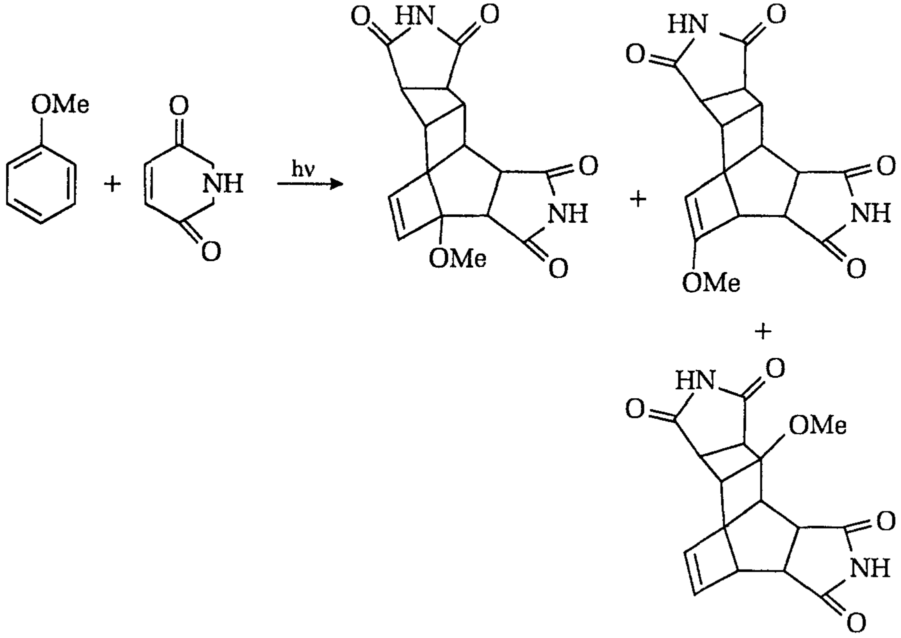
The addition reaction between benzene and Maleic anhydride is the best known example of ortho addition. The reaction is some what unusual in that it proceeds by either direct or sensitised photolysis and does not provides any *meta*-product.



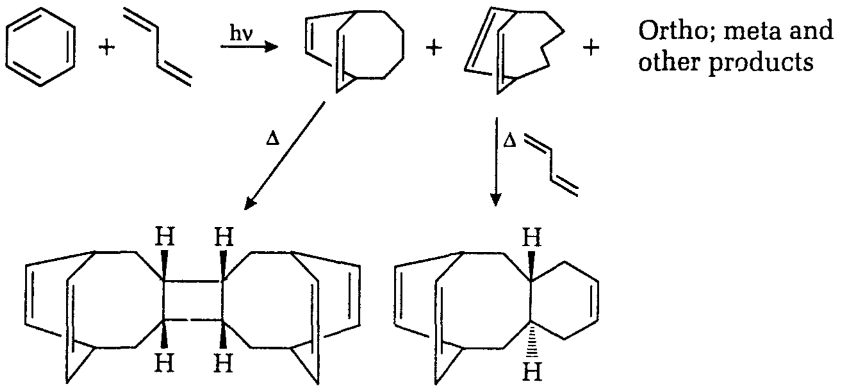
The streochemistry of addition is controlled by orientation of excited state complex. The electron deficient alkenes give mixture of exo- and endo- adducts in non-concerted process.



Photoaddition reaction between benzene derivative and maleimide gives all three possible products. The reaction is initiated by $n \rightarrow \pi^*$ excitation rather than by excitation of charge transfer complex.

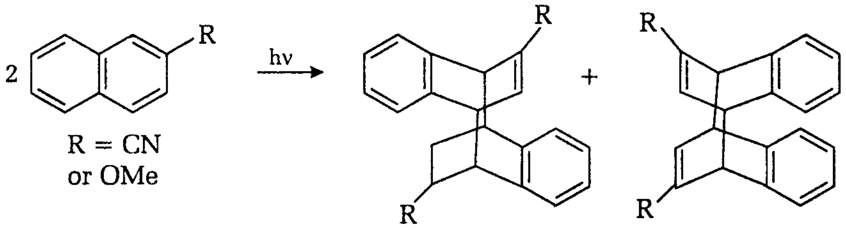


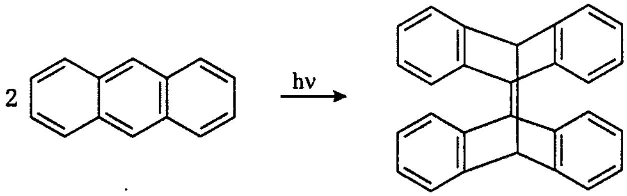
The 1, 4-addition reaction occurs with butadiene and benzene to give the *para*-adduct, containing *cis*- and *trans*-double bond along with *ortho*-, *meta*- and *para*- products.



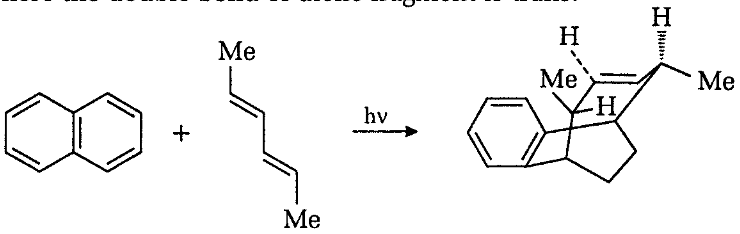
Other aromatic compounds like naphthalene, its derivatives, anthracene, its derivatives and other compounds shows photoaddition reactions. The photoaddition reaction may be between same compound or different compounds.

Cycloaddition reaction between two aromatic substrates yields dimerised products except benzene. For example, 2-substituted naphthalene and anthracene give dimerised product on photolysis.

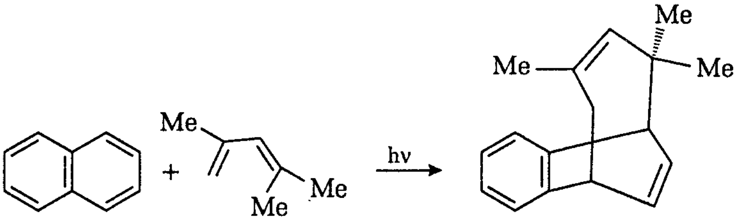




The photolysis of naphthalene and *trans, trans*-hexa-2, 5-diene gives the adduct where the double bond of diene fragment is trans.



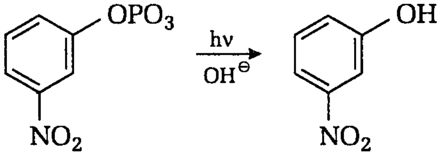
Reaction of naphthalene with 2, 4-dimethyl pent-1, 3-diene gives the adduct where the double bond is generated from the diene fragment.



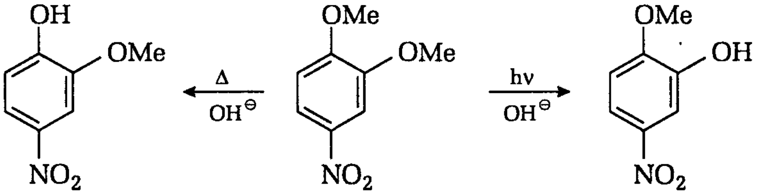
5.3 PHOTOCHEMICAL SUBSTITUTION ON AROMATIC COMPOUNDS

A number of aromatic compounds undergo nucleophilic substitution, while electrophilic photosubstitution on aromatic ring is rare. The photosubstitution is very conventially done on monocyclic, polycyclic and heterocyclic aromatic compounds. The electron donating substituents (Alkyl, —OH, —OMe etc.) on aromatic ring facilitate the nucleophile to attack on *ortho*- and *para*-positions while electron withdrawing substituents (—CN, —NO_2, —COMe, etc.) on the aromatic system, direct nucleophile to *meta*-position. Polycyclic aromatic compounds frequently exhibit "α-reactivity". Substrates with more than one substituent exhibit a resonance stabilisation in product formation.

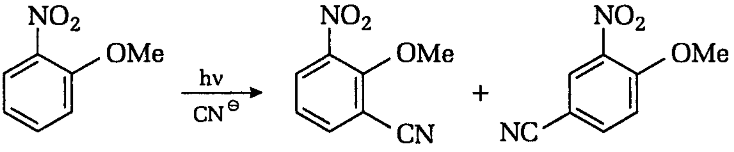
Substituents on aromatic systems make an effect on orientation, reaction rate and excited states. For example, photochemically induced substitution in 3-nitrophenyl phosphate is 300 times faster than that of *o*- or *p*- isomers.

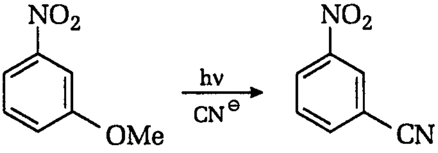


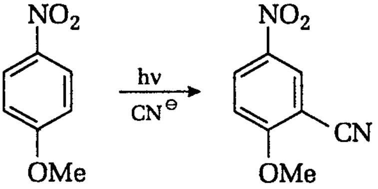
Nitro group activating *m*-position, which results in the formation of a excited state of longer life-time than *o*- or *p*-isomers. It is better understood, when we have *m*- and *p*-substituent in the same molecule. 1, 2-dimethoxy-4-nitrobenzene gives Hydroxyl substitution at *m*-position, while *para*-substitution occurs thermally.

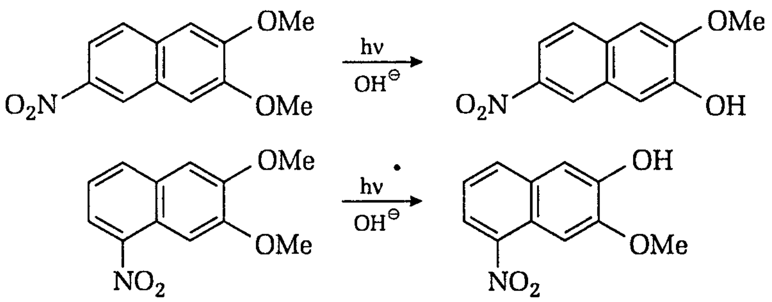


Photocyanation of nitrobenzene also support the *m*-directing effect. In the naphthalene derivatives, *meta*-activation is observed. These examples demonstrate that the chemistry of the photo-excited molecule in contrast with their ground state chemistry.

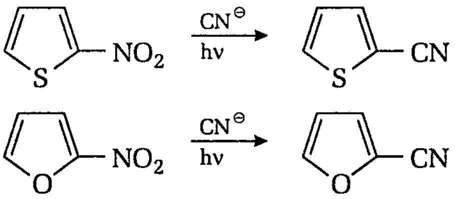




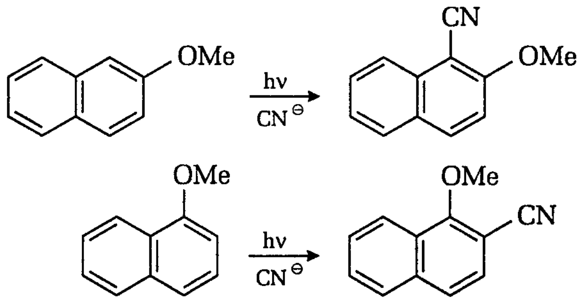




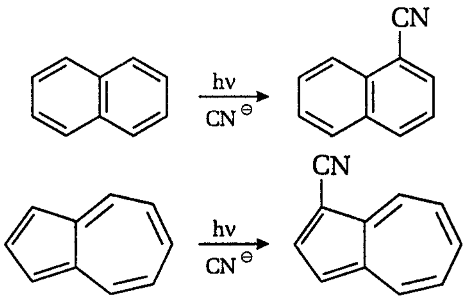
The photocyanation of 2-nitrothiophene and 2-nitrofuran is an S_N2 process. It involves ISC to triplet state and deactivation with ionisation.



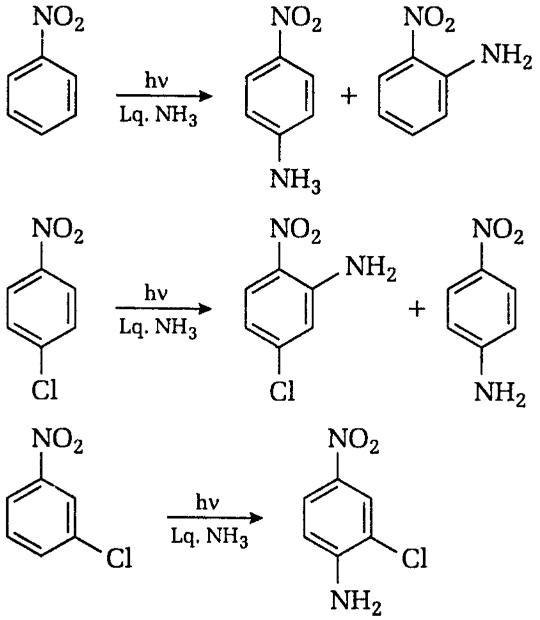
Electron donating group like —OMe present on aromatic system facilitate *o*- and *p*-substitution. The photochemical substitution of cyanide ion in 2-methoxy naphthalene and 1-methoxy naphthalene, yields *o*-products.



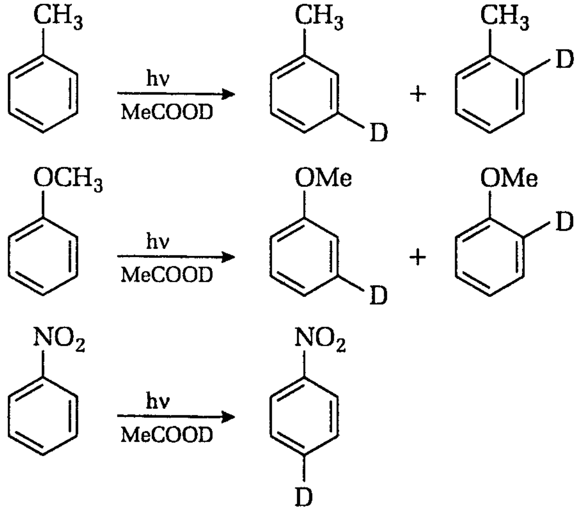
The photosubstitution of many polycyclic aromatic molecules demonstrate an α-effect. For example, photocyanation of naphthalene and Azulene give the 1-cyano derivatives and phenanthrene the 9-substituted compound.



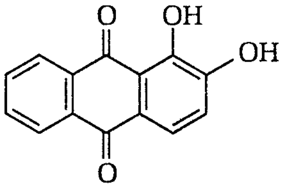
Nitrobenzene and 4-chloronitrobenzene are photoaminated in liquid ammonia with enhanced reactivity at the *ortho*- and *para*-positions; while 3-chloronitrobenzene undergoes photoamination at position-4, which is decided by the ground state effect of electron withdrawing nitro substituent.



Electrophilic substitution on aromatic systems is rare. They have been intensively investigated, and are of synthetic importance. Photodeuteration is important, and electron donating substituents like methyl or methoxy direct the electrophile precedently to *meta*-position while electron withdrawing substituents such as nitro group direct electrophile to *p*-position.

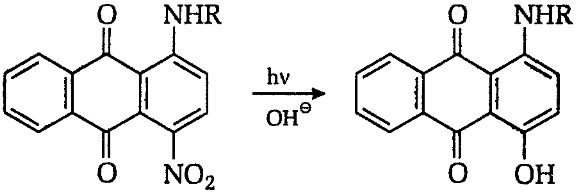


Nucleophilic substitution in aromatic ring of quinones has attracted attention because of its relevance to the light-fastness of antraquinone dyes (like alizarin).



Alizarin

Anthraquinone gives predominantly the 2-hydroxy derivatives on photolysis in aqueous propane-2-ol. The nitro group can be replaced by hydroxyl ion.



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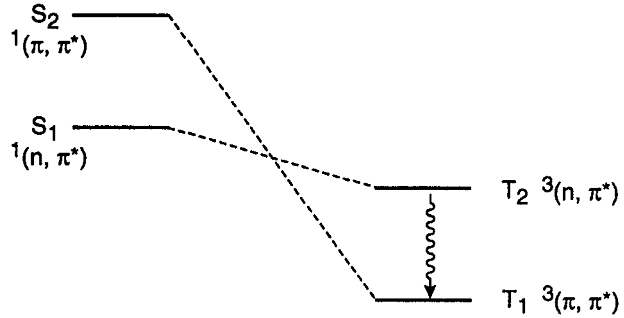
UNIT

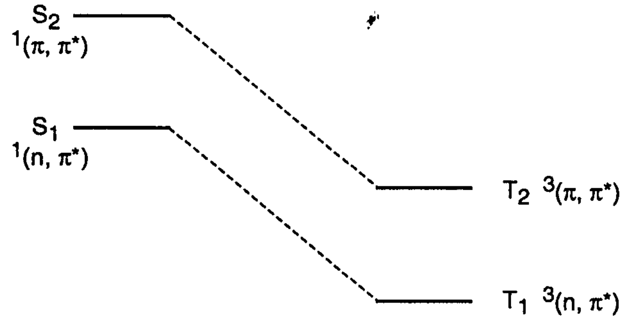
6

PHOTOCHEMISTRY OF CARBONYL COMPOUNDS

Organic molecules containing $>C{=}O$ group are known as carbonyl compounds. Carbonyl [$>C{=}O$] functional group shows either $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ or both electronic excitations. Out of these two readily accessible electronic transitions, the $n \rightarrow \pi^*$ transition is low energy transition and S_1 state has n, π^* configuration. The excitation to S_2 state will be followed by internal conversion and vibrational equilibration to S_1. The low-lying triplet state has either n, π^* or π, π^* configuration. This comes from the fact that the difference in energy between a $^1(\pi, \pi^*)$ and corresponding $^3(\pi, \pi^*)$ state is much larger than the energy difference between a $^1(n, \pi^*)$ and the corresponding $^3(n, \pi^*)$ state. The reactivity of an excited state carbonyl compound depends upon the multiplicity of the excited state and upon the electronic configuration of the excited state.



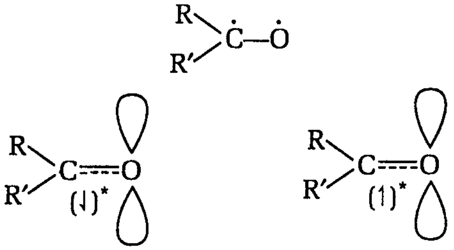
Low-lying π,π* triplet state



Low-lying n,π* triplet state

Fig. 6.1. Electroncally excited states.

We shall focus on the representation of n,π^* states, since, these are the states responsible for most of the interesting photochemical transformations of carbonyl compounds. The presence of an electron in the antibonding (π^*) orbital reduces the double bond character of carbon-oxygen bond, while the singly occupied n-orbital conveys radical like reactivity of oxygen atom.



$^1(n,\pi^*)$ $^3(n,\pi^*)$

Fig. 6.2. Orbital repeasentaton of (n, π^*) configuration of carbonyl compounds.

The photochemistry of carbonyl compounds may be studied under following categories :

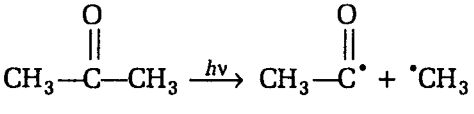
6.1 SATURATED ACYCLIC CARBONYL COMPOUNDS

The photochemical transformations of saturated acyclic carbonyl compounds are dominated by three reaction process, termed as :

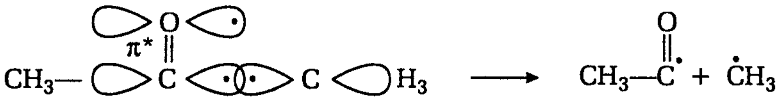
1. Norrish type I 2. Norrish type II 3. Photo reduction

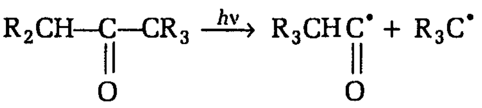
6.2 NORRISH TYPE I [α-CLEAVAGE]

The excited (n,π^*) saturated acyclic carbonyl compounds undergo an initial cleavage of carbon-carbonyl bond to give an alkyl and an acyl radical. This process is known by α-cleavage or Norrish type I cleavage.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{h\nu} CH_3-\overset{\overset{O}{\|}}{C}^{\bullet} + {}^{\bullet}CH_3$$





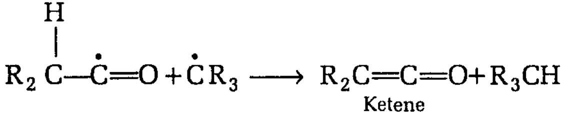
$$R_2CH-\underset{\underset{O}{\|}}{C}-CR_3 \xrightarrow{h\nu} R_3CH\underset{\underset{O}{\|}}{C}^{\bullet} + R_3C^{\bullet}$$

The mentioned reaction is initiated by low-lying $^3(n,\pi^*)$ state because triplet state cleaves more rapidly than the corresponding singlet state, instead of fact that cleavage from singlet is more exothermic.

The radicals formed in Norrish type I cleavage follow one of the following routes :

(i) α-Hydrogen Abstraction

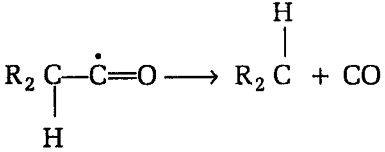
If there is α-Hydrogen present in acyl radical then an α-Hydrogen abstraction is takes place, which yields a ketene and alkane. The presence of ketene can be demonstrated by spectroscopic methods or in presence of a nucleophilic species as water or methanol, it is converted into carboxylic acid or ester derivative which gets trapped.



$$R_2\overset{H}{C}\text{—}\dot{C}{=}O+\dot{C}R_3 \longrightarrow \underset{\text{Ketene}}{R_2C{=}C{=}O}+R_3CH$$

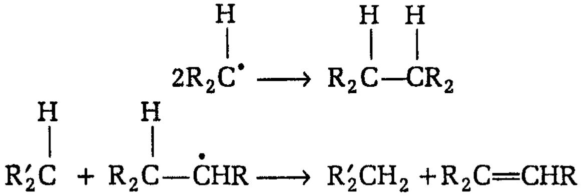
(ii) Decarboxylation

Decarboxylation of acyl radical yields carbon monoxide and an alkyl radical



$$R_2\underset{H}{C}\text{—}\dot{C}{=}O \longrightarrow R_2\overset{H}{C} + CO$$

The alkyl radical formed reacts with another alkyl radical to give an alkane or undergo H-abstraction to give an alkene and alkane.

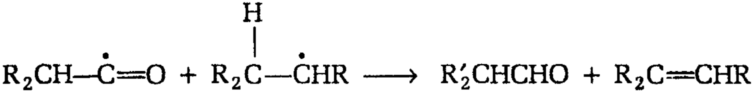


$$2R_2\overset{H}{C}^{\bullet} \longrightarrow R_2\overset{H}{C}\text{—}\overset{H}{C}R_2$$

$$R_2'\overset{H}{C} + R_2\overset{H}{C}\text{—}\dot{C}HR \longrightarrow R_2'CH_2 + R_2C{=}CHR$$

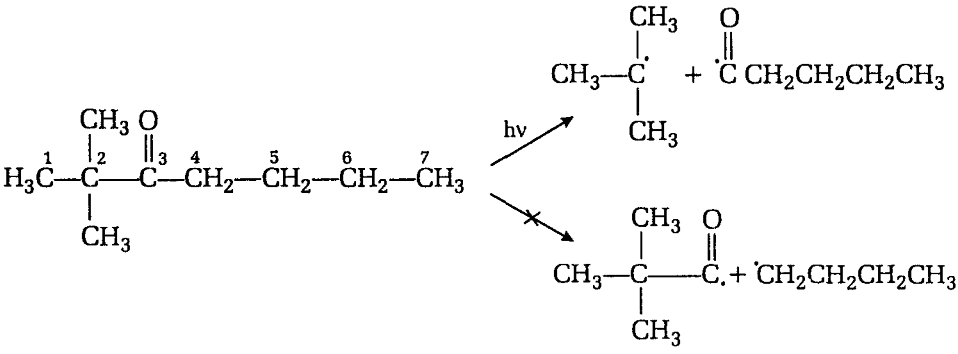
(iii) Intermolecular Hydrogen Abstraction

The acyl radical can pick-up a Hydrogen from alkyl radical and yields an alkene and aldehyde.

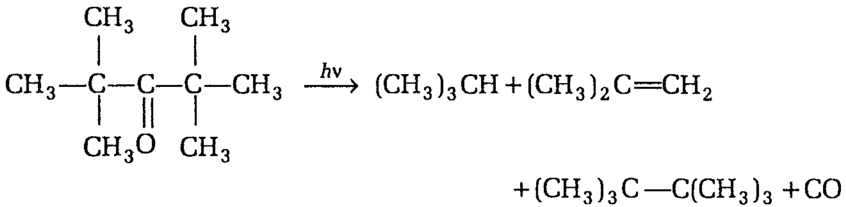


$$R_2CH\text{—}\dot{C}{=}O + R_2\overset{H}{C}\text{—}\dot{C}HR \longrightarrow R_2'CHCHO + R_2C{=}CHR$$

α-cleavage occurs in such a way that the most stable alkyl radical is formed. For example, α- cleavage of 2, 2-Dimethyl heptane-3-one at the bond between $C-2$ and $C-3$ to give tertiary butyl radical, instead of, cleavage of bond between $C-3$ and $C-4$ which yields less stable primary butyl radical.

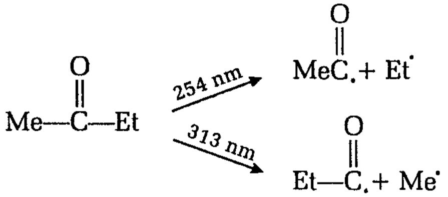


Photolysis of 2, 2, 4, 4- tetramethyl pentane-3-one, result in a high yield (~90%) of CO from both singlet and triplet excited state. The life-time of singlet excited state 4.5 to 5.6×10^{-9} S as compared with 0.11×10^{-9} S for triplet excited state. The Norrish type I cleavage occur 100 times faster from triplet than the singlet excited state.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{O}{\underset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{hv} (CH_3)_3CH+(CH_3)_2C{=}CH_2 + (CH_3)_3C-C(CH_3)_3+CO$$

As the excitation wavelength is reduced [energy increased], the selectivity of carbon-carbonyl bond cleavage decreases. For example, butan-2-one is little selective of band cleavage at 254 nm, but as the energy of the radiation is reduced, a greater preference for cleavage of the weaker bond is observed at 313 nm.

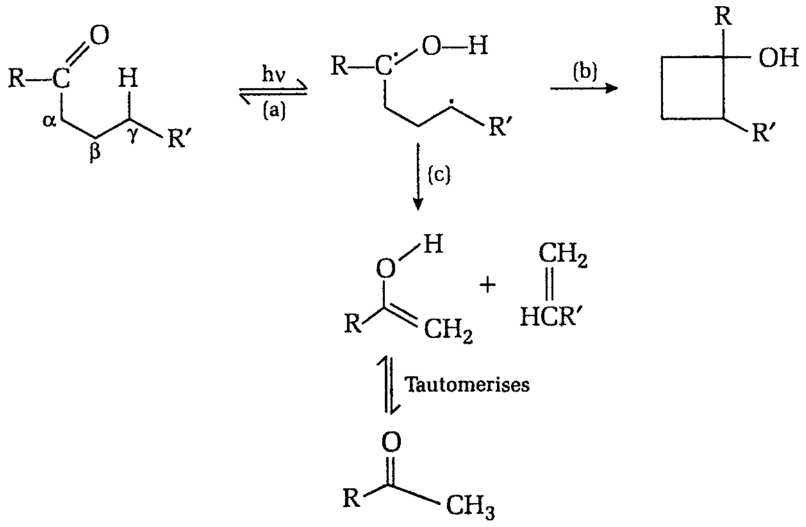


$$Me-\overset{O}{\overset{\|}{C}}-Et \xrightarrow{254\ nm} Me\overset{O}{\overset{\|}{C}}.+Et^{\bullet}$$

$$Me-\overset{O}{\overset{\|}{C}}-Et \xrightarrow{313\ nm} Et-\overset{O}{\overset{\|}{C}}.+Me^{\bullet}$$

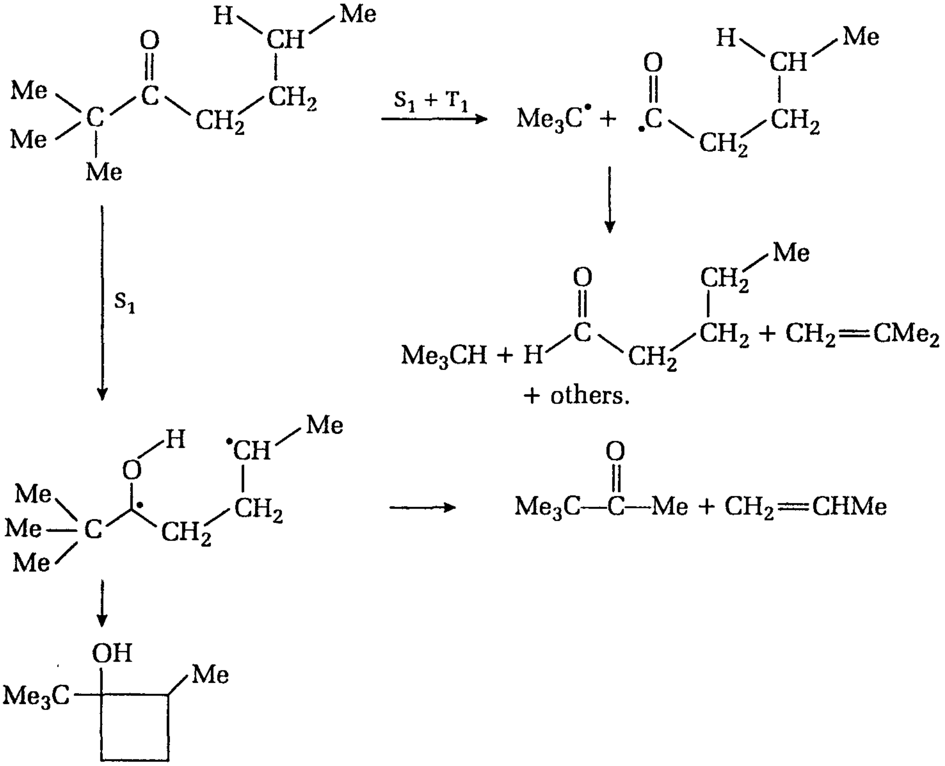
6.3 NORRISH TYPE II REACTIONS

As compared to α-cleavage, (n, π^*) ketone frequently undergo intramolecular hydrogen transfer from the γ-carbon atom to the carbonyl oxygen [γ-Hydrogen transfer], leading to a 1, 4-diradical. The 1, 4-diradical reverts to starting ketone (path. a). Intramolecular radical combination to form a substituted cyclobutanol (path. b) or the 1, 4-diradical can undergo fragmentation of the α, β-carbon-carbon bond to give a methyl ketone via the enol and an alkene (path. c). The process following patch *c*, is known as Norrish type II reaction.

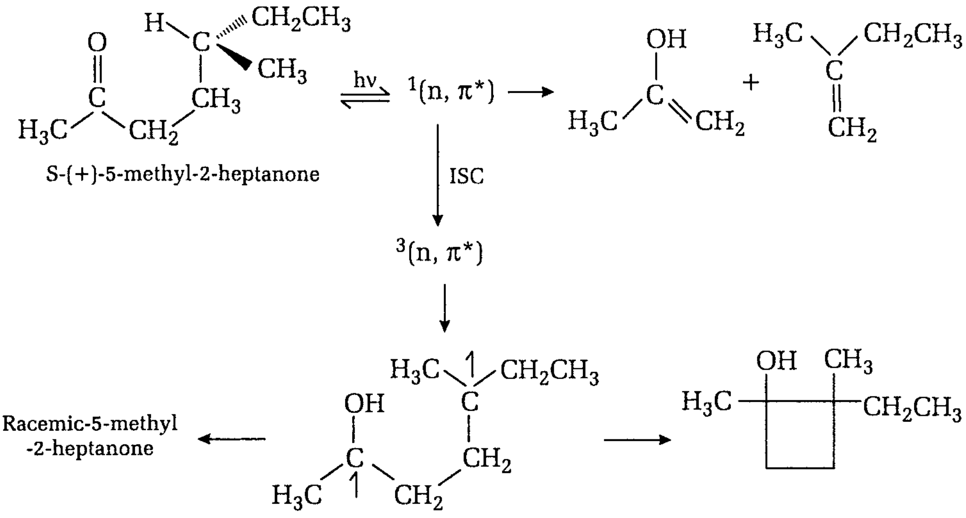


The feasibility of γ-Hydrogen transfer depends on the conformational mobility of the substrate and the life-time of the carbonyl excited state. If the life-time of the excited state is short the conformational distribution of the starting ketone will be important. The rate constant for Hydrogen abstraction by triplet ketones are such that conformational motion of alicyclic molecules can occur before the excited state undergoes reaction. Solvents that can stabilize the Hydrogen bond to the hydroxyl group of the 1, 4-diradical retard the reverse reaction. Replacement of the γ-Hydrogen by deuterium leads to formation of a 1, 4-diradical with a O—D bond. The energy required to break the O—H bond and consequently the reverse reaction is slower and an increase in the efficiency of overall reaction is observed.

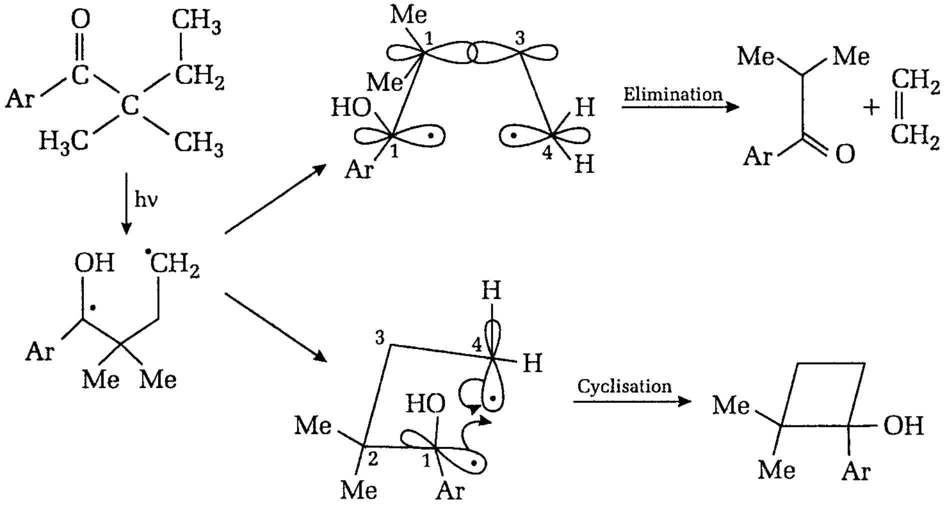
The condensed phase photolysis of 2, 2-dimethyl heptan-3-one, shows both Norrish type I and Norrish type II reactions. The Norrish type I (α-cleavage) occurs from both the excited singlet and triplet states. But the Norrish type II (γ-Hydrogen transfer) process occurs predominantly from excited singlet state.



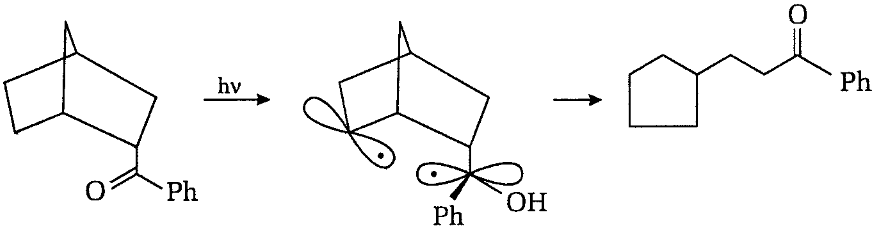
In some cases both singlet and triplet excited states give rise to γ-Hydrogen transfer. There are however, distinguishable differences in the singlet and triplet reactions. Irradiations of *S*-(+)-5-methyl-2-heptanone gives initially singlet excited state, which is capable of intersystem cross to the triplet excited state, return to optically active starting material or react to give products. The products probably are formed from a singlet diradical. The triplet excited state give rise to a triplet diradical which can decay to racemic starting material or go on to products. Racemization of the starting material occurs only by triplet excitation.



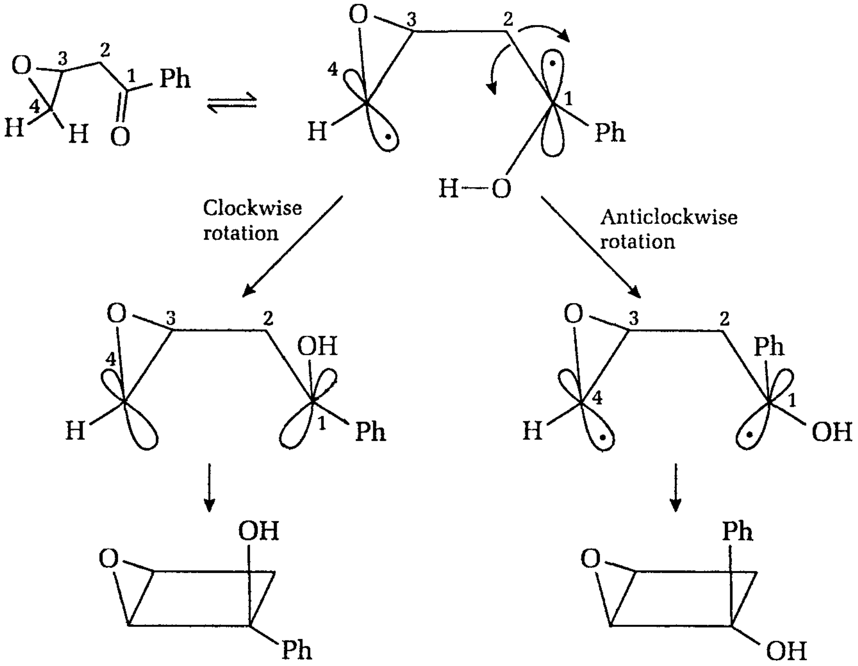
The formation of transition structure for cyclisation of a 1, 4-diradical only requires the overlap of the radical centres, carbon-carbon bond cleavage requires the radical centres to overlap with the bond undergoing cleavage. Photolysis of 2, 2 -dimethyl-1-phenyl butan-1-one gives mentioned eclipsing interactions which occur along with C_1—C_2 bond. Substitution on $C-2$, adjacent to the carbonyl group, increase the probability of cyclisation.



Photolysis of endo-2-benzolynorbornane gives photoelimination as major reaction.

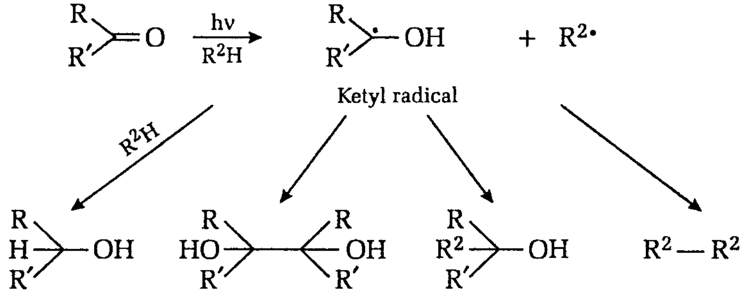


Photolysis of epoxyketones gives mixture of epoxycyclobutanol, due to orthogonality of orbitals of 1, 4-diradical.



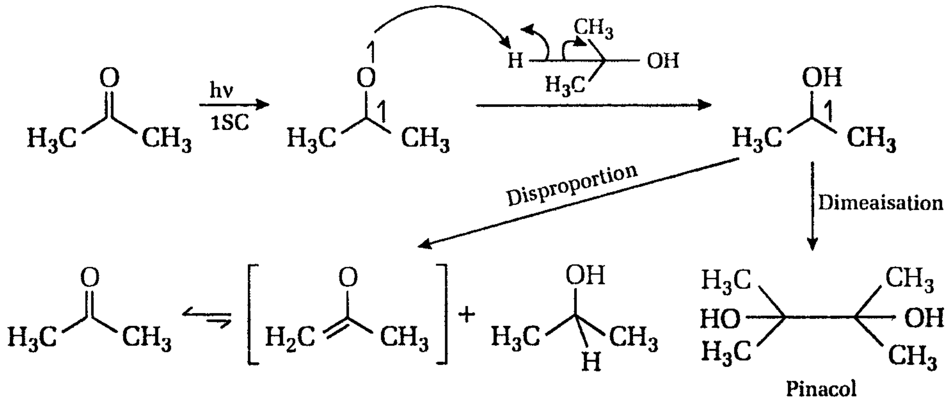
6.4 PHOTO REDUCTION

Photo reduction of ketones in the condensed phase occurs readily and can give rise to alcohols, 1, 2-diols and other products.

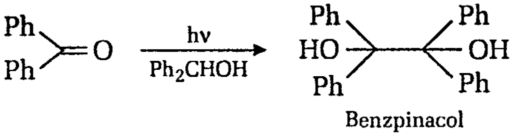


The reaction usually proceeds from the n, π * triplet excited state and involves abstraction of Hydrogen atom from a suitable donor [often the solvent] as the primary process. Subsequently stabilisation of formed ketyl radical occurs by one the mentioned secondary reactions.

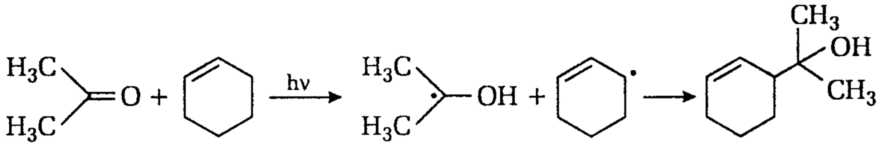
The photolysis of propanone in propan-2-ol results in hydrogen atom transfer to the ketone and two identical ketyl radicals are formed. The formed ketyl radical undergo disproportion and dimerisation reaction to get stabilised. The photolysis yields 2, 3-dimethylbutan-2, 3-diol (pinacol) as the sole product of the reaction.



Reductive coupling occurs for aromatic ketones also. Benzophenone gives benzpinacol as sole product when the reaction is carried out in benzhydrol as solvent.



Carbonyl compounds like ketones, aldehydes and quinones can also add photochemically to activated methylene groups by Hydrogen atom abstraction and subsequent radical recombination.



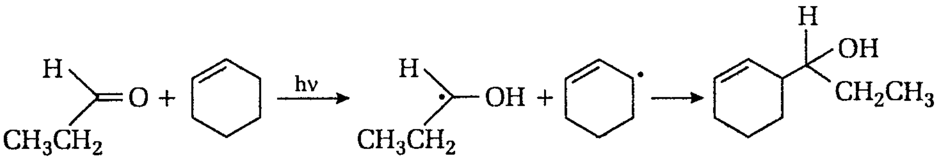
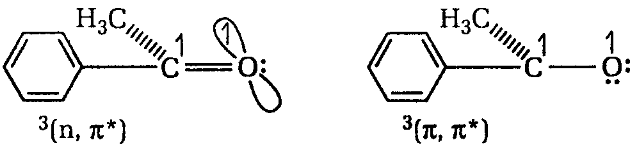
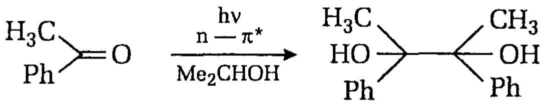


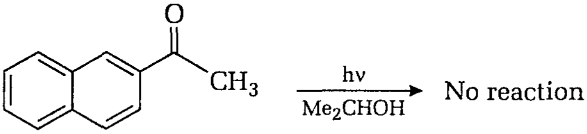
Photo reduction generally proceeds from $n \rightarrow \pi^*$ triplet state. However, with aromatic ketones both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ triplet states can be populated and $\pi \rightarrow \pi^*$ triplet state is more reactive and efficient in Photo reduction.



The reactivity of these two triplet states is different, the $^3(n, \pi^*)$ state behaves like alkoxy radical with one unpaired electron on the oxygen atom. While on $^3(\pi, \pi^*)$ state, the unpaired electrons are delocalised over both the carbon and the oxygen atom. For example, Photo reduction of acetophenone in isopropanol proceeds from (n, π^*) triplet state while of 2-acetylnaphthalene not.

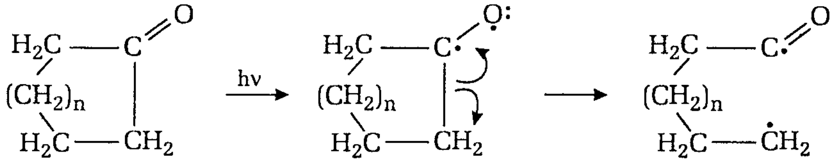


A pinacol



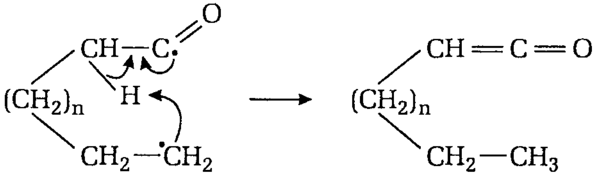
6.5 SATURATED CYCLIC CARBONYL COMPOUNDS

In saturated cyclic carbonyl compounds, the hydrogen if present on γ-carbon atom, will not be in a position to transfer to oxygen of carbonyl group. That's why, photochemistry of saturated cyclic carbonyl compounds is dominated by Norrish type I process, involving the initial cleavage of a carbon-carbonyl bond. The reaction proceeds from $^3(n-\pi^*)$ excited state because those ketones in which the $\pi-\pi$ * triplet state is of lower energy either cleave slowly or not at all. While the $n-\pi$ * singlet state is generally less reactive to α-cleavage than the $n-\pi$ * triplet state. Many α-cleavage reactions proceed from both excited states.

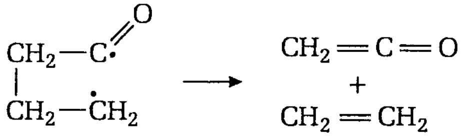


The acyclic diradical formed after photolysis undergoes following subsequent processes.

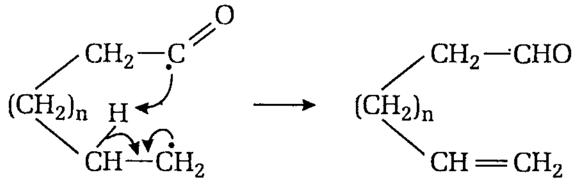
1. **Intramolecular Hydrogen abstraction** : The terminal alkyl radicals undergo intramolecular Hydrogen abstraction to produce a ketone.



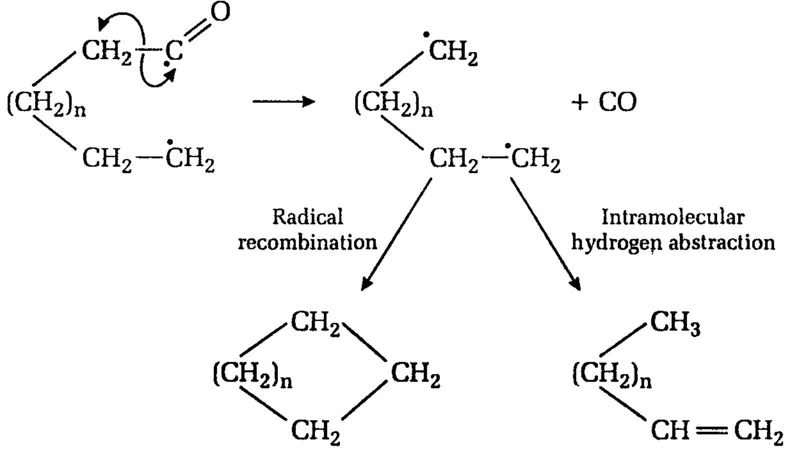
In case when $n = 0$, ketene and ethene are formed



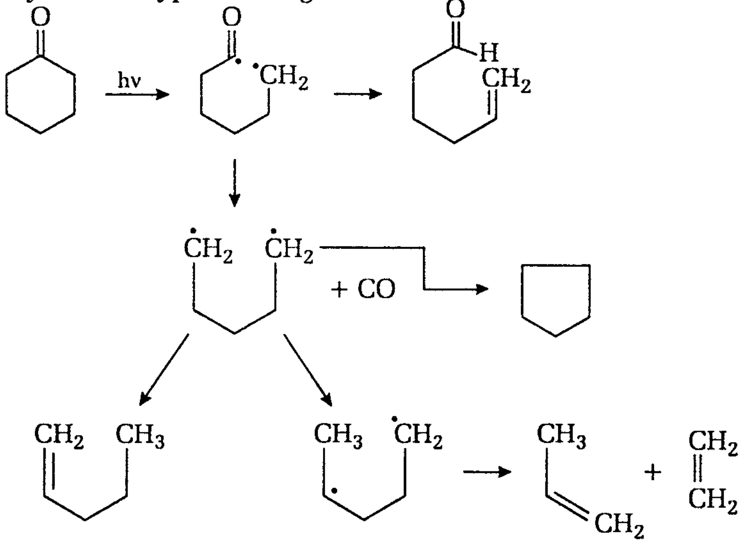
2. **Intramolecular Hydrogen abstraction by the carbonyl carbon atom**, to give an unsaturated aldehyde.



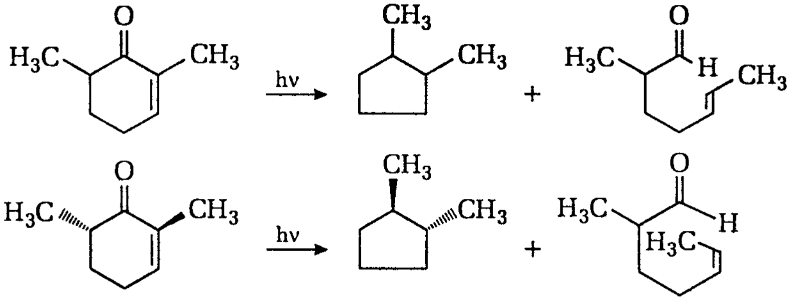
3. Photo-decarboxylation : Acyclic carbonyl diradical on decarboxylation give carbon monoxide, an alkene or a cyclic alkane or both.



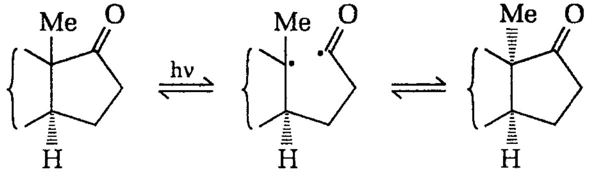
In the vapour-phase photolysis of cyclohexanone, the 1, 6- triplet diradical is formed by Norrish type I cleavage.

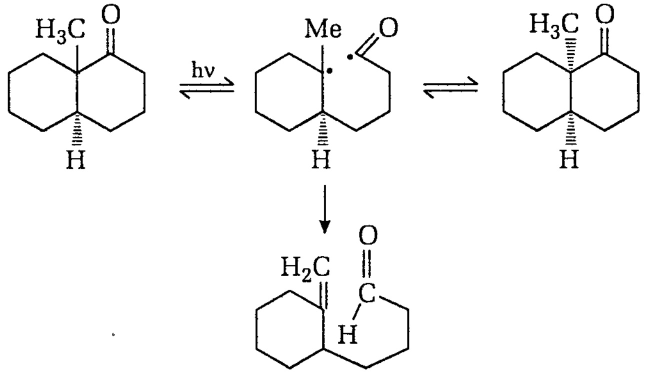


The vapour-phase photolysis of epimeric 2, 6- dimethyl cyclohexanone gives stereospecific reaction. In each case, product formation is faster than photochemical interconversion of the epimers and each epimer gives the stereospecific mixture of products.

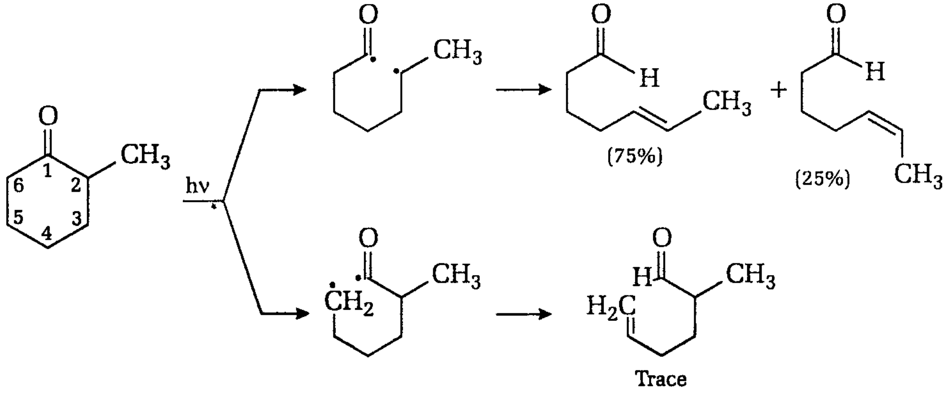


The isomerisation have already been reported. The formed diradical recombines, which gives rise to thermodynamically more stable isomer. The photochemical epimerisation of 17-ketosteroids and other mentioned saturated cyclic carbonyl compounds is through Norrish type I, α-cleavage.

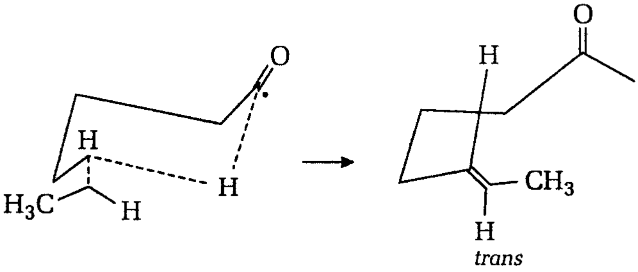


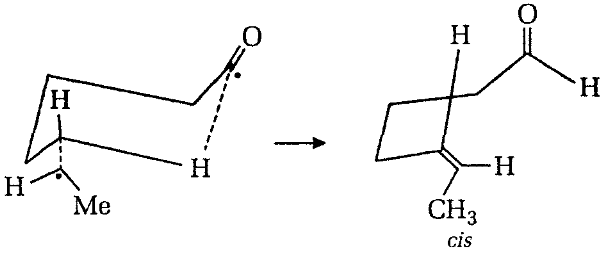


Photolysis of 2-methylcyclohexanone gives a 3 : 1 mixture of *trans*- and *cis*-hept-5-enal with only a trace of 2-methylhex-5-enal.



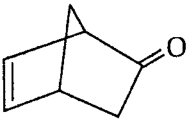
The preference for the formation of the *trans*-alkenal can be rationalised by a conformational preference in the six-membered, Hydrogen bridged, cyclic transition structure leading to this product.





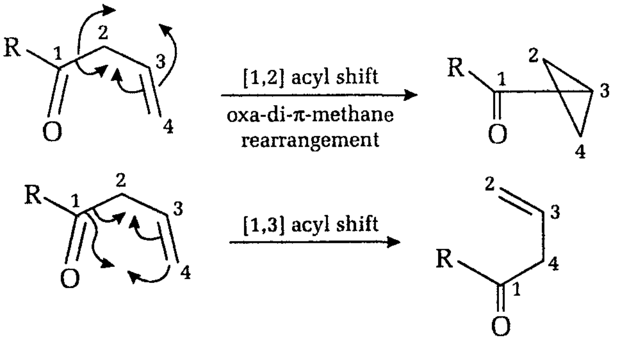
6.6 β, γ-UNSATURATED CARBONYL COMPOUNDS

The β, γ-unsaturated carbonyl compounds are non-conjugated systems and show remarkable properties in ultra-violet region. Bicylo [2.2.1]-hept-5-en- 2-one is an example and shows absorption at 308 nm.



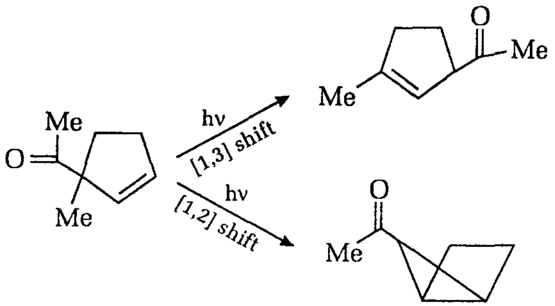
The $n \rightarrow \pi^*$ excitation is most favoured transition but some times, the absorption shifts to longer wavelength, because of mixing of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition.

β, γ-unsaturated ketones exhibit two reactions that depends upon the bichromophoric interaction. These two characteristic reactions are [1, 2] and [1, 3] acyl shift.



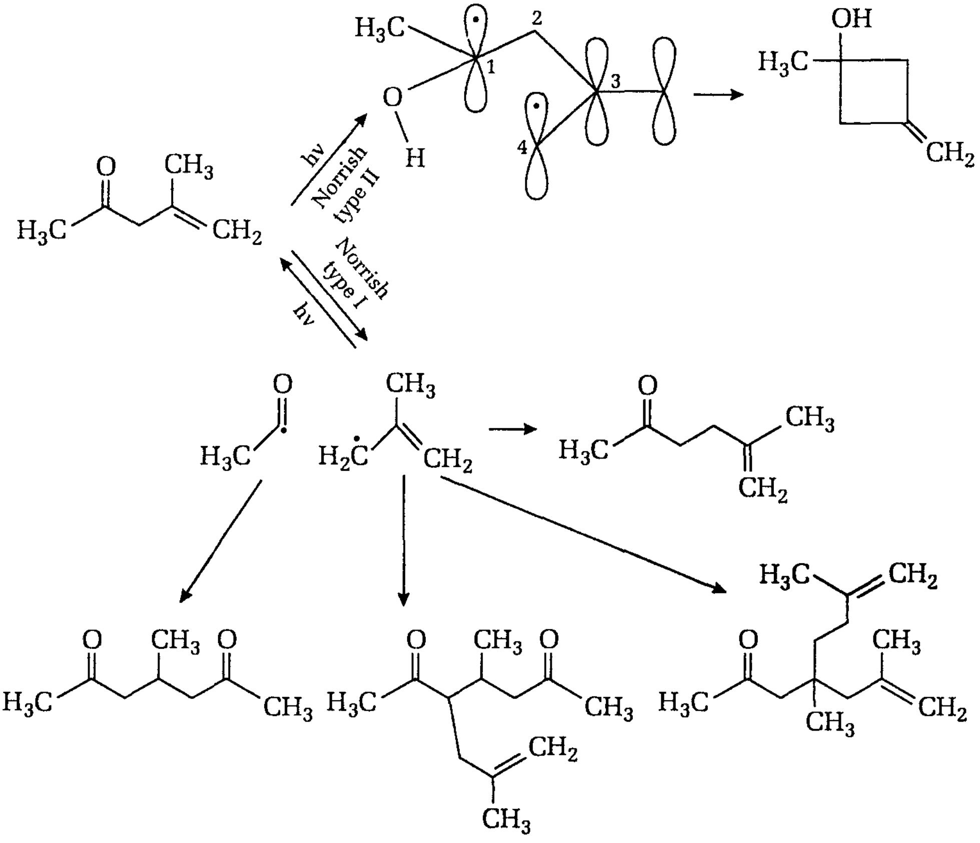
The [1, 2] sigmatropic reaction is also known as the oxa-di-π-methane rearrangement and is analogous to the di-π-methane rearrangement of 1, 4-dienes. The reaction involves the migration of the acyl group from C_2 to C_3 (termed as [1, 2] acyl shift), and formation of a new bond between C_2 and C_4. The [1, 3] acyl shift involves migration of the acyl group from C_2 to C_4 [termed as [1, 3] acyl shift) and relocation of the double bond between C_2 and C_3.

Photolysis of β, γ-enone, yields product through both [1, 2] and [1, 3] acyl shifts.



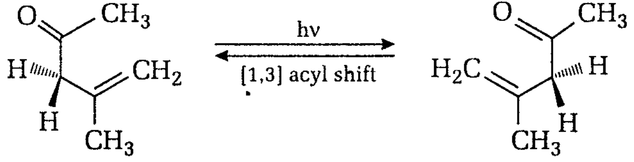
Beside [1, 2] shift and [1, 3] shift β, γ-unsaturated carbonyl compounds undergo characteristic reactions of chromophores, *i.e.*, dimerisation, oxetane formation, reduction, Norrish type I and Norrish type II reactions, are also reported.

Solution phase photolysis of 4-methylpent-4-en-2-one gives more common Norrish type I and Norrish type II reactions. The Norrish type I (α-cleavage) yield minor products due to subsequent reorganization and recapture of the radical fragments (cyclobutanol). Norrish type II yields major product of the reaction which proceeds from $n \rightarrow \pi^*$ singlet or from an exceedingly short-lived triplet state. The other products expected from fragmentation of 1, 4-diradical, namely acetone and alkene were not detected.

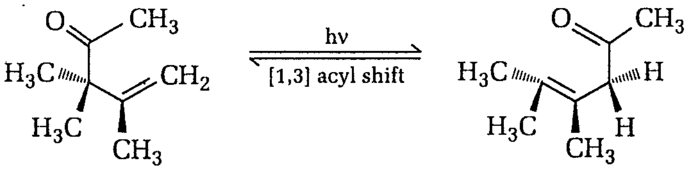


For this simple substrate the [1, 2] shift product is not observed and this is also a common feature of substrates which geometrically isomerise, thereby dissipating triplet energy which might be otherwise used to effect the oxa-di-π-methane rearrangement.

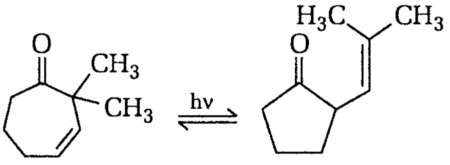
A [1, 3] shift of acyl group cannot be detected for this substrate since product of the process is identical with the substrate.



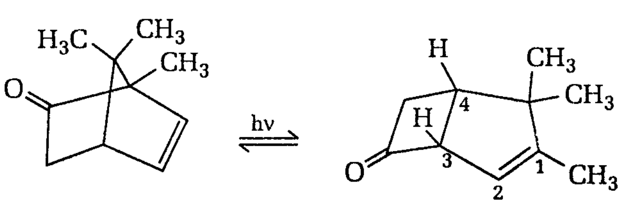
The introduction of two methyl substituents adjacent to the carbonyl group destroys the symmetry of the enone and a product resulting from [1, 3] acyl shift is observed. The product may result from a concerted shift of the acyl group or from α-cleavage and radical recombination in the cage containing the acyl and allylic radicals.

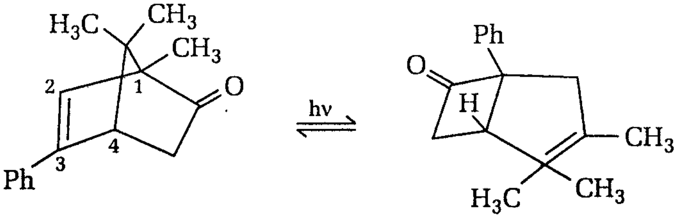


There are many examples of photochemical isomerisation of β, γ-enones which proceed with [1, 3] acyl shift. Photolysis of 2, 2-dimethylcyclohept-3-enone leads to a [1, 3] sigmatropic shift to a five membered ring ketone.



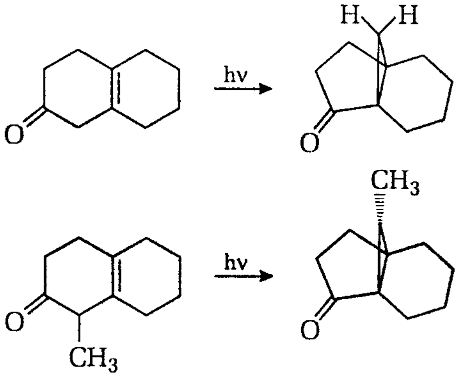
The following enones undergo acyl migration to give rearranged products :





The oxa-di-π-methane rearrangement of β, γ-unsaturated carbonyl compounds is most commonly observed in rigid systems where isomerisation of the alkene is inhibited. It occurs from the lowest π → π * triplet state and can be sensitised by triplet sensitiser.

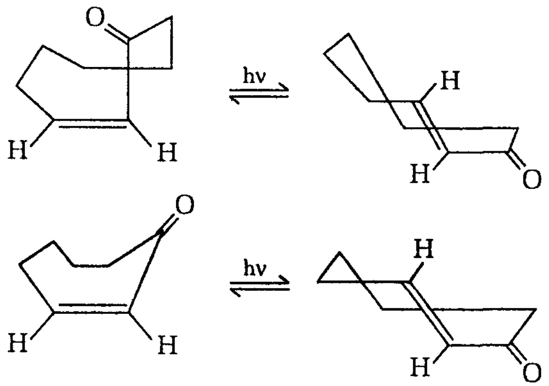
The bicyclic ketone, relatively rigid β, γ-enone, photolysis of which gives only tricyclic cyclopropyl ketone.



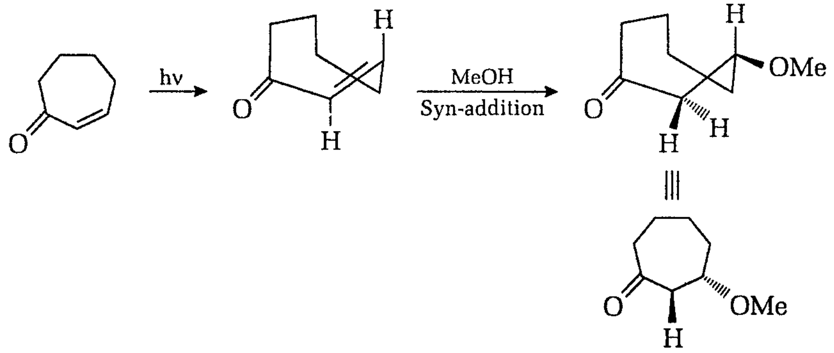
6.7 α, β-UNSATURATED CARBONYL COMPOUNDS

Most of α, β unsaturated compounds undergo photochemical change like migration of the alkenic π-bond to give a β, γ-unsaturated ketones, dimerisation by photochemically allowed [$\pi^2 s+\pi^2 s$] cycloaddition, rearrangement and *cis-trans* isomerisation. These are among the commonest photochemical reactions of α, β-unsaturated ketones.

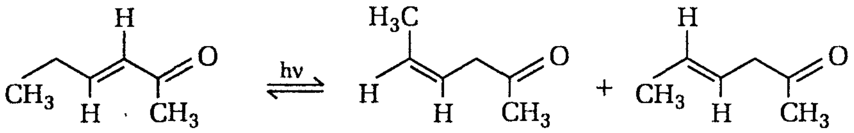
The primary and fastest photochemical reaction of acyclic and some cyclic α, β-unsaturated ketones is *cis-trans* isomerisation. This isomerisation is not expected for cyclopent-2-enone or cyclohept-2-enone because of high strain energy, but it has been reported for *cis*-cyclooct-2-enone and cis-cyclohept-2-enone. It is thought to occur from triplet excited state.



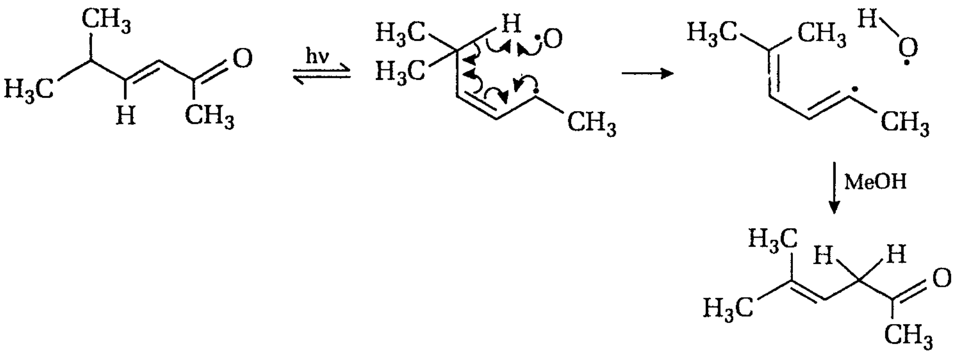
Flash photolysis of cyclohept-2-enone, yields isomerised product which may be detected by employing methanol which gives syn-addition to strained bond and formed product is already trapped.



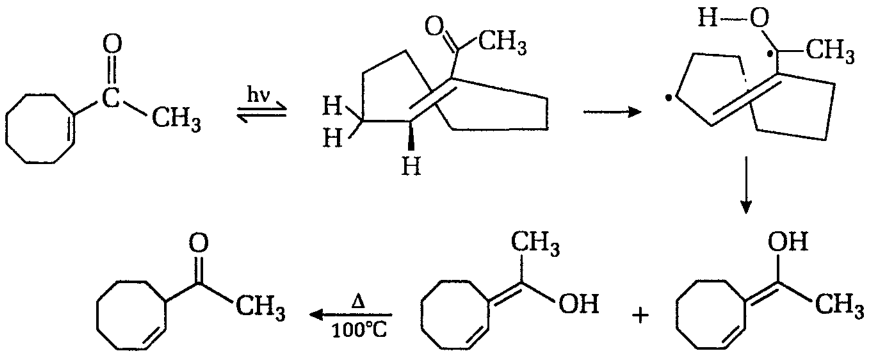
Isomerisation of α, β-unsaturated ketone to β, γ-unsaturated ketone is expected to involve π → π * excited state. The photolysis of Hex-3-en-2-one results in migration of the C—C double bond to give the β, γ-unsaturated isomers [*E*/*Z* mixture].



Photolysis of 5-methylhex-3-en-2-one gives only β, γ-isomeric product through intramolecular hydrogen abstraction from γ-position.

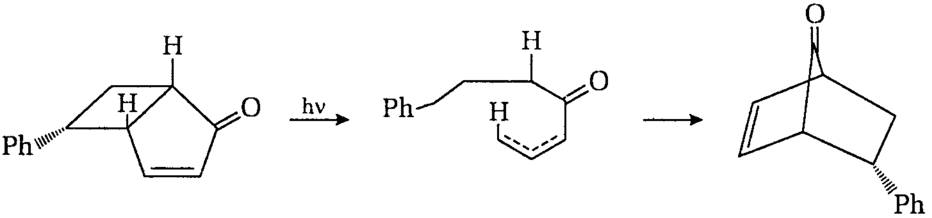


The conjugated 1, 3-dienol intermediate in the isomerisation of α, β- to β, γ-unsaturated ketones has been isolated from 1-acetylcyclooctene.

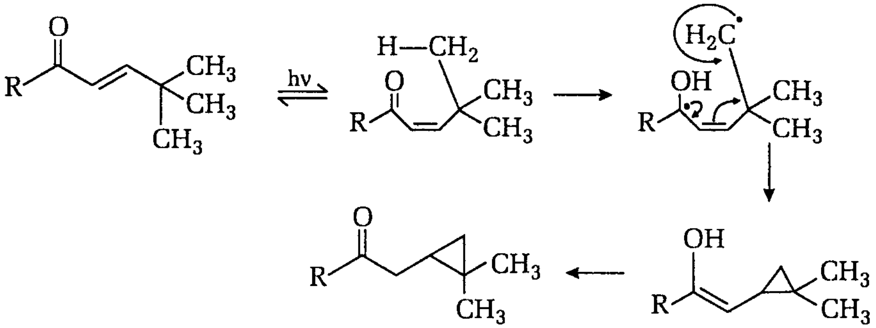


The α, β-unsaturated ketone is thought to undergo initial *cis-trans* isomerisation. Now carbonyl oxygen is in a position to abstract γ-Hydrogen atom, which further yield β, γ- isomer.

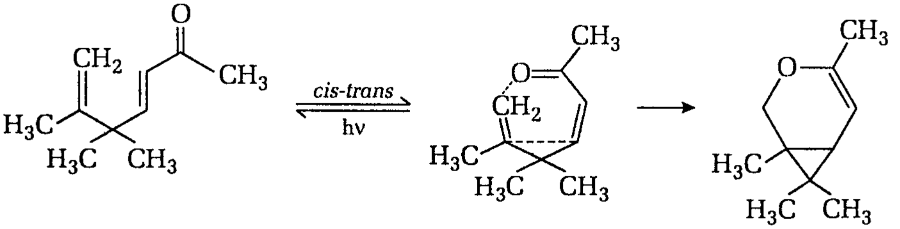
The photolysis of following α, β-unsaturated ketone yields β, γ-enone but through skeleton-rearrangement.

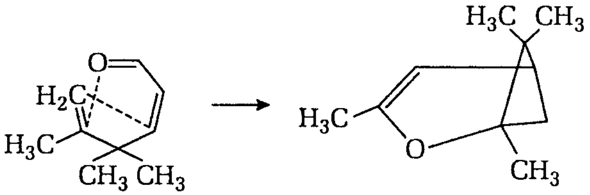


When an α, β-unsaturated ketone lacks a γ-hydrogen atom, photolysis usually results in an intramolecular δ-hydrogen transfer through a seven membered cyclic transition state.



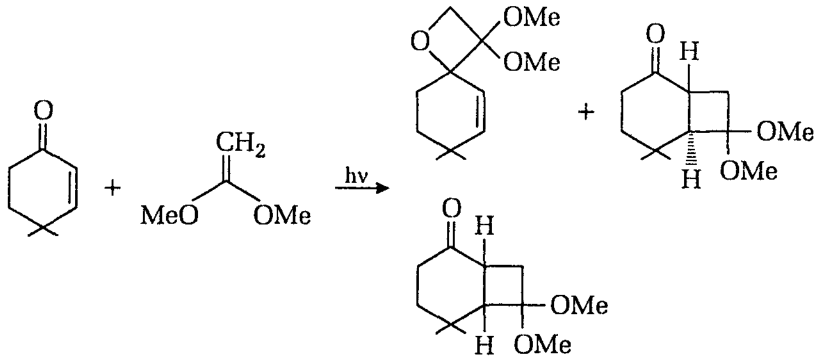
Intramolecular cycloaddition of α, β-unsaturated ketones have also been reported. For example,

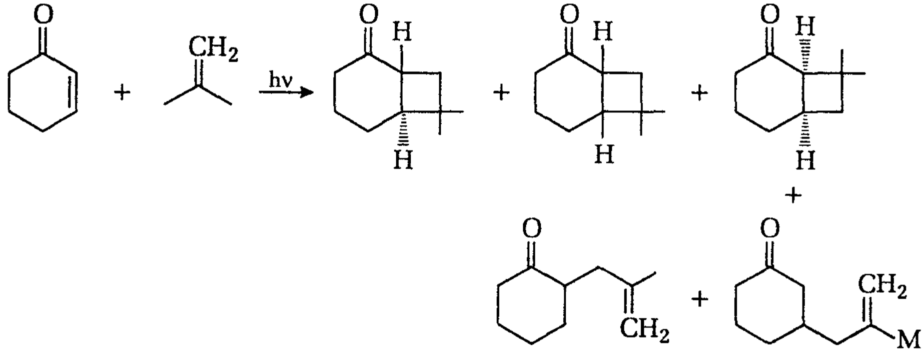




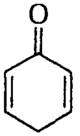
The major cycloaddition reactions of α, β-unsaturated ketones is intermolecular of $[\pi^2 + \pi^2]$ type. These involve photo induced geometrical isomerisation followed by a ground state reaction of highly reactive *trans*-cyclic enone.

Reaction of cyclohexenone with 2-methyl propene gives both of the possible cis- fused cyclobutane adducts, but the major product is the trans- fused ketone. The formation of trans-fused adducts is more common for reaction of enones with electron rich alkenes. But it is not observed for cyclopentenones, due to inability of twisting.

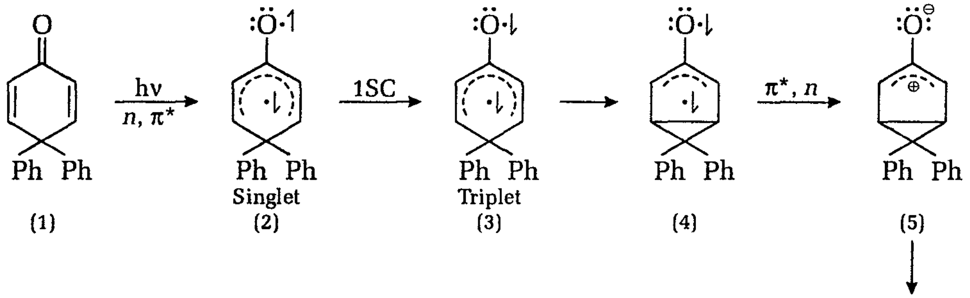


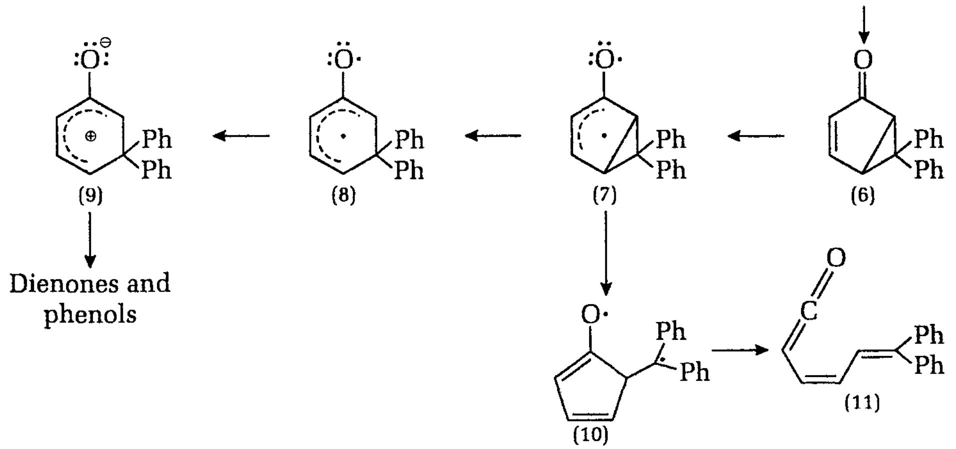


6.8 CYCLOHEXADIENONE



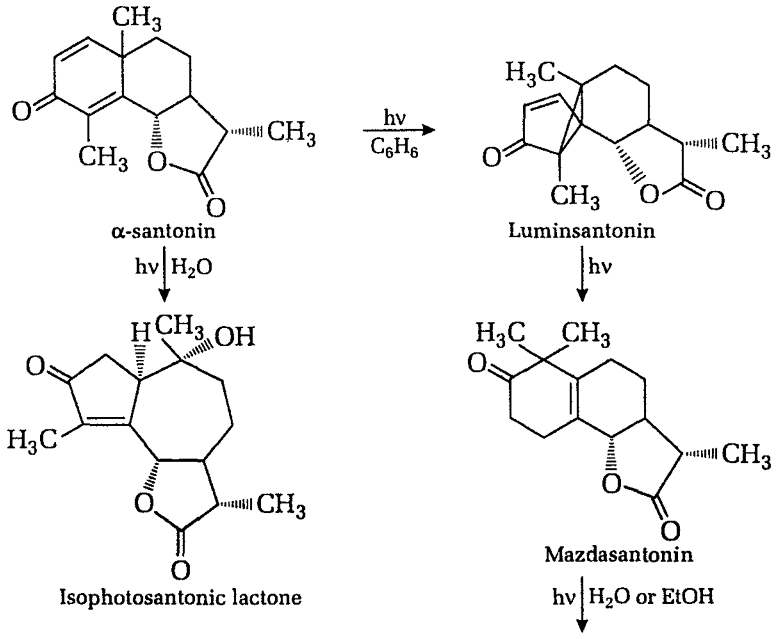
The reactive excited state of dienone is $n \rightarrow \pi^*$ triplet state. The excited cyclohexadienones undergo rearrangement reactions. The rearrangement has been extensively studied for 4, 4- diphenylcyclohexa-2, 5-dienone.

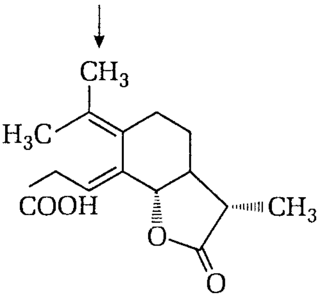




For the rearrangement of 4, 4-diphenyl cyclohexa-2, 5-dienone, the suggested mechanism involves $C_3 - C_5$ bonding from the excited triplet state (3). An examination of the molecular orbitals of the $n - \pi$ * triplet state of the dienone indicates that an increase in $C_3 - C_5$ bonding results from electron occupying the lowest π^*-molecular orbital. In this mechanism, the excitation energy gained in going from the ground state (1), to the excited triplet state (3), is lost after $C_3 - C_5$ bonding (4), to give the Zwitterion (5), which subsequently rearranges to the product 6, 6-diphenyl bicyclo [3.1.0] hex 3-en-2-one (6). The product (6) is itself photochemically labile and undergoes further rearrangement as shown above.

The first photochemical reaction of a cyclohexadienone chromophore in santonin was noted. α-Santonin undergoes photochemical rearrangement in an non-nucleophilic media to give the cyclopropyl ketone lumisantonin, which is itself photochemically labile and yields the linearly conjugated dienone mazdasantonin.

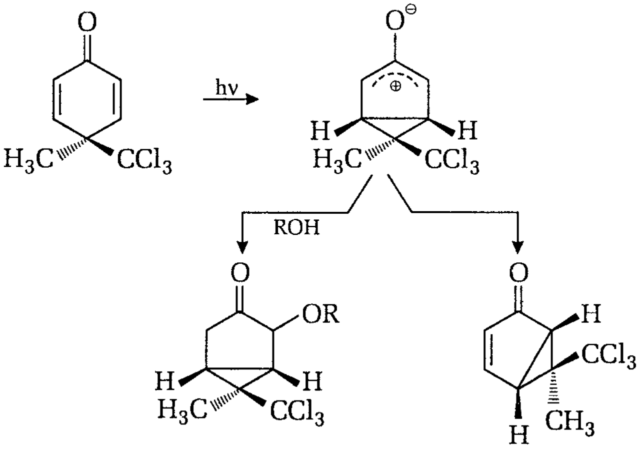




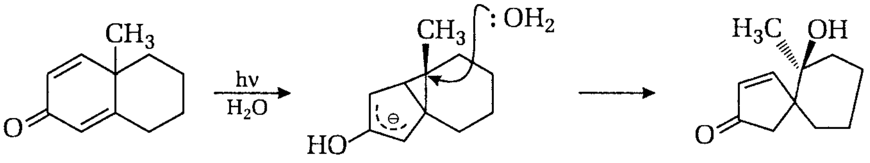
Acid derivative

Upon photolysis in nucleophilic media, like water or ethanol, mazdazantonin gives the ring cleaved acid or ester derivative while α-santonin when photolysed in water gives isophotosantonic Lactone.

The photolysis of mentioned dienone support the proposed mechanism.

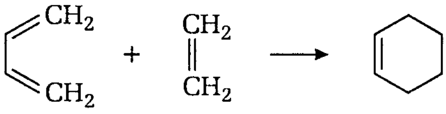


Photolysis in aqueous acid media causes the reaction to take a different course. The initially formed cyclopropyl Zwitterion is protonated and then cleavage of the three membered ring gives hydroxyalkene.



6.9 INTERMOLECULAR CYCLOADDITION REACTIONS

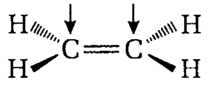
Cycloaddition reactions are one of the most important organic chemical reactions. Diel's-Alder reaction, is the most popular example of cycloaddition reaction and known to every serious student of organic chemistry. Cycloaddition provides route to synthesise cyclic compounds from acyclic reactants.



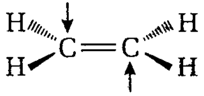
Classification

Cycloaddition reactions are classified with respect to three facts :

(i) Number of electrons participatating in the cycloaddition reaction.
(ii) The nature of the orbitals undergoing change (π or σ).
(iii) The stereochemical mode of cycloaddition (supra/antara).



Supra



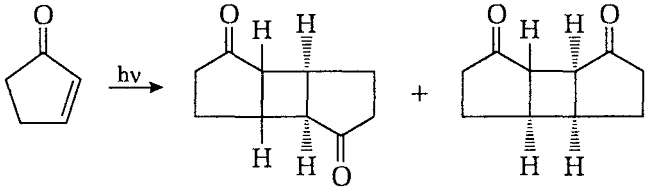
Antara

Photochemical cycloaddition process of carbonyl compounds are studied under two categories :

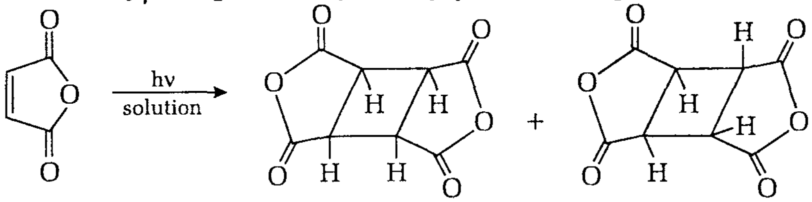
1. When both of reactants are same, *i.e.*, dimerisation reactions.
2. When one reactant is electronically excited ketone and other is ground state alkene-Oxetane formation.

6.10 PHOTODIMERISATION OF CARBONYL COMPOUNDS

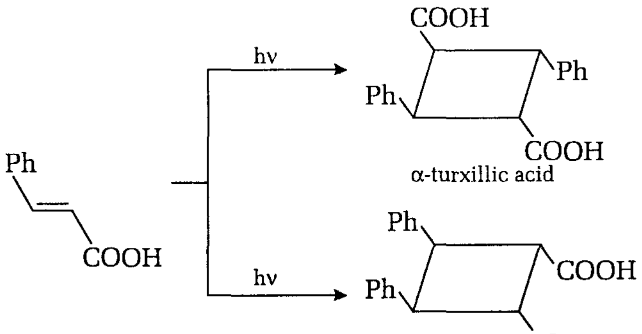
The $[\pi^2 s+\pi^2 s]$ photodimerisation reactions proceeds via involvement of 2π-electrons from each enone. These two π-bonds converted into intermolecular σ-bonds. The photodimerisation of cyclopentenone is an example of $[\pi^2 s+\pi^2 s]$ cycloaddition.



Maleic anhydride give same $[\pi^2 +\pi^2]$ cycloaddition photodimerisation.



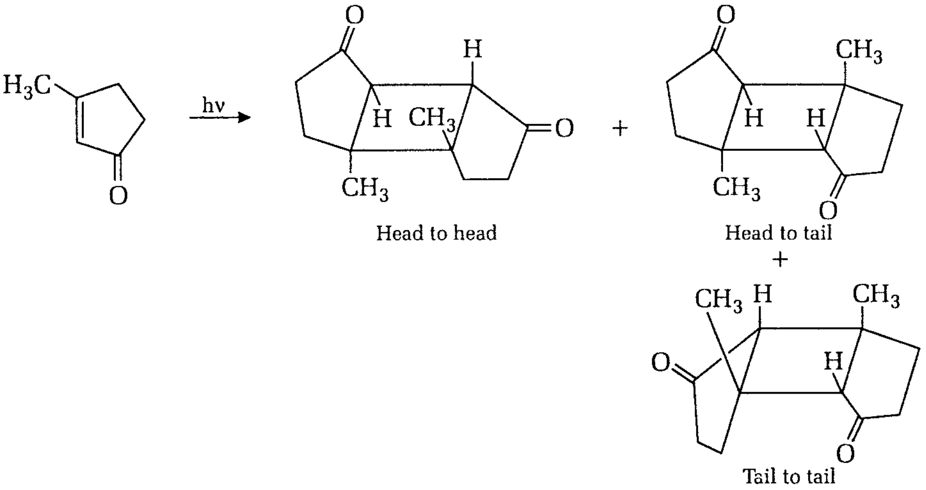
3-phenyl prop-2-en-1-oic acid give dimers α-Turxillic acid and β-turxillic acid on $[\pi^2 +\pi^2]$ photocycloaddition.

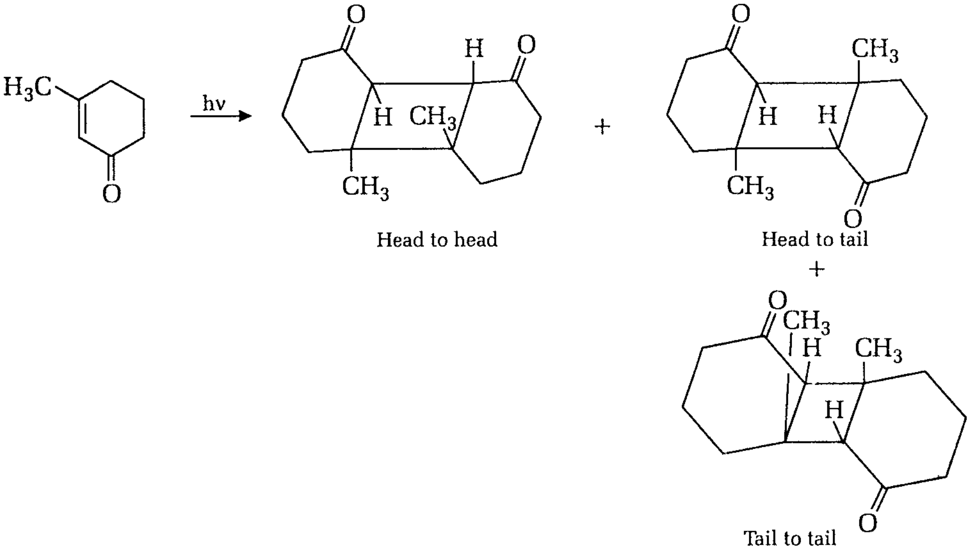


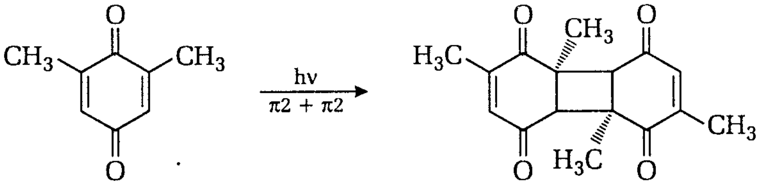
α-turxillic acid

β-turxillic acid

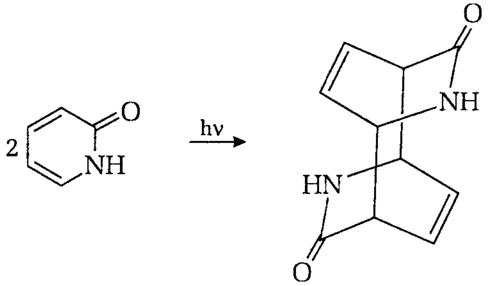
The photochemical dimerisation of α, β-unsaturated ketones provides a further class of $[\pi^2 + \pi^2]$ cycloaddition and is demonstrated for 3-methylcyclopent-2-enone and 3-methylcyclohex-2-enone, with the formation of head to head dimers and head to tail dimers. The α, β-unsaturated enone absorbs light of wavelength 300 nm and get n, π * excitation. The reaction is believed to occur from triplet state because ISC is efficient. While π, π * triplet excited enone also cause dimerisation.



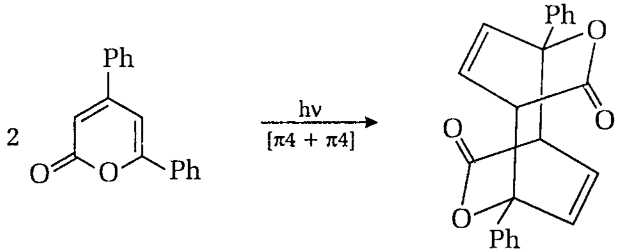




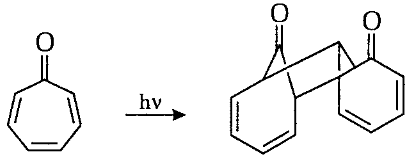
2-pyridones are known to undergo photodimerisation through $[\pi^4 s+\pi^4 s]$ cycloaddition.



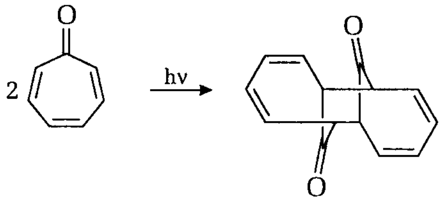
4, 6-diphenyl-α-pyrone also undergo $[\pi^4+\pi^4]$ cycloaddition and yields anti-dimer as the sole product. It undergoes photocyclisation in the solid state.



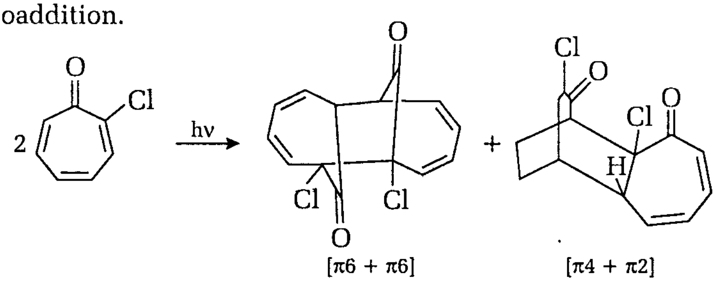
The $[\pi^6+\pi^2]$ photocycloaddition has also been reported in carbonyl compounds. The photolysis of tropone gives photodimerisation through $[\pi^6+\pi^2]$ cycloaddition.



Irradiation of a dilute acid solution of tropone gives a dimer resulting from an allowed $[\pi^6+\pi^6]$ cycloaddition.

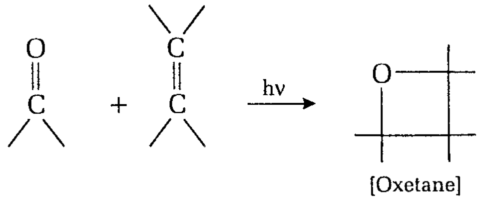


2-chlorotropone gives $[\pi^6+\pi^6]$ dimer as well as $[\pi^4+\pi^2]$ dimer on photocycloaddition.



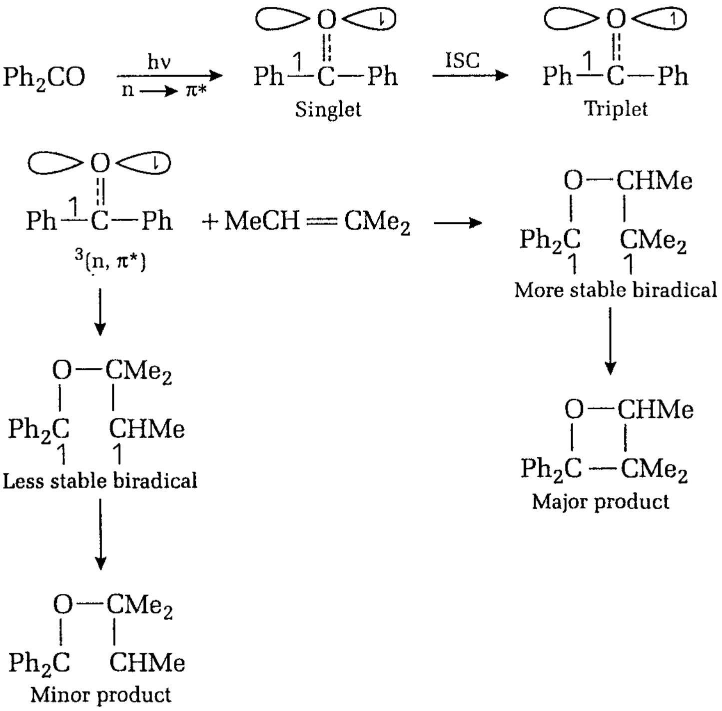
6.11 OXETANE FORMATION

In the presence of a olefin, photo excited ketone add to it and yields oxetane, the reaction is known as Paterno Büchi reaction.



This addition takes place by the absorption of light in the region of absorption of carbonyl group, hence it takes place by the excitation of carbonyl group rather than that of olefinic bond.

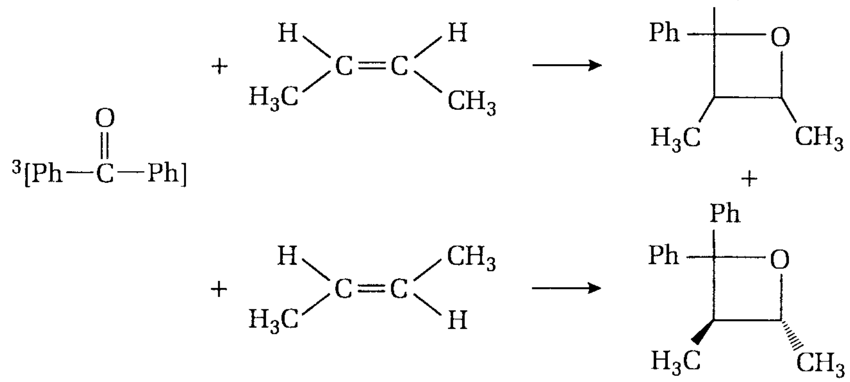
The reaction is initiated by low-lying n, π^* state. Most of the Paterno-Büchi reactions are reported to involve $^3(n, \pi^*)$ ketones. In some conjugated ketones it is difficults to distinguish between n, π^* and π, π^* transitions. Evidence support reactions by both of the transition states in conjugated ketones. It is assumed that the radical like oxygen atom of (n, π^*) ketone adds to the olefin to give preferentially the most stable biradical intermediate. In the addition of $^3(n, \pi^*)$ benzophenone to trimethylethylene the element of choice lies between a secondary radical and a tertiary radical, since both are same in other respects the tertiary radical is more stable and this mode of addition is preferred.



The biradical hypothesis is helpful in predicting the major product in Paterno-Büchi reaction. It is proposed that the reaction involves an exciplex (a complex of excited ketone and olefin), that break to the biradical.

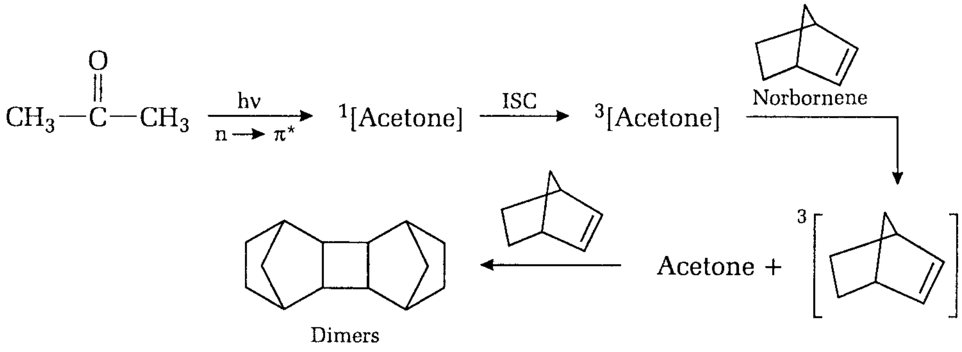
$$\begin{tikzcd}
\text{Ketone} \arrow[r, "h\nu"] & {}^{1}[\text{Ketone}] \arrow[r, "\text{ISC}", "\text{or sensitised}"'] & {}^{3}[\text{ketone}] \arrow[d, shift left, "\text{olefin}"] \\
\text{Oxetane} & \text{biradical} \arrow[l] \arrow[d] & \text{exciplex} \arrow[l] \arrow[u, shift left] \\
 & \text{Ketone + olefin} &
\end{tikzcd}$$

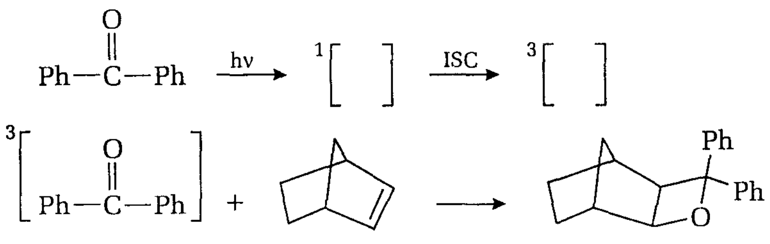
The biradical is a situation dependent intermediate because addition of ${}^{3}(n, \pi^{*})$ benzophenone to *cis*- and *trans*-2-butene gives the same mixture of adducts in each case.



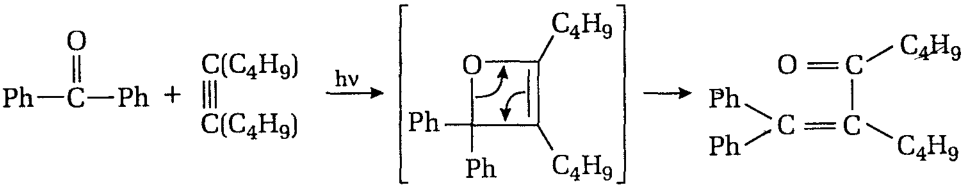
Two side reactions can limit the utility of the Paterno- Biichi reaction. The presence of active hydrogen [allylic hydrogen atom] on the olefin makes hydrogen abstraction by excited ketone which complete with Paterno-Biichi reaction. If the triplet energy of ketone is comparable to the triplet excitation energy of olefin, energy transfer will compete with the reaction.

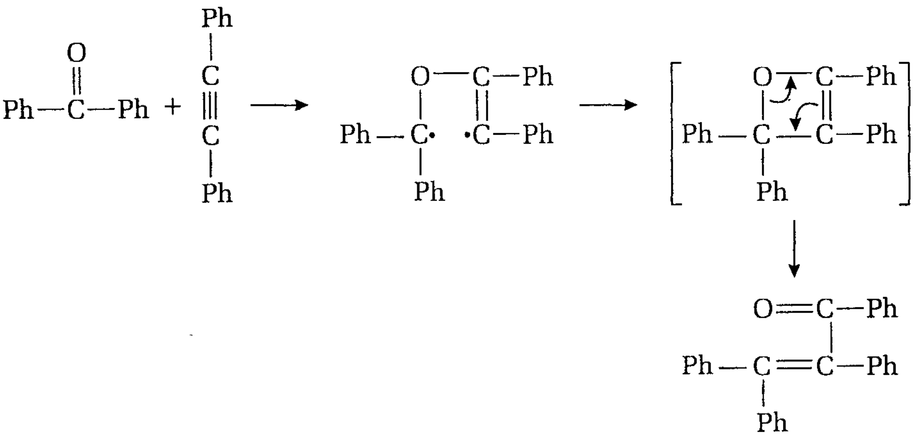
Acetone has triplet excitation energy comparable with the triplet energy of norborene. Therefore acetone acts as triplet sensitiser. Triplet excited norbornene produces dimes, while acetophenone do not act as triplet sensitiser and ordinary Paterno-Biichi reaction is observed. Therefore triplet excited benzophenone adds to norbornene.





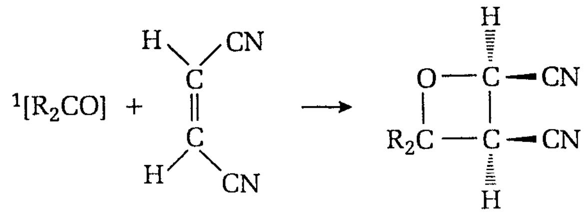
When acetylene is used in place of olefin, the initial adducts are assumed to be oxetenes, but only products isolated are α, β-unsaturated ketones.



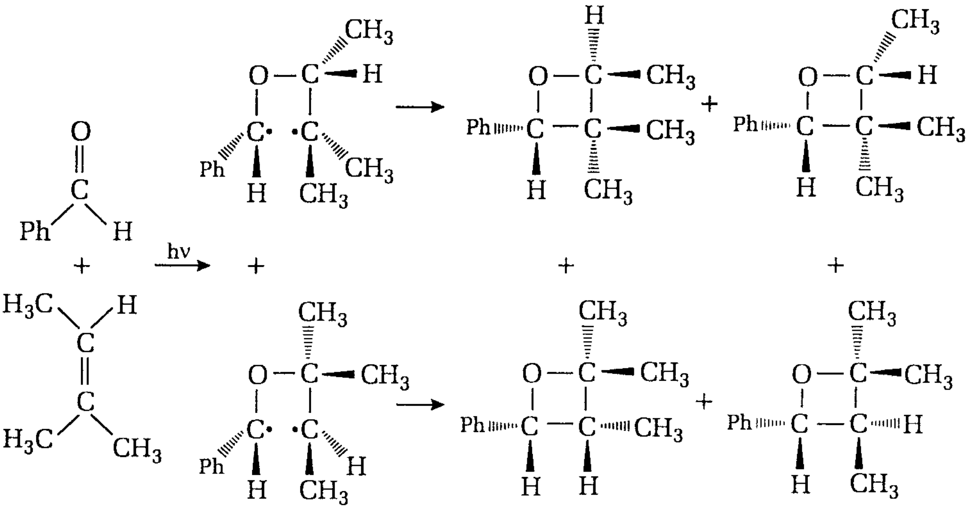


Oxetane formation from ${}^1(n, \pi^*)$ have also been reported. The reaction differs from the usual Paterno-Büchi reaction because the olefin is highly electronegatively substituted.

$$R_2CO \xrightarrow{h\nu} {}^1[R_2CO]$$



When benzaldehyde is irradiated in the presence of 2-methyl but-2-ene, four possible stereoisomeric oxetanes are formed.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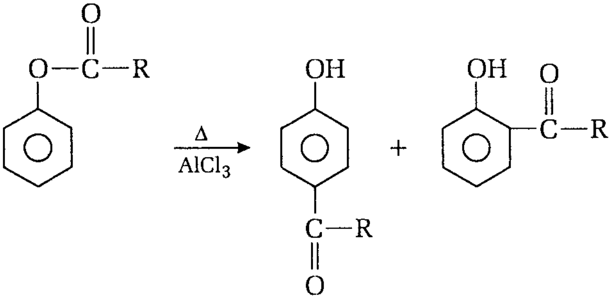
UNIT

7

MISCELLANEOUS PHOTOCHEMICAL REACTIONS

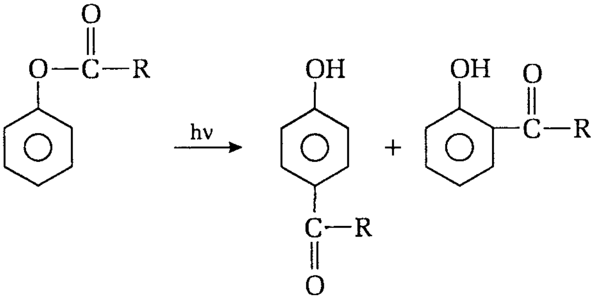
7.1 PHOTO-FRIES REARRANGEMENT

Phenolic esters can be rearranged into both *o*- and *p*-acyl phenols. This rearrangement could be carried out by heating the phenolic esters in presence of Friedel-crafts catalyst. This synthetically useful reaction is known as Fries rearrangement.

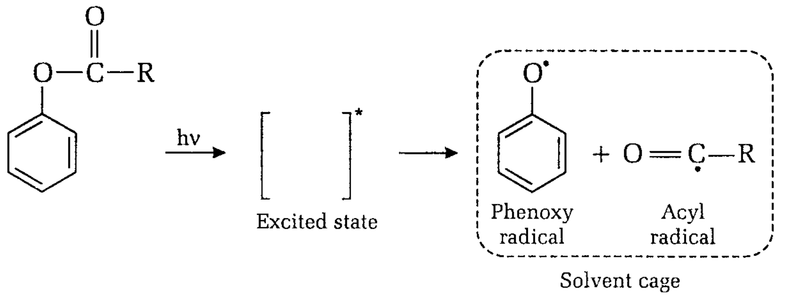


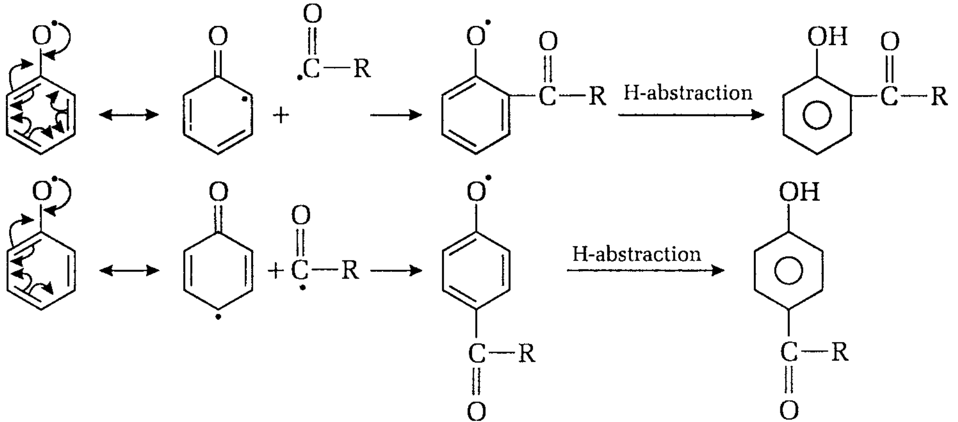
The Fries rearrangement can be carried out with UV light, in the absence of catalyst. This process is known as photo-Fries rearrangement.

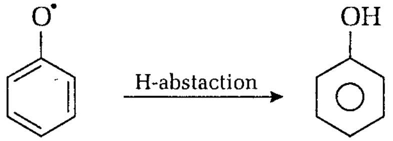
Photo-Fries rearrangement is an intramolecular free-radical process. Both *ortho*- and *para*-migrations of acyl group are reported on irradiation.



Evidences suggest that, in this rearrangement, the substrates dissociates into phenoxy and acyl radicals, which recombine within the solvent cage to give both the products. The phenol is always a side product, resulting from some phenoxy radical that leaks from solvent cage and abstract a hydrogen atom from a neighboring molecule. The mechanism is illustrated below :

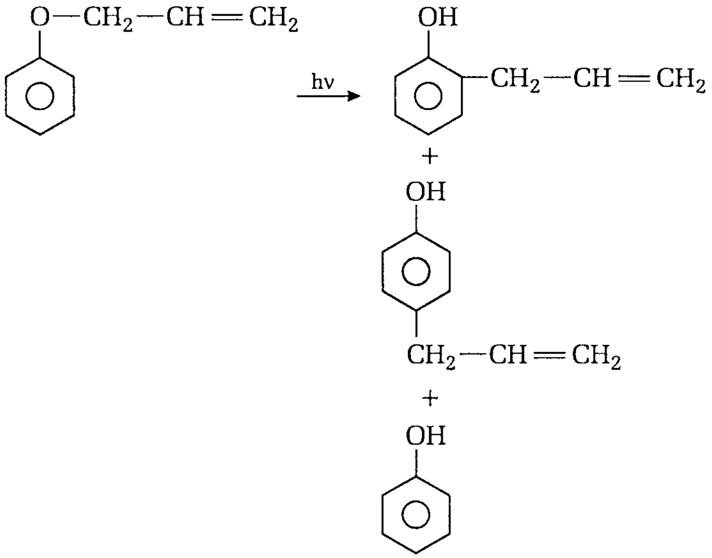






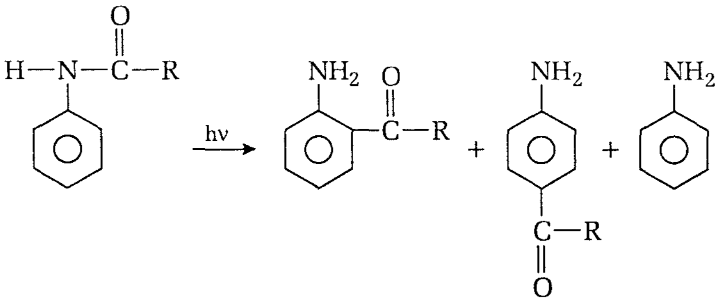
The idea of solvent cage is preferred because when the same reaction is carried out in gaseous phase, only phenol is formed.

Phenyl allyl ethers also give same rearrangement an photolysis.



7.2 PHOTO-FRIES REACTION OF ANILIDES

Photo-Fries rearrangement of anilides obeys the same mechanism as photo-Fries rearrangement of phenyl esters. The only difference is the replacement of bridging oxygen by Nitrogen.

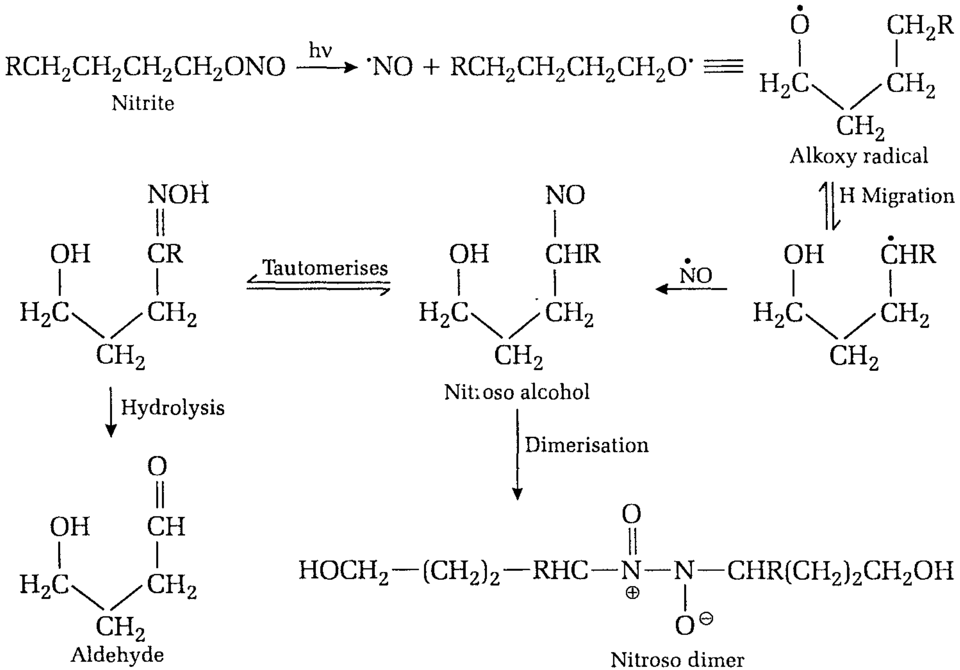


7.3 BARTON REACTION

Irradiation at wavelength greater than 330 nm, causes homolytic cleavage of O—NO bond of the nitrite to nitric oxide and alkoxy radical.

$$R—O—NO \xrightarrow{h\nu} R—O^{\bullet} + {}^{\bullet}NO$$

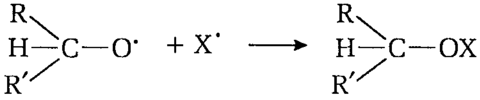
The nitric oxide generated in the photolytic step can recombine with the new allyl radical to produce a nitroso alcohol which can dimerise in presence of protic solvents and also forms an oxime [Scheme-1]. The reaction involving migration of nitric oxide is known as Barton reaction.



Scheme 1.

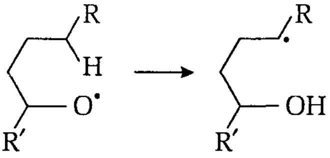
The nitric oxide and alkoxy radical formed on photolysis can undergo one of the following reactions :

(a) Radical recombination

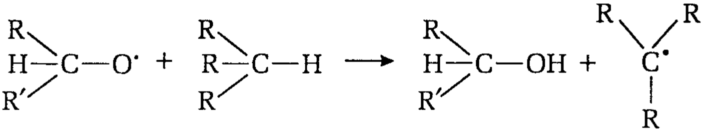


$$\mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}O^{\bullet}} + \mathrm{X^{\bullet}} \longrightarrow \mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}OX}$$

(b) The intermolecular Hydrogen abstraction takes place when γ-Hydrogen present.

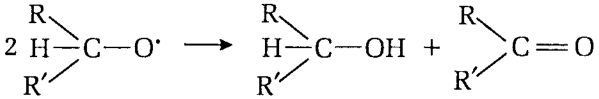


(c) Intermolecular Hydrogen abstraction



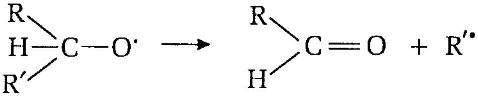
$$\mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}O^{\bullet}} + \mathrm{R{-}\overset{R}{\underset{R}{C}}{-}H} \longrightarrow \mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}OH} + \mathrm{\overset{R\;\;R}{\underset{R}{C^{\bullet}}}}$$

(d) Disproportion



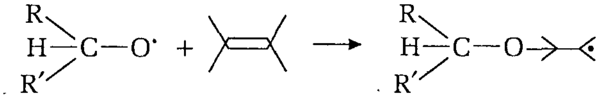
$$2\,\mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}O^{\bullet}} \longrightarrow \mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}OH} + \mathrm{\overset{R}{\underset{R'}{>}}C{=}O}$$

(e) Radical elimination



$$\mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}O^{\bullet}} \longrightarrow \mathrm{\overset{R}{\underset{H}{>}}C{=}O} + \mathrm{R'^{\bullet}}$$

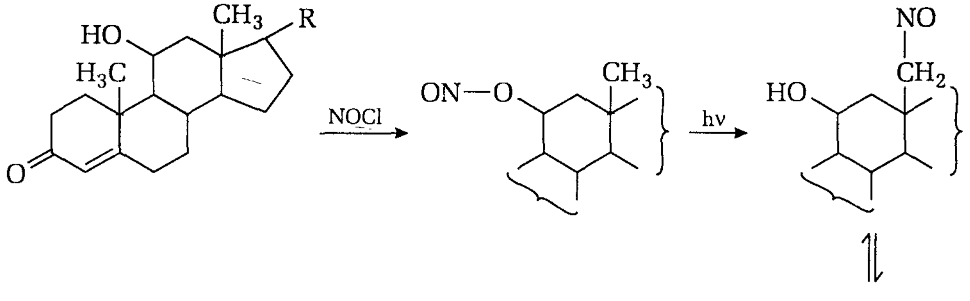
(f) Alkene addition.

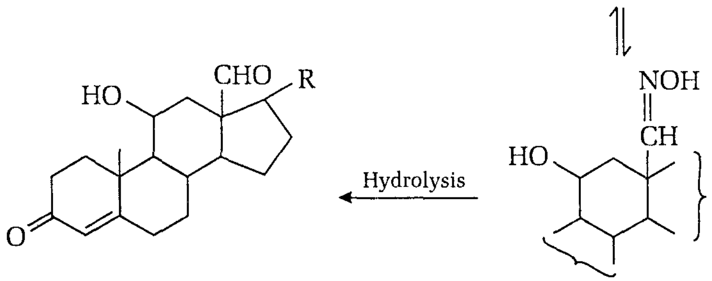


$$\mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}O^{\bullet}} + \mathrm{>C{=}C<} \longrightarrow \mathrm{H{-}\overset{R}{\underset{R'}{C}}{-}O{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}}$$

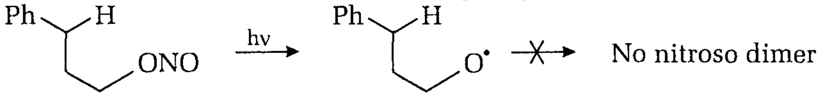
It provides a useful procedure for effecting substitution γ to an oxygen function. Provided there is a suitably positioned hydrogen atom the reaction is general for primary and secondary aliphatic nitrites. Thermally generated alkoxy radicals do not posses sufficient energy to abstract such a hydrogen and therefore do not undergo this reaction.

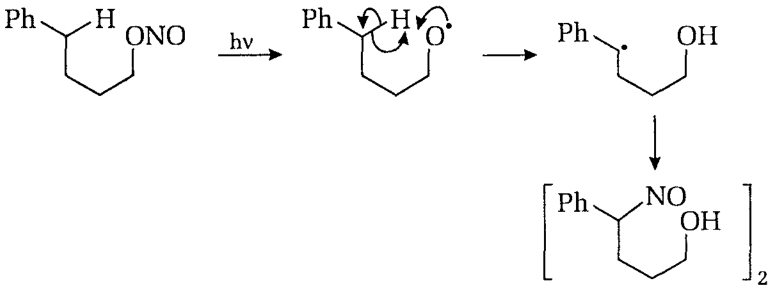
By the Barton reaction a methyl group in the δ-position to an Hydroxyl group can be oxidized to a —CHO group.

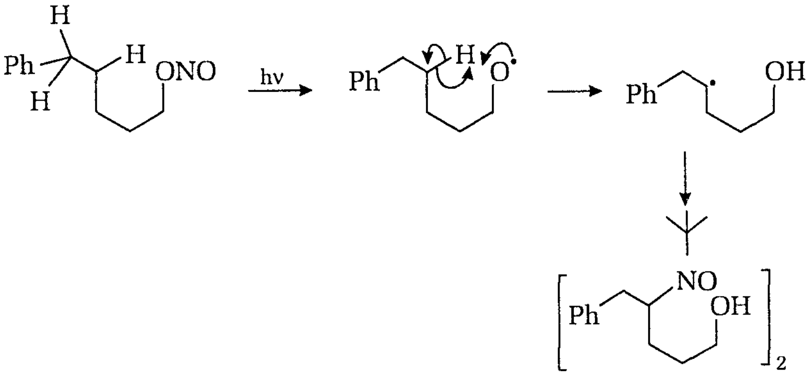




Like Norrish type I reaction, the intermolecular 1, 5-hydrogen transfer to alkoxy radical involves a six membered cyclic transition state structure, as demonstrated by the photolysis of series of ω-phenylalkyl nitrites.

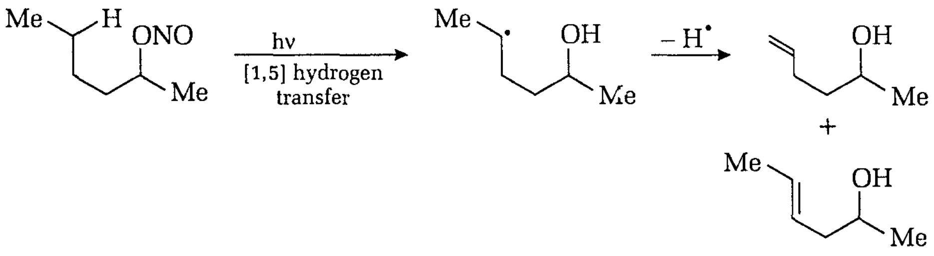




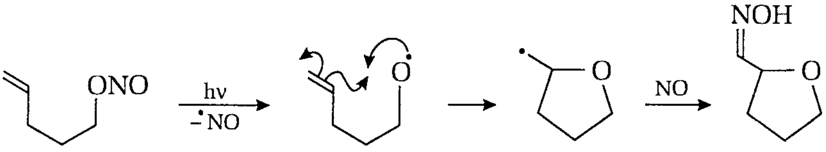


The propyl and pentyl nitrites are expected to transfer a benzylic hydrogen to the alkoxy radical through a five- and a seven-membered cyclic transition state but only 1, 5-Hydrogen transfer is observed.

Hexan-2-ol nitrite is converted into a mixture of unsaturated alcohols on photolysis. Here radical recombination is protected by copper(II) acetate.



A further variation to the reaction can occur with γ, δ-unsaturated nitrites whereupon radical ring closure produces a tetrahydrofuranyl derivative.



7.4 SINGLET MOLECULAR OXYGEN REACTION

It is known that photochemistry is the study of chemical changes produced by electronically excited species. Most of the photochemical transformations come from triplet excited state, due to its higher life-time. But oxygen molecule is a rare case, its ground state is a triplet while reactive state is electronically excited singlet state. The life time of electronically excited triplet state is relatively low, so significantly populated is singlet excited state.

II	Excited state	$\overset{\uparrow\quad\uparrow}{O{-}O}$	Triplet
I	Excited state	$\overset{\uparrow\quad\downarrow}{O{-}O}$	Singlet
	Ground state	$O\overset{\uparrow\uparrow}{=}O$	Triplet

The first excited state of electronically promoted molecular oxygen behave as an electrophile since it has two paired electrons while second excited state behave like radical. The singlet excited state of oxygen molecule is most stable state. Most of the photooxygenation reactions are shown by the singlet molecular oxygen.

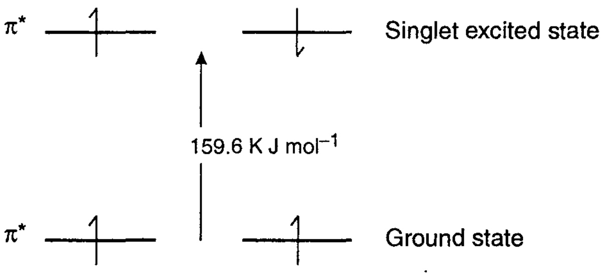
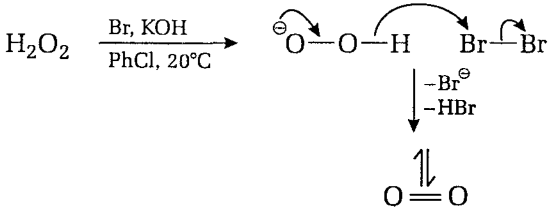


Fig. 7.1. Electronic states of oxygen molecules.

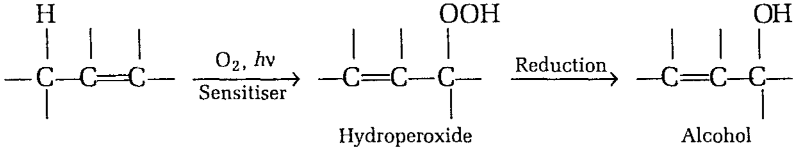
The most acceptable method for the generation of singlet molecular oxygen, is the direct irradiation of oxygen molecule in presence of a sensitiser. The photoexcitation of ground state molecule is carried out in the reaction mixture.



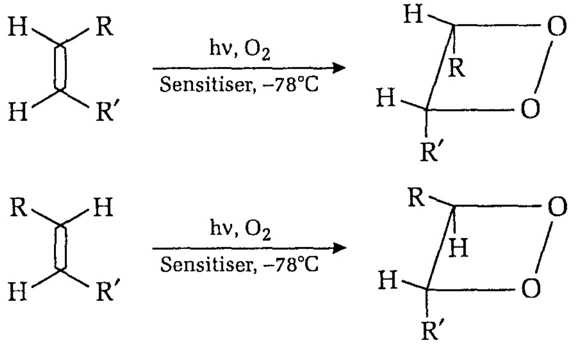
Another method for the generation of excited singlet molecular oxygen is by the oxidation of hydrogen peroxide with other oxidants like sodium hypochloride, alkaline solution of bromide or alkaline solution of peracids as given above.

Oxidation caused by singlet molecular oxygen is known as photosensitised oxygenation or photochemical oxygenation. The photo-oxygenation is not similar for all substances and is affected by the use of sensitiser or altering reaction conditions. It is well understood by the following examples :

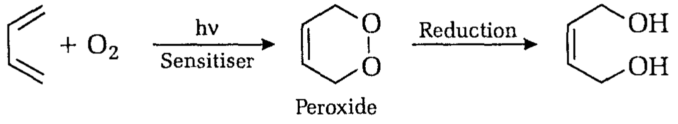
Singlet molecular oxygen reacts with alkenes to give hydroperoxides, which can be further convert into alcohol or corresponding ethers depending on situation. The reaction is carried out by the irradiation of alkene and oxygen with a sensitizer like chlorophyll or a dye.



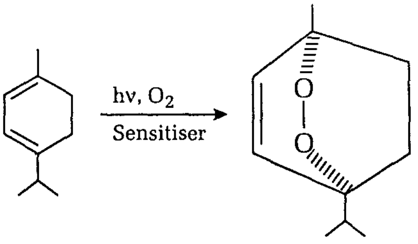
The activated alkenes not have acidic allylic hydrogen atom, to undergo addition with singlet oxygen on photolysis, with the formation of dioxetanes. The addition is stereospecific.



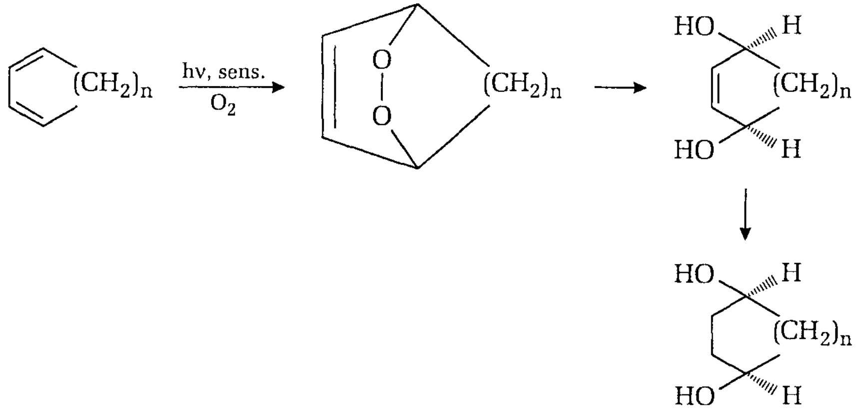
The photo-oxygenation of conjugated dienes provides a route to cycloperoxides, which may be further reduced. The reaction is same as photo-oxygenation of alkenes.



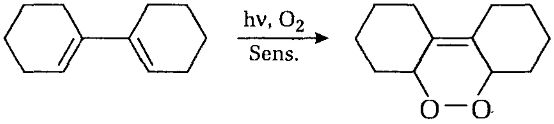
The formation of cyclic 1, 4-peroxides (endoperoxides), by the sensitised photo- oxygenation of cisoid 1, 3- dienes is well established.



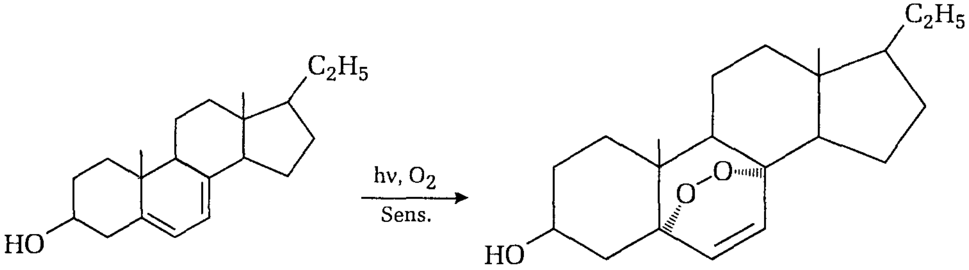
The carbocyclic dienes afford isolable endoperoxides which are easily reduced to unsaturated or saturate 1, 4-diols.



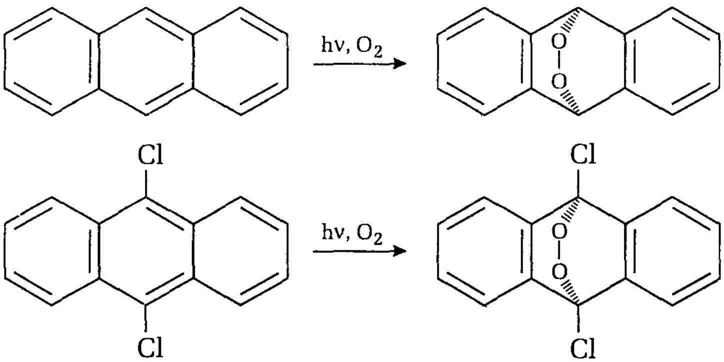
Cycloaddition of oxygen is not confined to monocyclic cisoid dienes, bicyclohexenyl diene also undergoes cycloaddition to give tricyclic peroxides.



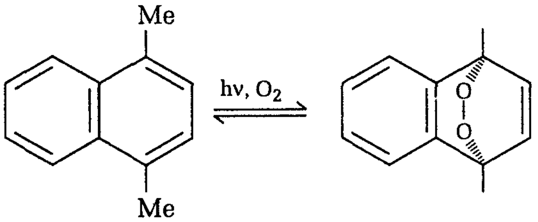
Steroidal dienes undergoes stereospecific photo-oxygenation, the endoperoxide being formed by the addition of molecular singlet oxygen to the least hindered face of molecule.



Aromatic systems gives very effective photo-oxygenation with excited singlet oxygen molecule and undergo direct photo-oxygenation, without any need of sensitiser. Anthracene gives 9, 10- endoperoxide without any sensitiser.



Endoperoxide formation from naphthalene derivatives has also been observed but the product have limited stability and undergoes retro-Diels-Alder reaction.



Poly methoxy benzenes and N, N-dimethylanilines on photo-oxygenation yields initial endoperoxides, but non-benzenoid peroxide has yet been isolated.

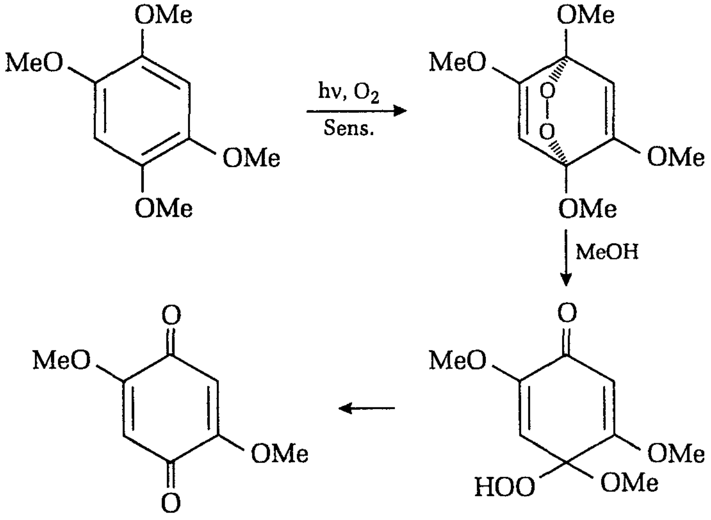
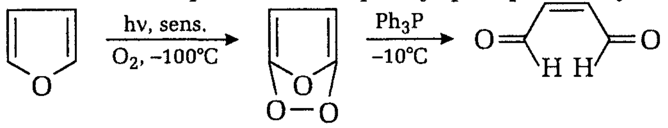
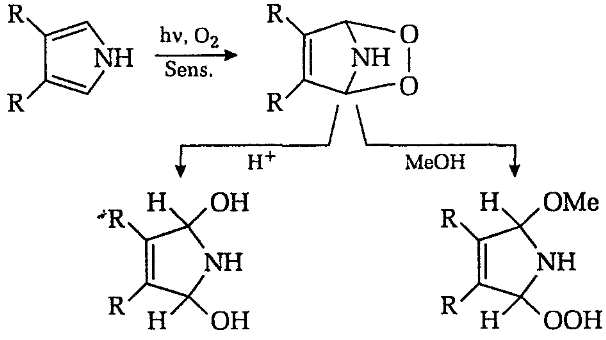
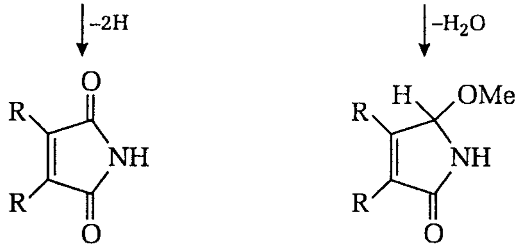


Photo-oxygenation of furan gives the ozonide which decomposes explosively at –10°C, in the presence of triphenyl phosphine to yield butendial.

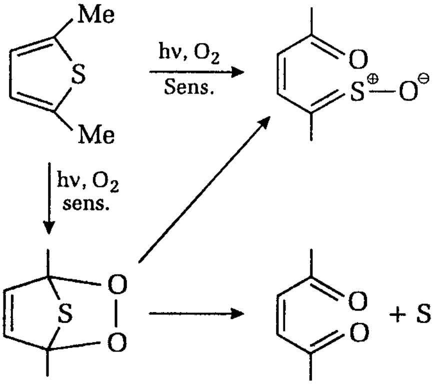


The sensitivity of pyrrole towards singlet molecular oxygen is well known. The first step of oxygenation is the formation of endoperoxide, but this peroxide is yet to be isolated.

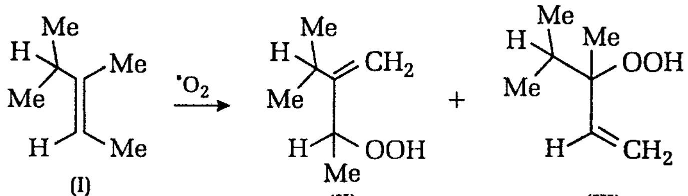




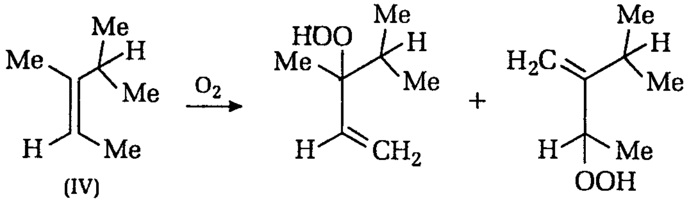
But photo-oxygenation of thiophenes yields analogous situation.



Apart from high stereo selectivity, the reaction also demonstrates a high and unusual regioselectivity. The reaction of alkene (I) with singlet oxygen yield equal amount of (II) and (III), resulting from hydrogen abstraction from the *cis*-methyl functionalities. But *trans*-compound (IV) behaves differently.



(I) (II) (III)

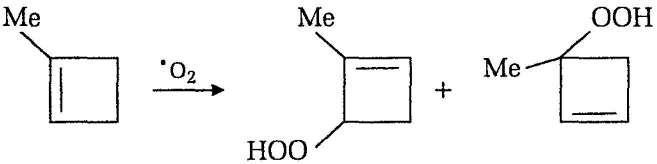


(IV)

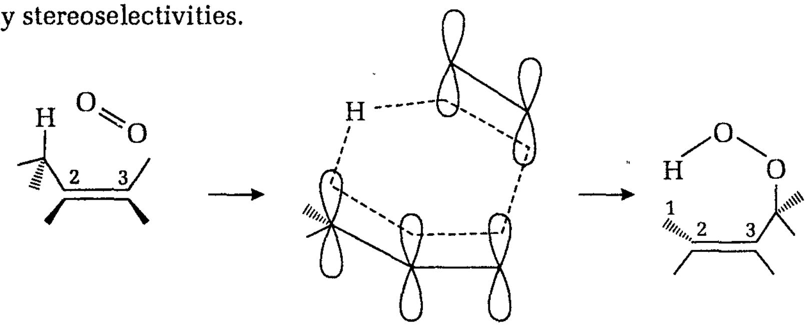
The photo-oxygenation of organic compounds has generated a successful wave for a number of synthetically important compounds, which is not possible by ordinary dark reactions.

Mechanism

The methyl cyclobutene on photo-oxygenation gives regioselective products.



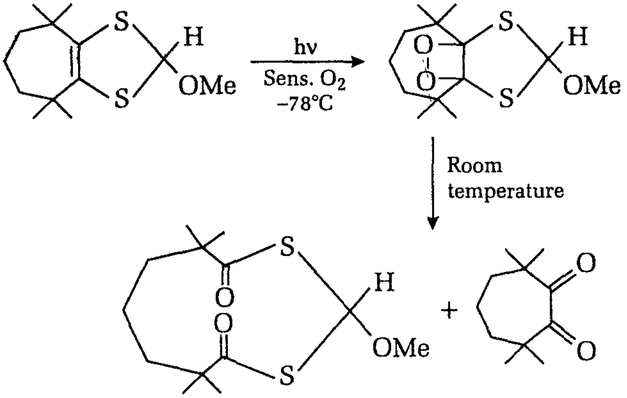
These hydroperoxide forming reactions proceed with a very low activation energies, usually below 20 kJ mol^{-1}. Those mechanism are favoured which satisfiy stereoselectivities.



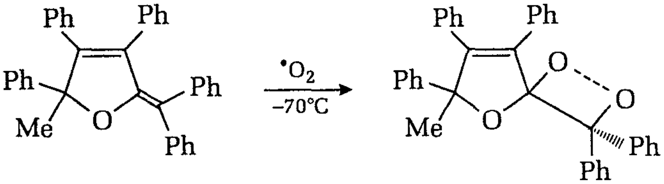
Ene mechanism

Some more examples :

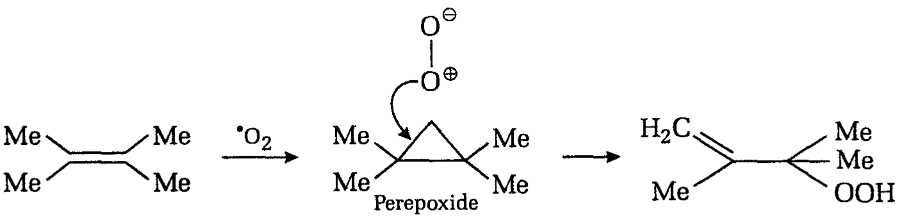
1. Thiophene reacts with singlet molecular oxygen



2. Furan derivatives gives



3. Substituted alkene gives peroxide through perepoxide intermediate.



7.5 PHOTOCHEMICAL FORMATION OF SMOG

In metropolitan cities, with a lot of industries of different kinds and dense automobile traffic, the atmosphere is polluted by the smoke coming out from the chimneys of the factories and exhaust of the petroleum fuel driven automobiles. Smog is the combination of smoke and fog, which undergoes a lot of photochemical changes. The photochemical smog so formed, have high concentration of ozone and nitrogen dioxide.

Smoke is the mixture of unsaturated hydrocarbons, Nitrogen oxides and some sulphur compounds. In the early morning, atmospheric Nitrogen oxide concentration is high but, after sun-rise. Nitrogen oxide disappears and Nitrogen dioxide appears. Photochemical reaction between Nitrogen oxide and ozone gives Nitrogen dioxide.

$$NO + O_3 \longrightarrow NO_2 + O_2$$

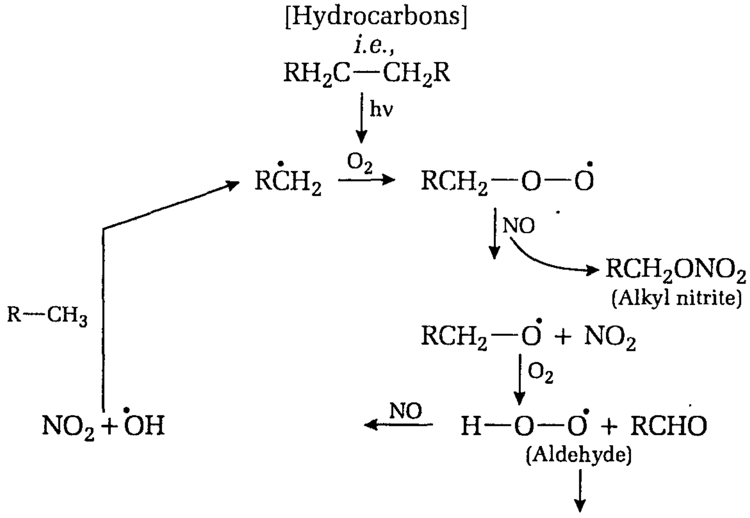
This reaction makes depletion of ozone which is regenerated by the reaction with O-atoms.

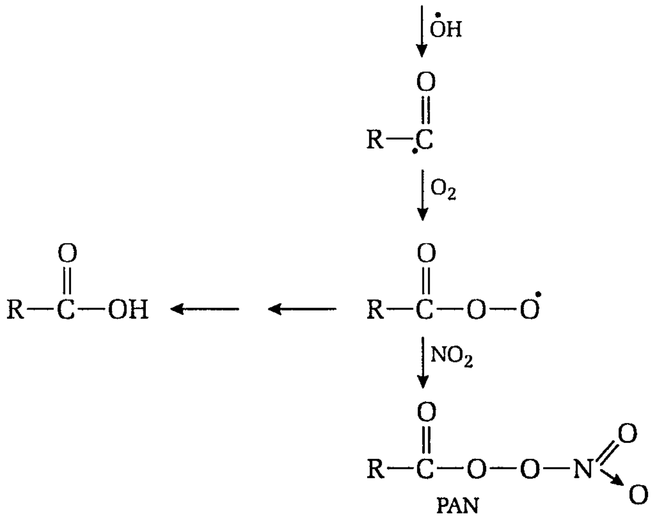
$$O + O_2 \xrightarrow{M} O_3 \qquad \{\text{M- moderator}\}$$

Hydrocarbons and other organic compounds in the atmosphere are assumed to oxidize through a series of steps of photochemical reactions. They do not react directly with sun-light, but react with photochemically formed species. The hydrocarbons identified in atmosphere are methane, ethane, ethene, ethylene, propane, *n*-butane, isopentane, etc. Hydrocarbons are removed from the atmosphere by several chemical and photochemical reactions. For instance, oxidation, to convert them into CO_2, acids and aldehydes are formed.

The automobile pollutants in the atmosphere are exposed to intense sunlight, which yields photochemical oxidants. This phenomenon give rise to photochemical smog. Three specific eye irritants have been already identified in the photochemical smog—Formaldehyde, acrolein and peroxyactyl nitrate (PAN). The possible reaction sequence is as follows :

Mechanism of Smog Formation :





Effects of Smog

There are certain serious bad-effects of smog on human-life, which are already recognized and mentioned below :

(i) Peroxy acyl nitrate (PAN) is photochemically produced in atmosphere, which is phototoxic substance and effects plants, heabs and Trees. PAN with acrolein and formaldehyde are specific eye-irritant.

(ii) Smog contains oxidants, which damage rubber and other polymers.

(iii) Smog reduces the human visibility.

(iv) Smog causes respiratory disorders.

7.6 PHOTOCHEMICAL DEGRADATION OF POLYMERS

In nintees, the white cloths used to get yelloish after few washes. The washerman was blamed that he did not washes cloths properly. But after some time, the cause was identified. It was due to **photodegradation of cloth fibers.** Photodegradation of polymers has two contrary features, beneficial as well as non-beneficial.

(i) UV and visible radiation are harmful to synthetic as well as natural polymers. The photodegradation of synthetic polymers reduces its life-time. Radiation are harmful to bio-polymers like, DNA, poly seccharides, proteins etc. Their photolysis produces a number of disorders.

(ii) More and more use of synthetic plastics and other polymers in everyday life has created a problem of disposal. The one of the cheapest and natural way is their photodegradation.

The photochemical degradation can occur in two ways after photo-initiation :

(a) Homolytic cleavage : The homolytic cleavage may lead to elimination at weaker bond, after photo- initiation.

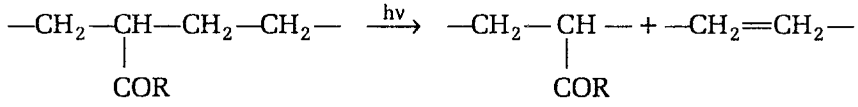
(b) **Heterolytic cleavage :** The heterolytic cleavage leads to formation of ions. The energy needed for weaker bond may be directly absorbed or achieved by intramolecular energy transfer.

The polymers are converted into photo-stable units through photodegradation.

Due to the exposure of polymers to UV-visible radiation, especially in the presence of atmospheric oxygen, most of the organic polymers undergo photodegradation. This chemical change brings a decrease in mechanical properties of the bulk of polymer. In some contexts, durability is the necessary factor, like in building and automobile industries. Photo stabilisation is desirable in order to extend the life-time of the material. On the other hand, the persistence of plastics and plastic packaging materials after disposal has gained environmental concern. Therefore efforts are made to make thes polymers light sensitive.

The photo-degradation process involves a light initiated auto-oxidation process. The reduction in photodegradation process can be achieved by reducing the rate of initiation or propagation of chain reaction or by increasing chain termination. The rate of initiation can be reduced by the reduction of residual impurities while propagation can be reduced by protection from atmospheric oxygen. The rate of initiation can also be reduced by the protection of polymer material from light. Photodegradation is confined to the polymer surface. The use of white oxides of zinc and titanium makes the reflection of light. In order to prevent the relatively long- lived triplet carbonyl compounds which partcipitate into secondary photoinitiation, quenchers may be used.

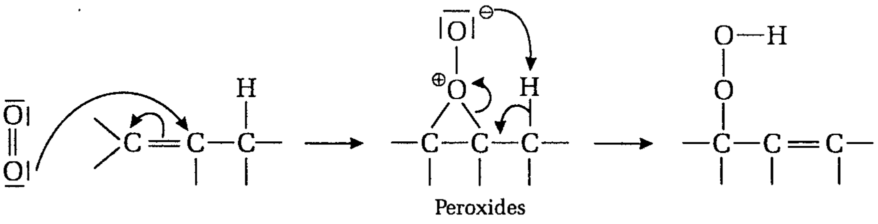
In order to manufacture environmental friendly qualities of polymers, a photo-active group may be introduced into the polymer. For example, light sensitive polymers are obtained by the co- polymerisation of ketonic species with hydrocarbons. The photodegradation of resulting polymeric material involves. Norrish type II process of the polymer chain rather than a radical mediated photo-oxidation.



$$-CH_2-\underset{\substack{|\\ COR}}{CH}-CH_2-CH_2- \xrightarrow{h\nu} -CH_2-\underset{\substack{|\\ COR}}{CH}- + -CH_2{=}CH_2-$$

Photodisposal of agricultural film or packaging should undergo a sharp and controlable degradation initiated by exposure to UV light.

The another use of photodegradation is to use sunny hours, because sun-light damage the DNA sequence. Due to this fact bacteria when exposed to light get damaged.



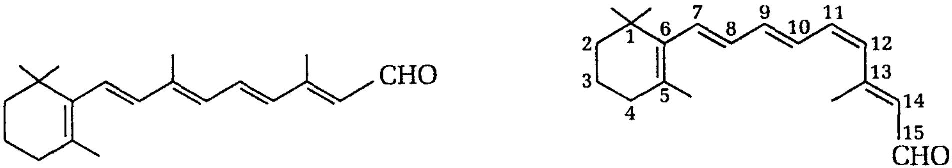
7.7 PHOTOCHEMISTRY OF VISION

"The most precious gift given by GOD is vision". Scientifically, eye is a bio-organic instrument which is able to convert radiation energy [visible region of electromagnetic radiation] into chemical energy then into electrical energy. The procedure of vision starts with the absorption of photon [Radiation particle], followed by isomerisation (chemical change) which creates electrical pulses, neurons conduct these pulses to brain where brain read it.

A lot of research has been done in recent time targeting photochemistry of vision. The eye is an extraordinary instrument, sensitive within visible region [400 nm to 800 nm]. The sensitivity can be understood by the fact that a fully darken eye can clearly detect object in light so dim that only 10,000 quanta absorbed per second by retina, that is one quanta per three minutes to receptor cell on the retina.

Eye is a system of lens and retina. There are two types of light sensitive cells are found in retina, known as RODS and CONES. Both the cells act as receptor of photon. The rods have been found highly sensitive and functioning at low light intensity. Hence rods are responsible for vision in dim light. While cones are low sensitive and work as colour selector. The cones are more is number than rods and responsible for detail colour vision in good light. Central part of visual field in retina are made up only of cones while sides by rods.

The photosensitive compounds present in Human and most other mammals are two proteins-opsin and retinal. Out of these two proteins retinal act as receptor of photon and use to give geometrical isomerisation.



All *trans*-retinal

11-*cis*-retinal

Fig. 7.2. Structure of retinal.

The photosensitive pigment found in rods is called rhodopsin or visual purple. Its retinal is 11-*cis*-retinal and its opsin is scotopsin. Rhodopsin shows absorption maximum at ≈ 500 nm. Human rhodopsin has molecular weight 41000 and 348 amino acid residues. The 90% of the total protein in the membrane of red disk are made up of rhodopsin. It is coupled with G-protein as :

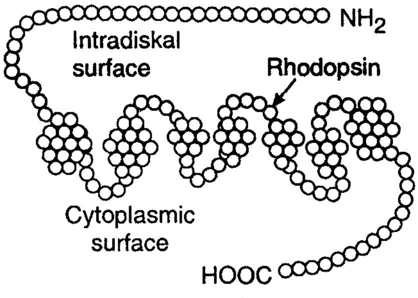


Fig. 7.3. Surface of G-proteins to Rhodopsin.

Retinal is parallel to the surface of membrane and is attached to a lysin residue at position 296 in the seventh *trans* membrane domain.

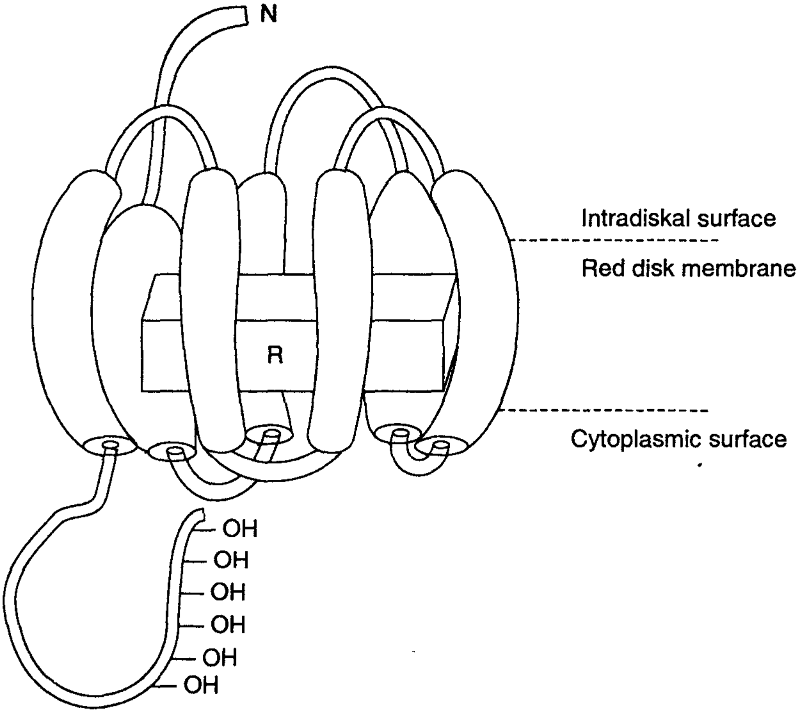


Fig. 7.4. Digramatic representation of the surface of rhodopsin, showing the position of 11-*cis*-retinal (*R*) in the red disk membrance.

$$\underset{\text{Retinal}}{C_{19}H_{27}CHO} + \underset{\text{lysin of scotopsin}}{RNH_2} \longrightarrow \underset{\text{Schiff's base}}{C_{19}H_{27}CH{=}N{-}R} + H_2O$$

The linkage between the scotopsin back bone and retinal results from addition reaction followed by elimination reaction between aldehyde group (—CHO) of retinal and on α-amino group of lysine of scotopsin.

The process of vision is a sequence of changes in phototransduction of photosensitive pigments [rods and cones]. These events may be summerise as follows :

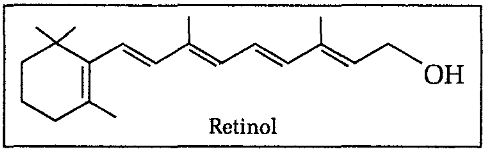
(i) Incident light [Visible region only.]
(ii) Structural change in the 11-*cis*-retinal of photopigment.
(iii) Conformational changes in photopigments.
(iv) Activation of transduction.
(v) Activation of phosphodiesterase.
(vi) Reduction in concentration of intercellular cGMP.
(vii) Closure of $Na^{\oplus}$ channels.
(viii) Hyper polarisation.
(ix) Decrease in release of synaptic transmitter.
(x) Resonance in bipolar cells and other neutral elements.

Rods are very sensitive towards the light and the main research interest is towards the photochemistry of transduction of rods. The following sequence of steps occurs during the phototransduction of rods.

(i) Light activates rhodopsin
(ii) Activated rhodopsin activates transduction.
(iii) Activated transduction binds with GTP [phosphodiesterase].
(iv) Activated phosphodiesterase catalyses the conversion of cyclic GMP [cGMP] into 5′-GMP.
(v) This makes reduction in protoplasmic concentration of a GMP.
(vi) This reduction causes closure of a cGMP-gated ion channels.

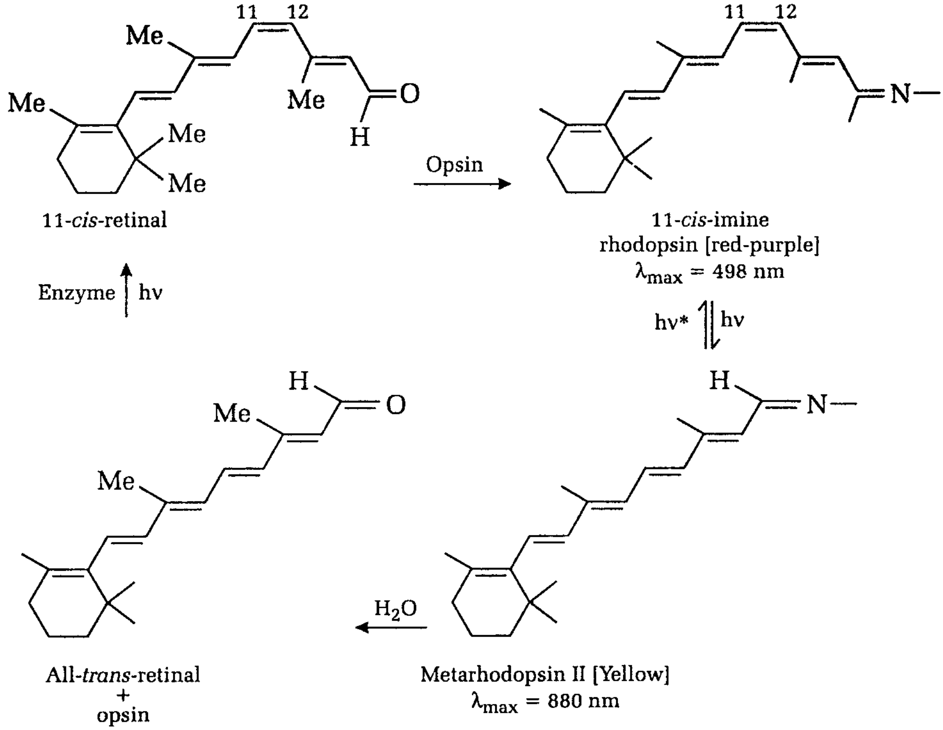
In the dark retinal in rhodopsin is in the 11-*cis*-configuration. Irradiation of rhodopsin leads to a series of conformational changes which can be noted by the disappearance and appearance of various intermediates of different colours.

$$\begin{tikzcd}
\text{Rhodopsin [red]} \arrow[r, "h\nu"] \arrow[d, shift right, leftarrow] \arrow[d, shift left, "\text{Scotospin}"] & \text{Bathorhodopsin [red]} \arrow[d, "\text{Thermal}"] \\
\text{11-}cis\text{-retianl} \arrow[dd, shift right, leftarrow] \arrow[dd, shift left] & \text{Lumirhodopsin [orange-red]} \arrow[d, "\text{Thermal}"] \\
 & \text{Metarhodopsin-I [orange]} \arrow[d, "\text{Thermal}"] \\
\text{All trans-rentinal + opsine [colourless]} \arrow[d, shift right, leftarrow, "\text{NAD}^{\oplus}"'] \arrow[d, shift left, "\text{NADH}"] & \text{Metarhodospin-II [yellow]} \\
\text{Retinol} &
\end{tikzcd}$$


Retinol

Rhodopsin which is a brown [Red] coloured chromoprotein found in rods and synthesized from vitamin A, get bleached in presence of light and resynthesized in dark. The first step is the conversion of Rhodopsin into Bathorhodopsin after the absorption of light. This conversion needs only tens of picoseconds and each subsequent step is $10^2 - 10^3$ times slower than its previous step. Current opinion ascribes the changes to the inability of the straight all-trans-retinal to be sterically accommodated on the surface of the opsin, only bent 11-*cis*-retinal fitting into the protein. In the dark, the retinal in rhodopsin is in the 11-*cis* conformation. Absorption of photon leads to photoisomerisation of the double bond of the 11-*cis*-retinal in rhodopsin. This alters the configuration of the opsin and opsin changes activities of the associated hetero trimeric G protein, which is called transducin or Gt 1. Photoisomerisation leads to the formation of strained structure and finally brings about the cleavage of the protein-retinal bond. The transition to bathorhodopsin involves the isomerisation to nearly all *trans*-forms but one that has not yet adopted its lowest energy geometry. The most relaxed all-*trans*-isomer appears at the lumirhodopsin. At each step the protein backbone rearranges, with prominent changes in one or more buried carboxyl groups becoming apparent in meta rhodopsin-I. Formation of metarhodopsin-II causes deprotonation of the Schiff's base as well as significant changes in the lipid structure.

The photochemistry of vision is triggered by absorption of a photon and induces *cis-trans* isomerisation. The conjugated polyenal, 11-*cis*-retinal and the protein opsin combine in retina to give the red-purple 11-*cis*- amine, rhodopsin.



11-*cis*-retinal

11-*cis*-imine
rhodopsin [red-purple]
λ_{max} = 498 nm

All-*trans*-retinal
+
opsin

Metarhodopsin II [Yellow]
λ_{max} = 880 nm

When the absorption of light occurs the *cis*-double bond is isomerized to give the yellow all-*trans* metarhodopsin II and a nerve impulse is triggered. Unlike its 11-*cis*-imine isomer the all- *trans* product does not fit to the site on the protein surface and the carbon-nitrogen double bond is exposed and hydrolysed to give all-*trans*-retinal and opsin. The all-*trans* retinal can be converted back to the 11-*cis*-isomer in the retina by enzyme and light of much shorter wavelength. In bright light metarhodopsin II can be converted to 11-*cis*-imine rhodopsin, by trans-cis isomerisation of the 11, 12-carbon-carbon double bond. This is an example of a reversible photoinduced isomerisation where colour changes occur upon *cis-trans* isomerisation. Such system are termed as photochromic systems.

Interaction of excited retinal with opsin leads to bathochromic shift [decrease in energy], the shift get larger and stronger interaction. As more strained lumirhodopsin changes into metarhodopsin the absorption maximum moves towards blue shift [hypsochromic shift]. The cascade of reactions occurs very rapidly and amplifies the light signal. The amplification helps to explain the remarkable sensitivity of red photoreceptors. These receptors are capable of producing and executable response to as little as one photon of light. When the 11-*cis*-retinal is converted to the all *trans* configuration, it separates from the opsin [bleaching]. Some of the rhodopsin is regenerated directly, while some of the 11-*cis*-retinal is reduced by enzyme alcohol dehydrogenase in the presence of NADH to vit. A_1, retinol, and this reacts with scotopsin to form rhodopsin. All these reactions, except the formation of bathorhodopsin are independent of light intensity, occurring equally in light and dark. The amount of rhodopsin in the receptors changes inversely with the level of incident light. Hence the concentration of rhodopsin decreases on exposing in light.

The photosensitive pigment in the cones is called iodopsin and its opsin is photopsin. There are three kinds of cones in primates. The colour vision receptors, respond maximally to light at wavelengths 440 nm, 535 nm and 565 nm [blue, green and red wavelength region]. Each contains 11-*cis*-retinol and opsin separately. The opsin and photopsin resembles with the rhodopsin, and spans the cone membrane seven times and has a characteristic structure in each type of cone. The cell membrane of cones is investigated to form the saccules but these are not separate intracellular disks like those in rods. The mechanism of cones responding towards light are well similar with rods. The mechanisms might be as, light activates 11-*cis*-retinal, and sequently activate Gt_2 (differ from rod transduction). Gt_2 activates phosphodiesterase, which catalyses the conversion of GMP to 5′ GMP. This results in closure of $Na^{\oplus}$ channels between the extracellular fluid and the cone cytoplasm, cause an increase in intracellular $Na^{\oplus}$ concentration and hyperpolarisation of the cone outer segments. This is sequence of events in photoreceptors by which incident light leads to production of a signal in the next succeeding neural unit in the retina. These signals read by brain and a Bio-organic photochemical procedure completes.

❑❑❑

UNIT

8

PROBLEMS AND SOLUTIONS

8.1 1INTRODUCTION

PROBLEMS

1. Visible region of electromagnetic spectrum is from 4000 Å to 8000 Å. How much energy variation will be in the photons of visible region?
2. Absorption of microwave radiation leads to change in the rotational energy levels of a molecule. If molecule absorbs at 10^{-1} cm. What will be energy separation between its rotation levels?
3. It is stated that only UV-visible region of light is able to produce chemical change, while others are not. Why?
4. Give three examples of Naturally occurring photochemical reactions?

SOLUTIONS

1. The energy of radiation is given by

$$E = \frac{hc}{\lambda}$$

When $\lambda = 4000 \text{ Å} = 4 \times 10^{-7}$ m

$$E = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{4 \times 10^{-7} \text{ m}}$$

$$= 4.9695 \times 10^{-19} \text{ J} = 1.14 \times 10^{5} \text{ J mol}^{-1}$$

When $\lambda = 8000 \text{ Å} = 8 \times 10^{-7}$ m

$$E = \frac{6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{8} \text{ ms}^{-1}}{8 \times 10^{-7} \text{ m}}$$

$$= 2.4847 \times 10^{-19} \text{ J} = 5.72 \times 10^{4} \text{ J mol}^{-1}$$

The energy associated with photons of visible region varies from 5.72×10^{4} J mol^{-1} to 1.14×10^{5} J mol^{-1}.

2. Wavelength absorbed $\lambda = 10^{-1}$ cm $= 10^{-3}$ m

Energy associated $$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{10^{-3}}$$

$$= 1.98 \times 10^{-22} \text{ J/photon.}$$

The energy separation of rotational level in molecule is 45.7 J.

3. The essential condition for chemical transformation is electronic excitation. UV-visible region of electromagnetic spectrum contains energy 36 – 143 k cal mol^{-1} which is sufficient for electronic excitation from one molecular orbital to higher molecular orbital of an organic molecule. Hence, only UV-visible region produce chemical change while other radiations [higher or lower wavelength] do not make any contribution in photochemistry.
4. Three examples of naturally occurring photochemical reactions are :
   (i) Photosynthesis
   (ii) Photodegradation of polymers
   (iii) Photochemistry of vision

8.2 BASIC PRINCIPLES

PROBLEMS

1. Calculate energy [in calories] associated with 1 mole of radiation of wavelength 2000 Å?
2. For the following photochemical reaction

$$A \xrightarrow{hv} B$$

1.0×10^{-5} mole of B was formed on absorption of 6.626×10^{7} ergs of energy of ratiation of wavelength 3600 Å. Calculate the quantum yield?

3. Radiation of wavelength 2540 Å was passed through a reaction cell containing 10 ml of solution of 0.0495 molar oxalic acid and 0.01 molar uranyl sulphate. After the absorption of 8.81×10^{8} ergs of radiation, the concentration of oxalic acid was reduced to 0.0383 molar. Calculate the quantum yield for the photochemical consumption of oxalic acid at given wavelength?
4. Calculate the energy (in electron volts) associated with per Einstein of radiation of wavelength 220 nm?
5. The bond energy of molecule H—X is 142.95 k cal mol^{-1}. What will be the longest wavelength of light, capable of bond dissociation?
6. The bond dissociation energy of HCl is 102 k cal mol^{-1}. If HCl is illuminated with a radiation of wavelength 2530 Å. Calculate the fraction of radiation energy converted into kinetic energy of fragments?
7. In a reaction vessel 15 mole of oxygen and 12 mole of chlorine taken and a radiation pulse of wavelength 4200 nm of 10 Einstein passed. After it, 5 mole of oxygen recovered. Calculate the quantum efficiency of the reaction?
8. Match the following

(A) Colour of visible light	(B) Wavelength (Å)
1. Violet	(a) 6500–7600
2. Indigo	(b) 5500–5800
3. Blue	(c) 4300–4500
4. Yellow	(d) 4900–5500
5. Orange	(e) 5800–6500
6. Green	(f) 3800–4300
7. Red	(g) 4500–4900

9. State "Grotthus-Draper's Law" of photochemistry?
10. Write down full form of the following terms?
    (i) VC (ii) IC (iii) ISC

SOLUTIONS

1. Frequency of radiation

$$\nu = \frac{c}{\lambda} = \frac{3\times10^{10}}{2000\ \text{Å}}$$

$$= \frac{3\times10^{10}\ \text{cm sec}^{-1}}{2\times10^{-5}\ \text{cm}} = 1.5\times10^{15}\ \text{sec}^{-1}$$

∴ Energy associated $E = h\nu$

$$= (6.626\times10^{-27}\ \text{erg. sec})\ (1.5\times10^{15}\ \text{sec}^{-1})$$

$$= 9.939\times10^{-12}\ \text{ergs.}$$

Now energy per mole $= N\times E$

{where, N is Avogadro constant}

$$= (6.023\times10^{23}\ \text{photons mole}^{-1})\ (9.939\times10^{-12}\ \text{ergs. photon}^{-1})$$

$$= 5.986\times10^{12}\ \text{ergs mole}^{-1}$$

$$= \frac{5.986\times10^{12}}{10^7}\ \text{Joule mol}^{-1} \qquad [\because\ 1\ \text{Joule} = 10^7\ \text{ergs}]$$

$$= 5.986\times10^{5}\ \text{Joule mol}^{-1}$$

$$= \frac{5.986\times10^{5}}{4.184}\ \text{cal mol}^{-1} \qquad [\because\ 1\ \text{cal} = 4.184\ \text{Joule}]$$

$$= 1.431\times10^{5}\ \text{cal mol}^{-1}$$

or $= 143.1\ \text{k cal mol}^{-1}$

The energy associated with 1 mole of radiation of wavelength 2000 Å is 143.1 k cal mol^{-1}.

2. No. of molecules [B] formed $= 1.0\times10^{-5}\times6.023\times10^{23}$

$$= 6.023\times10^{18}\ \text{molecules}$$

No. of quanta absorbed $= \dfrac{\text{Total energy absorbed}}{\text{Energy of one quantum}}$

$$= \frac{6.626\times10^{7}\ \text{ergs}}{h\nu} = \frac{6.626\times10^{7}\ \text{ergs}}{hc/\lambda}$$

$$= \frac{(6.626\times10^{7}\ \text{ergs})\times(3.6\times10^{-5}\ \text{cm})}{(6.626\times10^{-27}\ \text{ergs sec})\ (3\times10^{10}\ \text{cm/sec})}$$

$$= 1.2\times10^{19}$$

∴ quantum yield of the given reaction

$$\phi = \frac{\text{No. of product formed}}{\text{No. of quanta absorbed}} = \frac{6.023\times10^{18}}{1.2\times10^{19}} = \mathbf{0.5019}$$

3. 10 ml of 0.0495 molar oxalic acid

$$= \frac{10\times0.0495}{1000} = 4.95\times10^{-4} \text{ mole}$$

10 ml of 0.0383 molar oxalic acid

$$= \frac{10\times0.0383}{1000} = 3.83\times10^{-4} \text{ mole}$$

∴ Amount of oxalic acid consumed

$$= (4.95\times10^{-4}) - (3.83\times10^{-4}) = 1.12\times10^{-4} \text{ mole}$$

No. of molecules of oxalic acid decomposed by light

$$= 1.12\times10^{-4}\times6.023\times10^{23} = 6.745\times10^{19} \text{ molecules}$$

The no. of quanta absorbed

$$= \frac{\text{Energy absorbed}}{\text{Energy of one quantum}} = \frac{8.81\times10^{8}\text{ ergs}}{h\nu} = \frac{8.81\times10^{3}}{hc/\lambda}$$

$$= \frac{(8.81\times10^{8}\text{ ergs})\times2.54\times10^{-5}\text{ cm}}{(6.626\times10^{-27}\text{ ergs sec})\times(3\times10^{10}\text{ cm. sec}^{-1})}$$

$$= 1.126\times10^{15}$$

$$\text{Quantum yield} = \frac{\text{No. of Oxalic acid decomposed}}{\text{No. of quanta absorbed}}$$

$$= \frac{6.745\times10^{19}}{1.126\times10^{20}} = \mathbf{0.5990}$$

4. Energy per quantum $= h\nu$

$$h = 6.626\times10^{-34}\text{ Joule sec.}$$

$$\nu = \frac{c}{\lambda} = \frac{3\times10^{10}\text{ cm sec}^{-1}}{220\times10^{-7}\text{ cm}} = 1.364\times10^{15}\text{ sec}^{-1}$$

$$\therefore \quad E = (6.626\times10^{-34}\text{ Joule sec})\ (1.364\times10^{15}\text{ sec}^{-1})$$

$$= 9.038\times10^{-19}\text{ Joule} = 5.444\times10^{5}\text{ Joule/mole}$$

$$\because \quad 1\text{ eV} = 1.6\times10^{-19}\text{Joules}$$

$$\therefore \quad 5.44\times10^{5}\text{ Joule/mole} = 3.4025\times10^{24}\text{eV}$$

5. Bond energy of molecule $= 142.95$ k cal mol^{-1}

$$E = \frac{142.95\times10^{3}\times4.184}{6.023\times10^{23}}\text{ Joule per molecule} \quad \{\because 1\text{ calorie} = 4.184\text{ Joule}\}$$

$$E = h\nu$$

$$\therefore \quad \nu = \frac{9.9303\times10^{-19}\text{ J}}{6.626\times10^{-34}\text{ Js}} = 1.4987\times10^{15}\text{ s}^{-1}$$

$$\because \qquad \nu = \frac{c}{\lambda}$$

$$\therefore \qquad \lambda = \frac{c}{\nu} = \frac{3\times10^{8}\ \mathrm{ms}^{-1}}{1.4987\times10^{15}\ \mathrm{s}^{-1}}$$

$$= 2.001\times10^{-7}\ \mathrm{m} = 2001\ \text{Å}$$

Hence, Radiation of wavelength 2001 Å will be the highest wavelength radiation causes bond dissociation of H—X.

6. Bond dissociation energy of HCl = 120 k cal mole^{-1}

$$= \frac{102\times10^{3}\times4.814}{6.023\times10^{23}}\ \text{Jule per molecule}$$

$$E = 7.086\times10^{-19}\ \mathrm{J} \qquad \ldots(1)$$

Energy associated with a quantum of radiation of wavelength 2530 Å

$$E' = h\nu = \frac{hc}{\lambda}$$

$$= \frac{6.626\times10^{-34}\ \mathrm{Js}\times3\times10^{8}\ \mathrm{ms}^{-1}}{2530\times10^{-10}\ \mathrm{m}}$$

$$= 7.857\times10^{-19}\ \mathrm{J} \qquad \ldots(2)$$

Now the energy difference between energy of a photon and bond dissociation energy of a molecule of HCl (the energy converted into kinetic energy).

$$E' - E = 0.771\times10^{-19}\ \mathrm{J}$$

∴ The fraction converted into K.E.

$$= \frac{0.771\times10^{-19}}{7.857\times10^{-19}}\times100 = 9.79\%$$

7. The reaction is $O_2 + Cl_2 \xrightarrow{h\nu} Cl_2O_2$

Oxygen used during the reaction = 10 mole

Number of Einstein of light used = 10 Einstein

$$\therefore \text{Quantum efficiency } \phi = \frac{\text{No. of moles reacting in given time}}{\text{No. of einsteins absorbed in some time}} = \frac{10}{10} = 1$$

Quantum efficiency of the reaction is 1.

8.

(A)	(B)
Colour of visible light	Wavelength (Å)
1. Violet	(a) 3800–4300
2. Indigo	(b) 4300–4500
3. Blue	(c) 4500–4900
4. Yellow	(d) 5500–5800
5. Orange	(e) 5800–6500
6. Green	(f) 4900–5500
7. Red	(g) 6500–7600

9. Grotthus-Draper's Law : [Also known as Ist law of photochemistry]

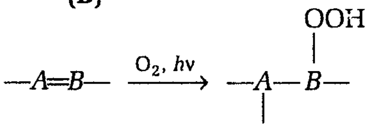
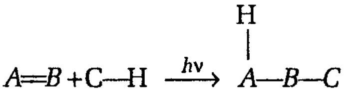
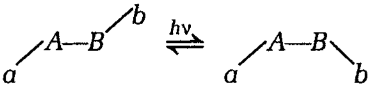
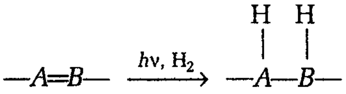
   When light falls an any substance, only the fraction of incident light which is absorbed by reacting species can bring about a chemical change.

10. VC : Vibration cascade
    IC : Internal conversion
    ISC : Intersystem crossing

8.3 DETERMINATION OF REACTION MECHANISM

PROBLEMS

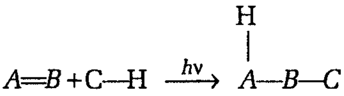
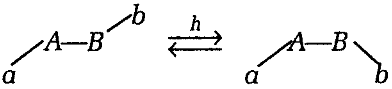
1. What are the factors to be considered during the determination of reaction mechanism of photochemical reactions?
2. Match the following

(A)	(B)
(i) Photodissociation	(a)  $-A=B- \xrightarrow{O_2,\,h\nu} -\underset{\vert}{A}-\overset{\overset{OOH}{\vert}}{B}-$
(ii) Photoaddition	(b) $n(A=B) \xrightarrow{h\nu} \left[A-B\right]_n$
(iii) Photoisomerisation	(c) $A-B \xrightarrow{h\nu} A^{\cdot}+B^{\cdot}$
(iv) Photopolymerisation	(d)  $A=B+C-H \xrightarrow{h\nu} \overset{\overset{H}{\vert}}{A}-B-C$
(v) Photooxidation	(e) 
(vi) Photoreduction	(f)  $-A=B- \xrightarrow{h\nu,\,H_2} -\overset{\overset{H}{\vert}}{A}-\overset{\overset{H}{\vert}}{B}-$

SOLUTIONS

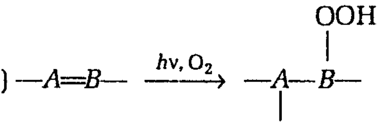
1. Following factors are considered during the determination of mechanism of photochemical reaction :
   - (i) Detect the formed products.
   - (ii) Determine the kinetics of the photochemical reaction
   - (iii) Determine short-lived intermediates.
   - (iv) Calculate quantum yield.
   - (v) Calculate life-time of excited states (singlet or triplet).

2.

(A)	(B)
(1) Photodissociation	(c) $A-B \xrightarrow{h\nu} A^{\cdot}+B^{\cdot}$
(2) Photoaddition	(d)  $A=B+C-H \xrightarrow{h\nu} \overset{\overset{H}{\vert}}{A}-B-C$
(3) Photoisomerisation	(e) 

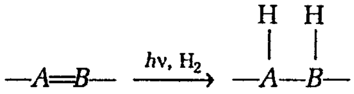
(4) Photopolymerization (b) $n(A{=}B) \xrightarrow{h\nu} \left[A{-}B\right]_n$

(5) Photooxidation (a)



$-A{=}B- \xrightarrow{h\nu,\,O_2} -\overset{|}{A}-\overset{\overset{OOH}{|}}{B}-$

(6) Photoreduction (f)



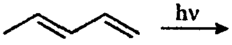
$-A{=}B- \xrightarrow{h\nu,\,H_2} -\overset{\overset{H}{|}}{A}-\overset{\overset{H}{|}}{B}-$

8.4 PHOTOCHEMISTRY OF ALKENES

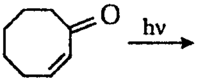
PROBLEMS

1. Predict the product?

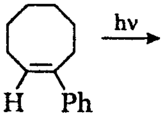
(1)



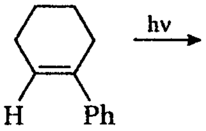
(2)



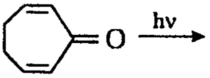
(3)



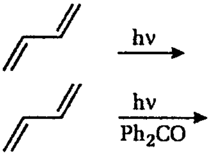
(4)



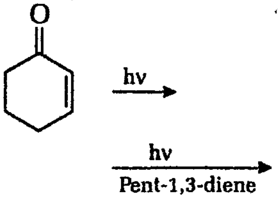
(5)



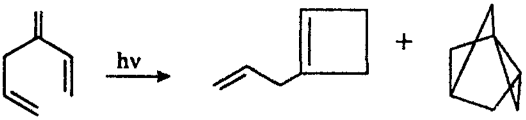
2. Complete the reaction and explain their difference?



3. Complete the reaction and explain difference?

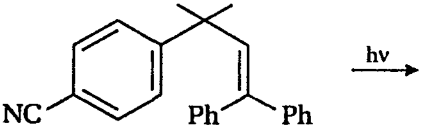


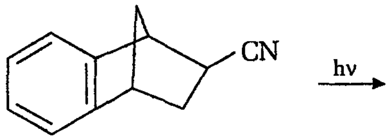
4. Give the reaction mechanism of the following photo- cyclisation reaction?

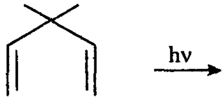


5. Give the product of the following di-π-methane rearrangements?

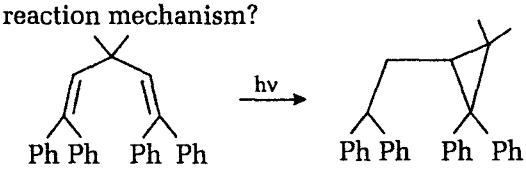
(1)



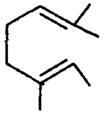
(2) 

(3) 

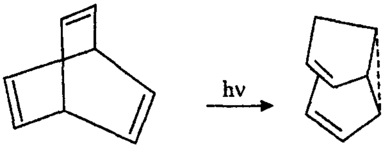
6. Write down reaction mechanism?



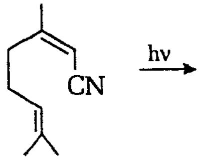
7. Give the possible products formed after the irradiation of.



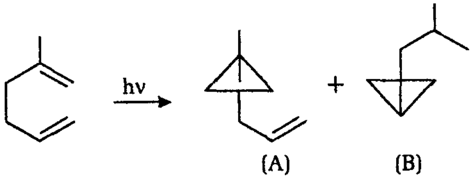
8. Give reaction mechanism?



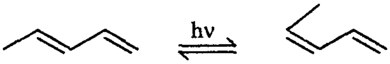
9. Predict the product formed after photo excitation of following 1, 5-diene?

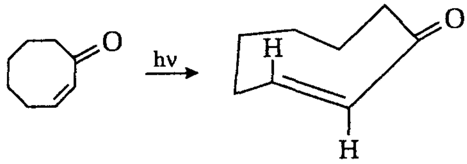


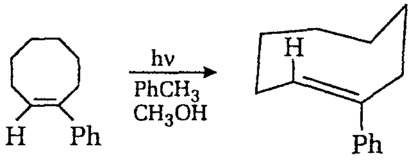
10. In the above example, substituted 1, 5-diene gives (*A*) as major product on photochemical rearrangement. Why?

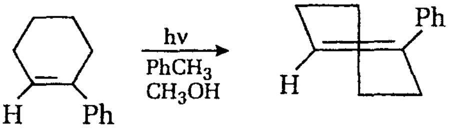


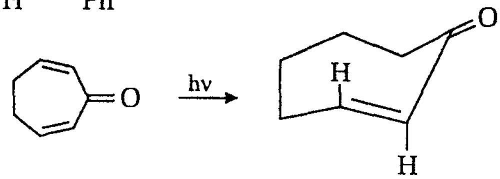
SOLUTIONS

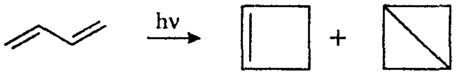
1. (1) 

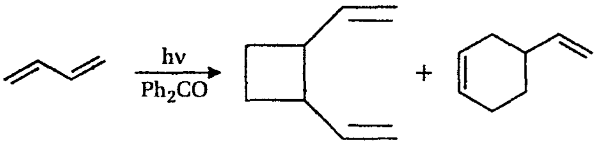
(2) 

(3) 

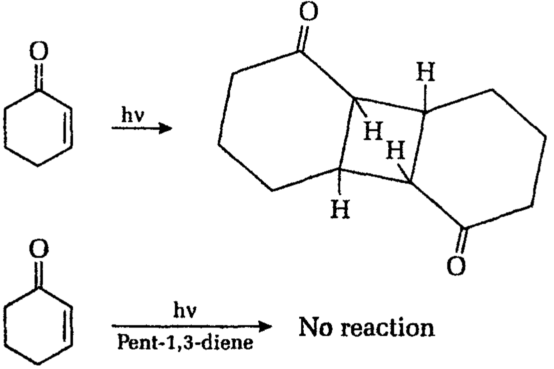
(4) 

(5) 

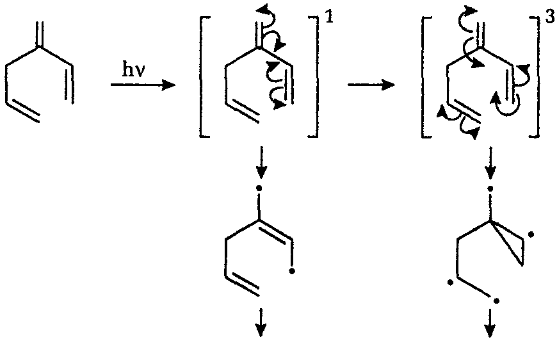
2. 

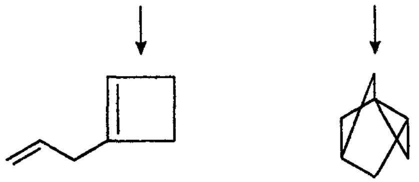


First reaction is a direct photochemical reaction while the second is a sensitised photochemical process.

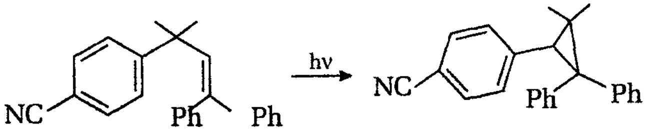
3. 

First reaction is a direct photochemical transformation while second is an quenched photochemical process, where pent-1, 3-diene act as quencher.

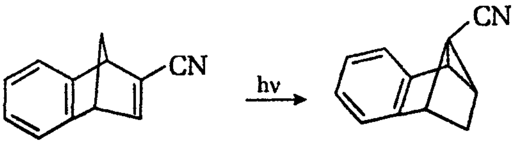
4. 



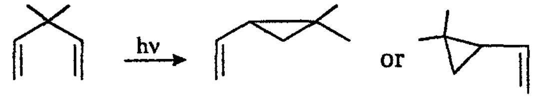
5. (1)



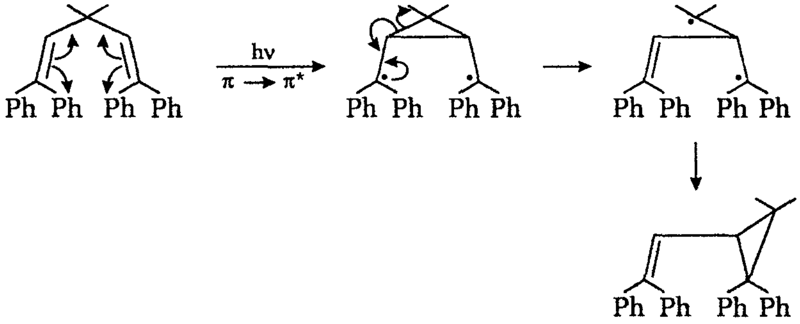
(2)



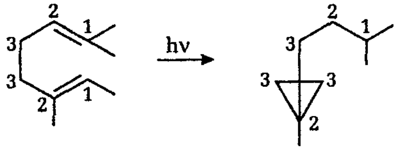
(3)



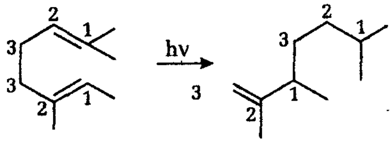
6.



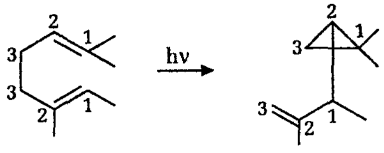
7.



[1,2] product

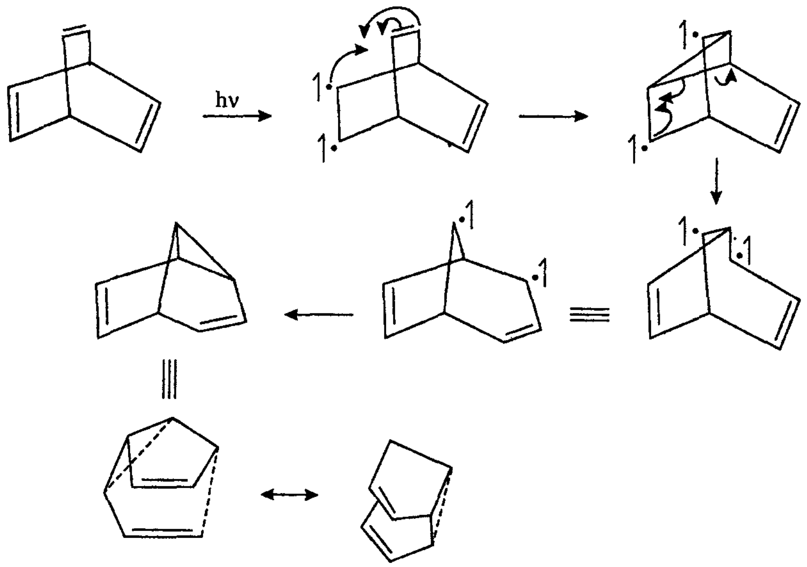


[1,3] product

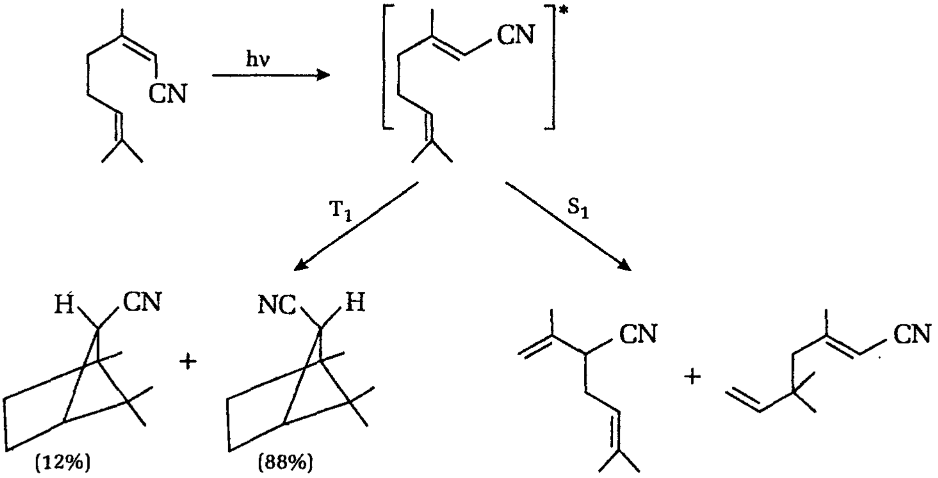


[3,2] product

8.



9.



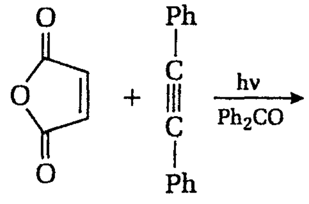
10. The formation of three membered ring is regioselectively favourable and occur preferentially across the more substituted allyl moiety. Hence, 1, 5-diene gives (*A*) as major product on rearrangement.

8.5 PHOTOCHEMISTRY OF AROMATIC COMPOUNDS

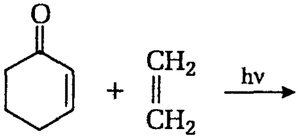
PROBLEMS

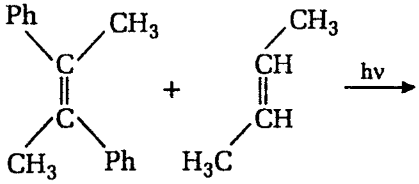
1. Complete the following photochemical addition reactions.

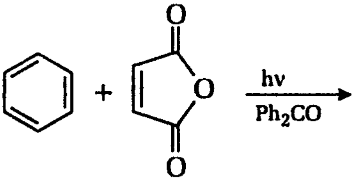
(1)

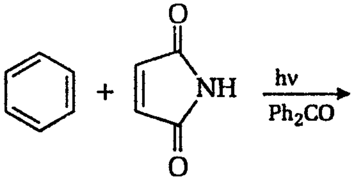


(2)

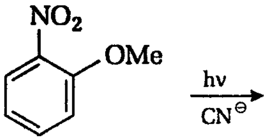


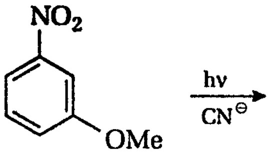
(3)


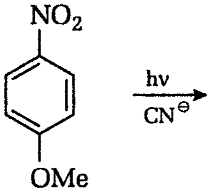
(4)


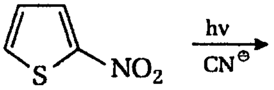
(5)


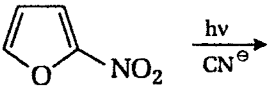
2. Complete the following photochemical substitution reactions?

(1)


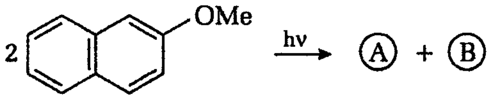
(2)


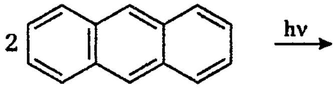
(3)


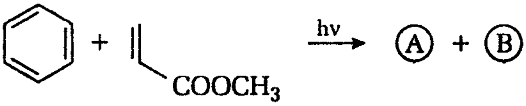
(4)


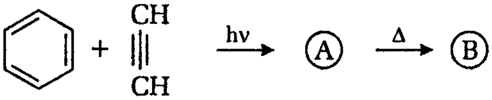
(5)


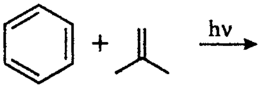
3. Give the products?

(1)


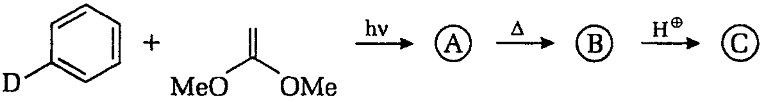
(2)


(3)


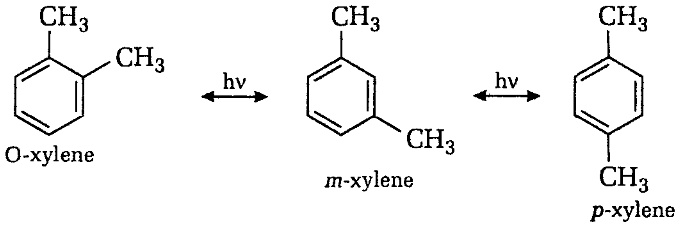
(4)


(5)


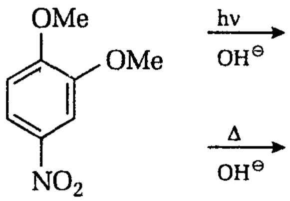
4. Write down intermediates and final product of the following photochemical reaction?



5. Give the mechanism of the following rearrangement.

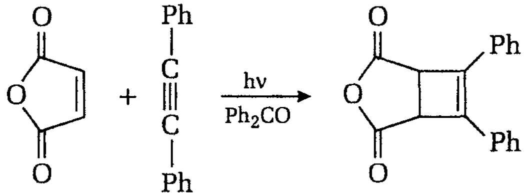


6. Give products?

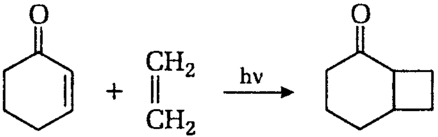


SOLUTIONS

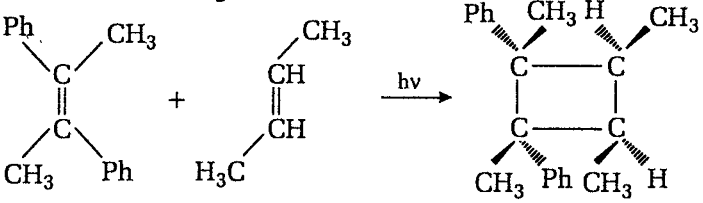
1. (1)



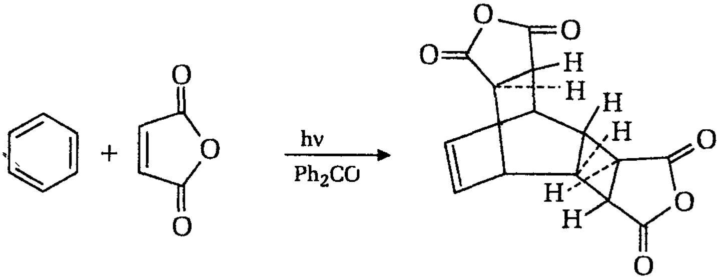
(2)



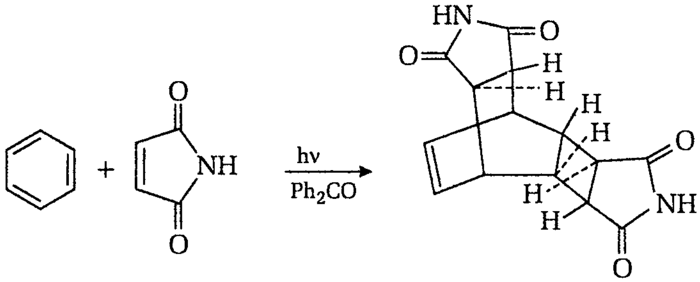
(3)



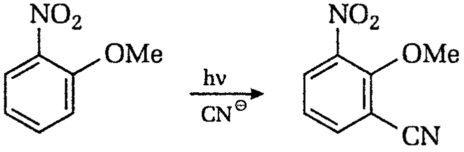
(4)



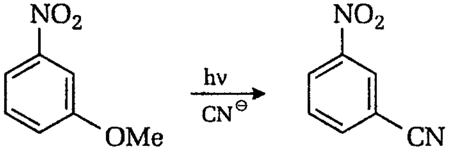
(5)


hν
Ph$_2$CO
NH
HN
O
H

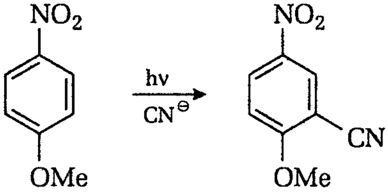
2. (1)


NO$_2$
OMe
hν
CN$^\ominus$
CN

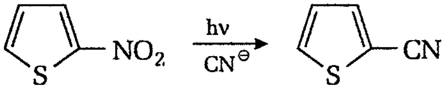
(2)


NO$_2$
OMe
hν
CN$^\ominus$
CN

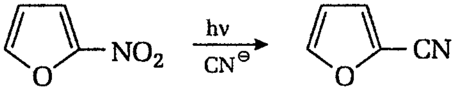
(3)


NO$_2$
OMe
hν
CN$^\ominus$
CN

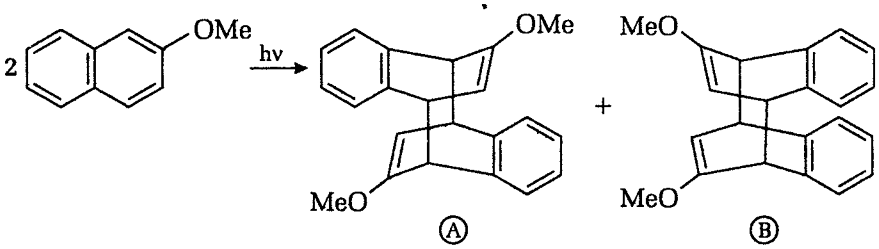
(4)


NO$_2$
S
hν
CN$^\ominus$
CN

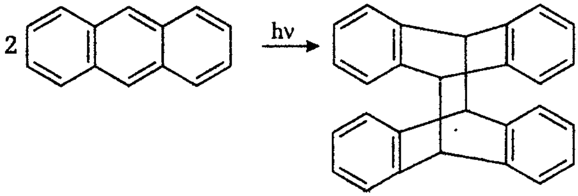
(5)


NO$_2$
O
hν
CN$^\ominus$
CN

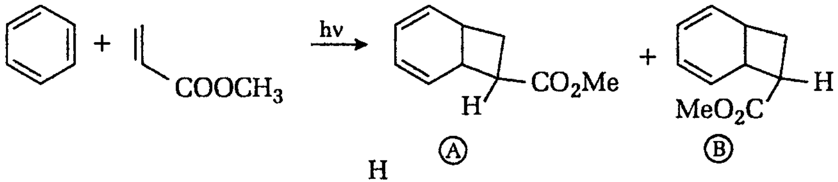
3. (1)


2
OMe
hν
MeO
+
Ⓐ
Ⓑ

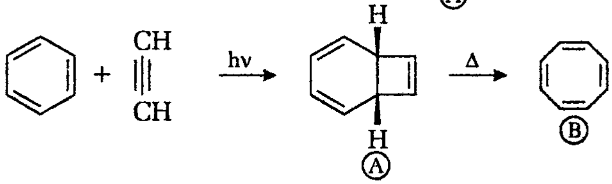
(2)


2
hν

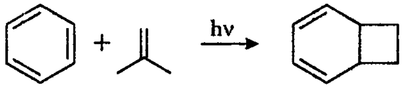
(3)



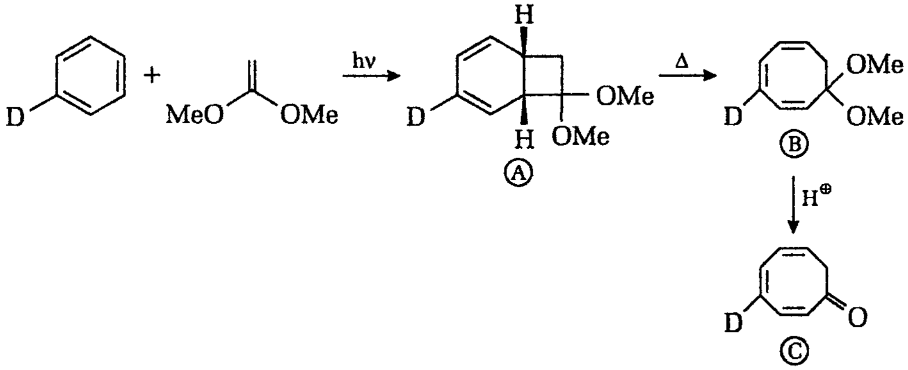
(4)



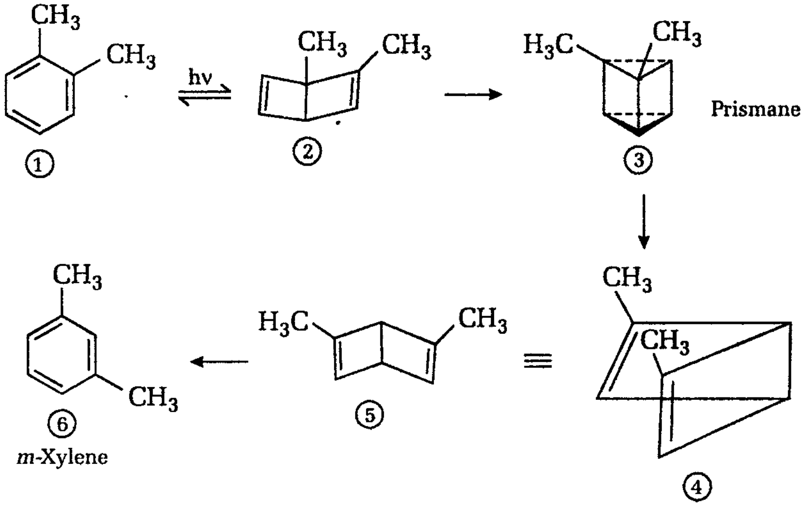
(5)

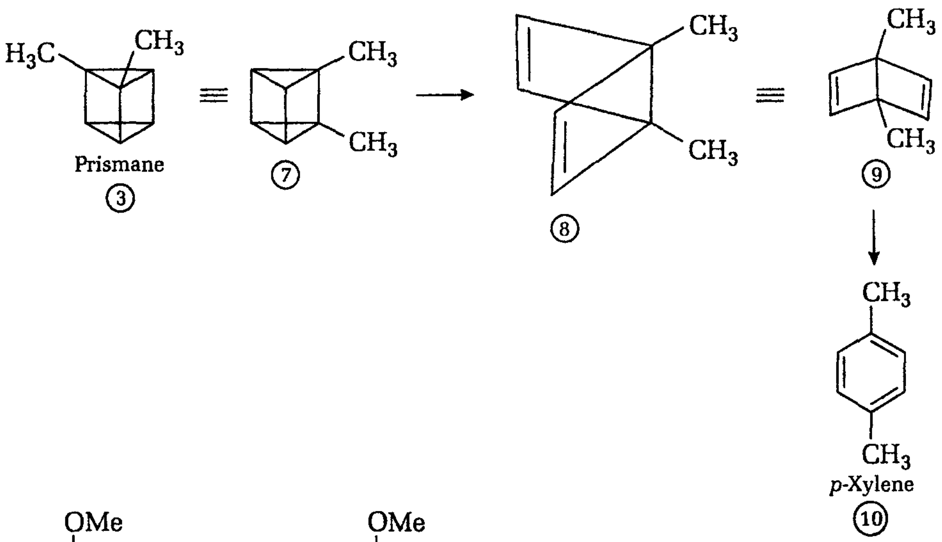


4. The reaction of benzene with substituted ethylene gives an orthocyclo adduct which undergoes disrotatory electrocyclic ring opening to give cyclooctatrienone.

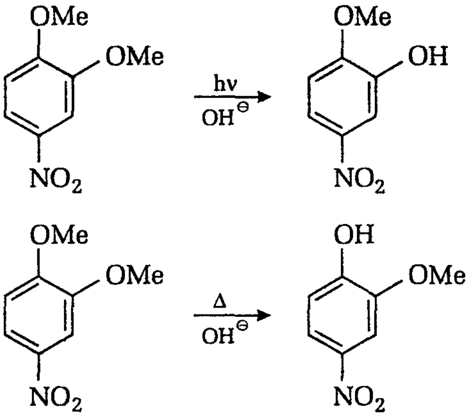


5.





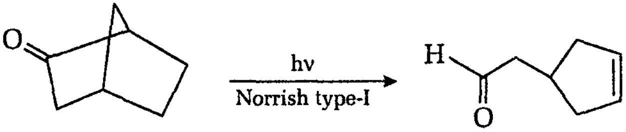
6.



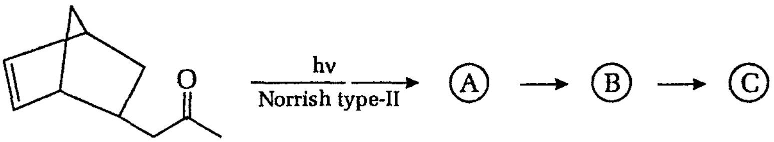
8.6 PHOTOCHEMISTRY OF CARBONYL COMPOUNDS

PROBLEMS

1. Write down the mechanism of the following photochemical reaction?

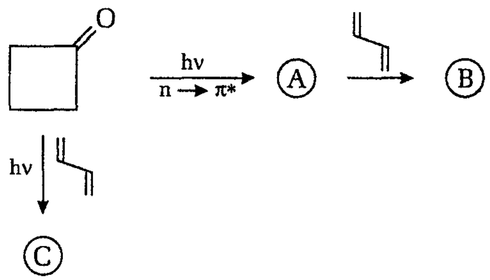


2. Complete the following reaction and predict the products?



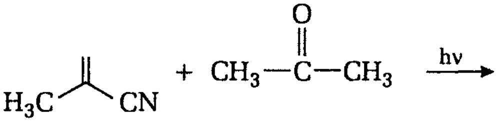
3. Give the product (s) formed after the photolysis of the following saturated carbonyl compound?

(1)

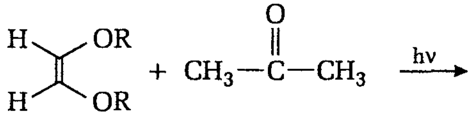


4. Predict the products?

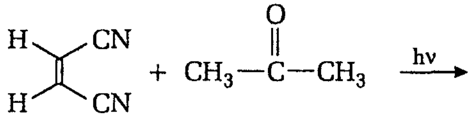
(1)



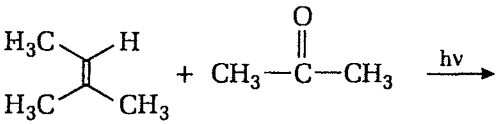
(2)



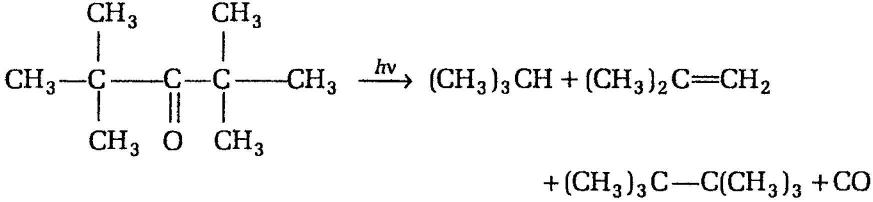
(3)



(4)



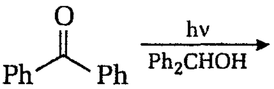
5. Give the mechanism of the following reaction?



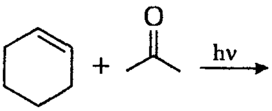
$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{\underset{O}{\|}}{C}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow{h\nu} (CH_3)_3CH + (CH_3)_2C{=}CH_2 + (CH_3)_3C-C(CH_3)_3 + CO$$

6. Give the product (s)?

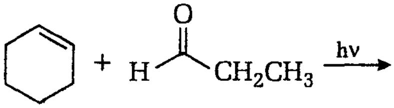
(1)



(2)



(3)



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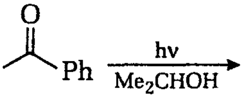
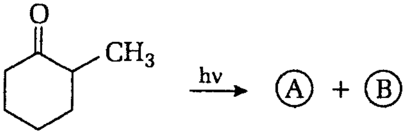


7. Complete the following reactions?

(1)



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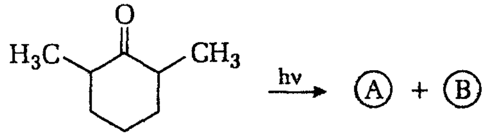
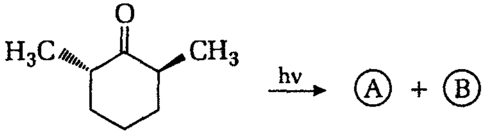
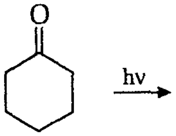


(3)

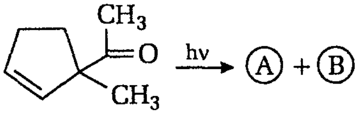


8. Write down reaction mechanism and product (s) formed on vapour phase photolysis of cyclohexanone?



9. Write down the products formed after the photolysis of following β,γ-unsaturated carbonyl compounds?

(1)



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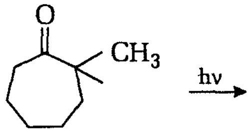

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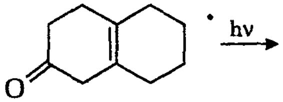
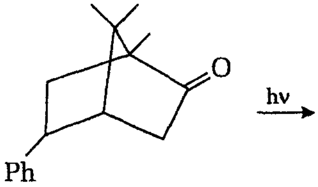
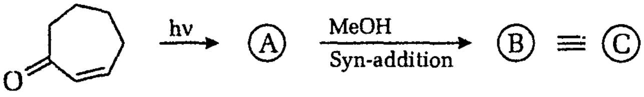


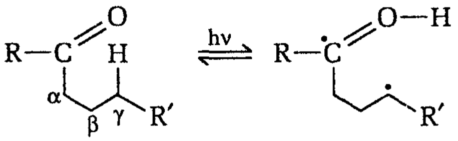
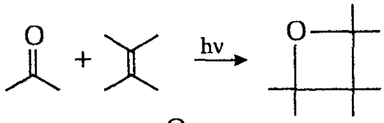
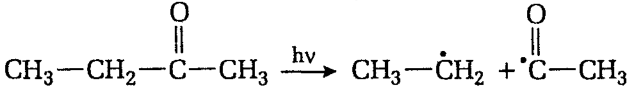
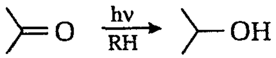
(4)



10. Identify the intermediates formed and final product of photolysis of cyclohept-2-enone?

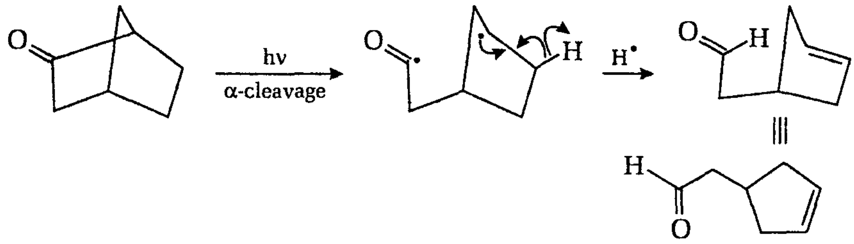


11. Match the following?

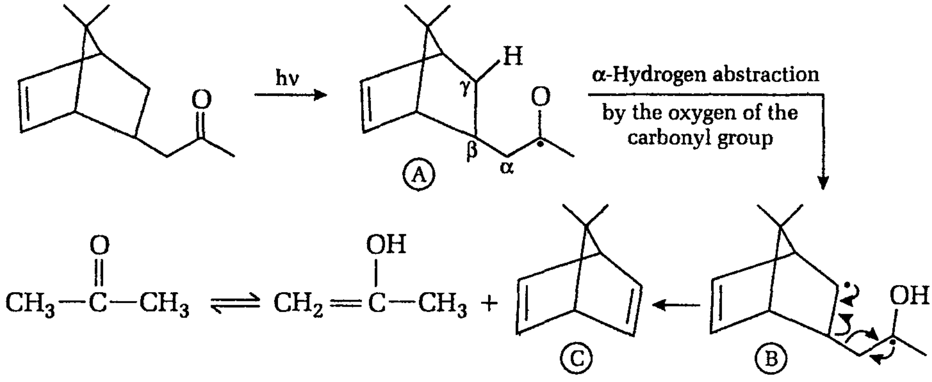
(A)	(B)
(1) Norrish type-I	(i) 
(2) Norrish type-II	(ii) 
(3) Oxetane formation	(iii)  $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{h\nu} CH_3-\dot{C}H_2 + {}^{\bullet}\overset{O}{\overset{\|}{C}}-CH_3$
(4) Photoreduction	(iv) 

SOLUTIONS

1.



2.



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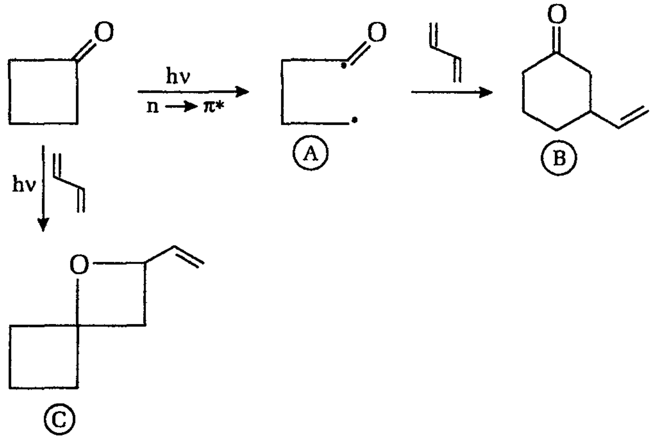
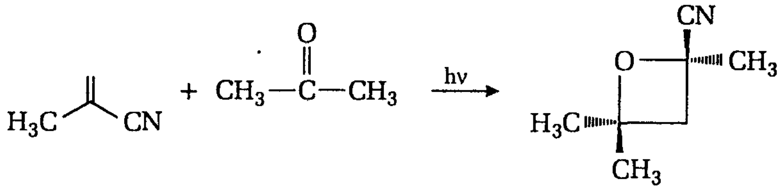
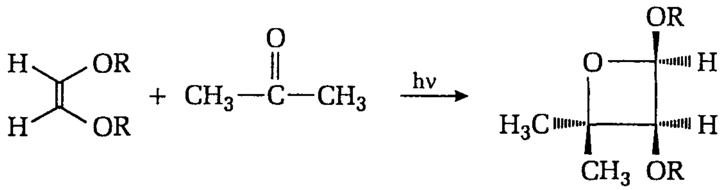


4. (1)



(2)



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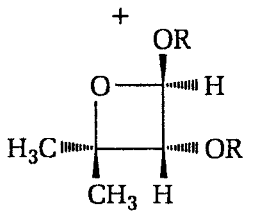
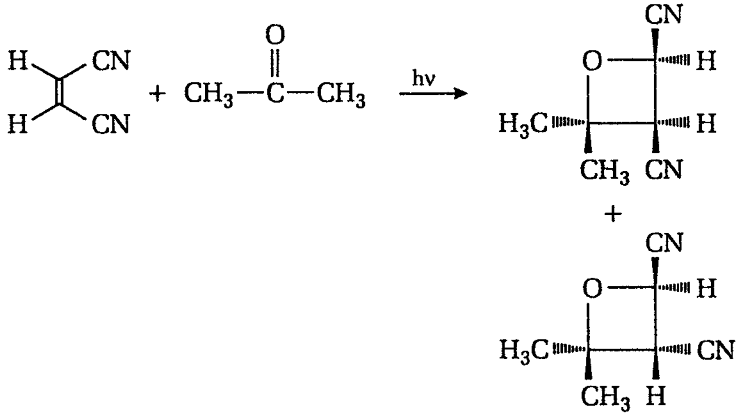
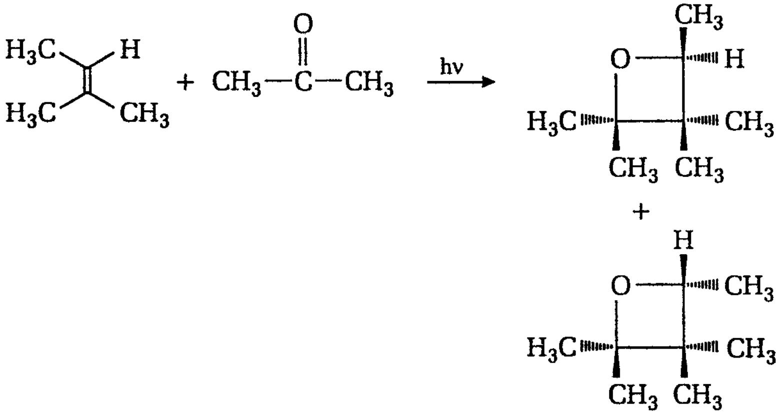


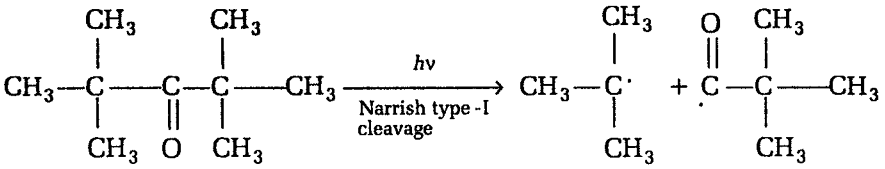
(3)



(4)



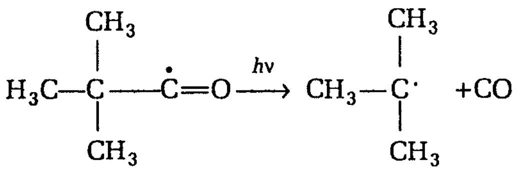
5.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\underset{O}{\|}}{C}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\text{Narrish type -I cleavage}]{h\nu} CH_3-\underset{CH_3}{\overset{CH_3}{C}}\cdot + \underset{\cdot}{\overset{\overset{O}{\|}}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

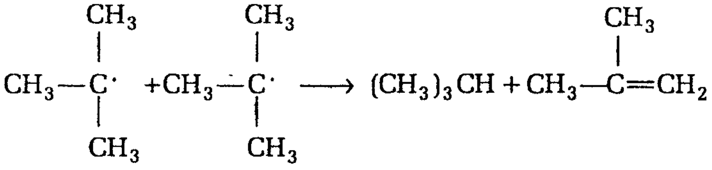
Now following process occurs

(1) Decarboxylation



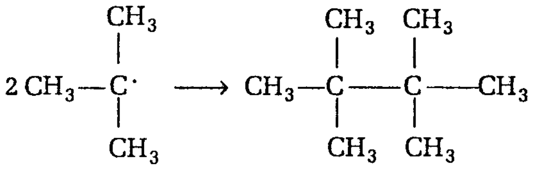
$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\dot{C}=O \xrightarrow{h\nu} CH_3-\underset{CH_3}{\overset{CH_3}{C}}\cdot \quad +CO$$

(2) Intermolecular Hydrogen abstraction



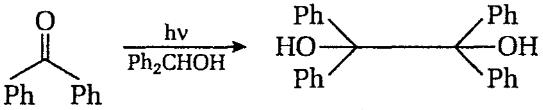
$$CH_3-\overset{CH_3}{\underset{CH_3}{C^\cdot}} + CH_3-\overset{CH_3}{\underset{CH_3}{C^\cdot}} \longrightarrow (CH_3)_3CH + CH_3-\overset{CH_3}{C}=CH_2$$

(3) Free-radical recombination



$$2\,CH_3-\overset{CH_3}{\underset{CH_3}{C^\cdot}} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

6. (1)



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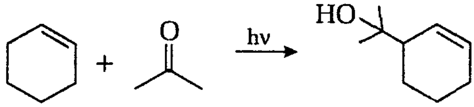

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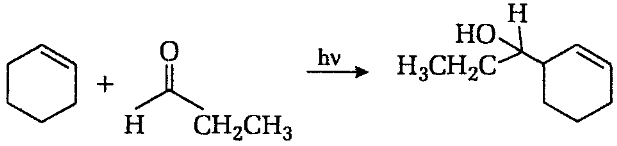

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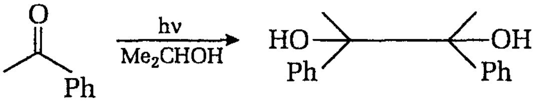
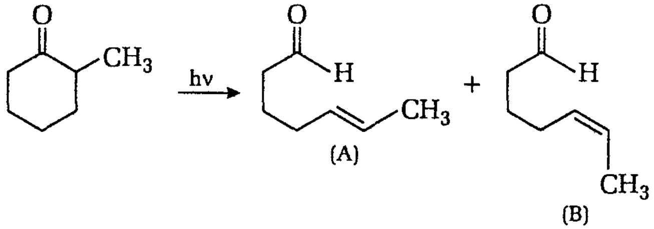


7. (1)



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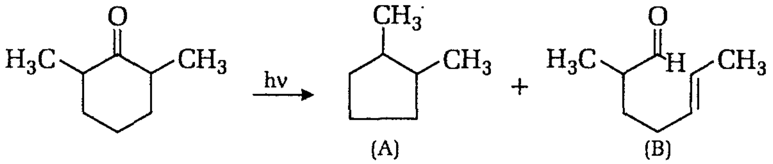
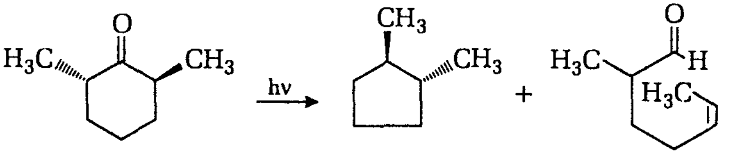
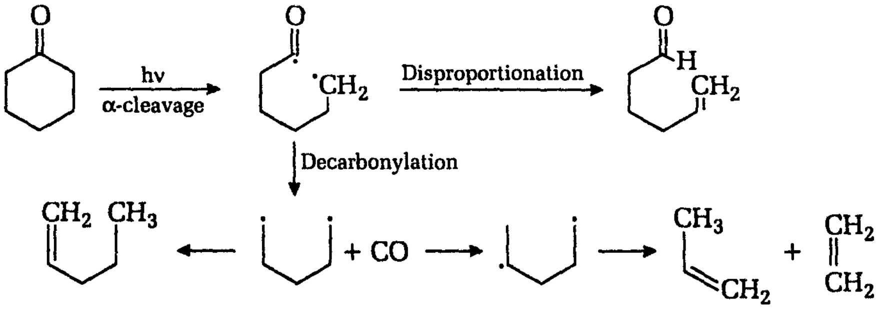


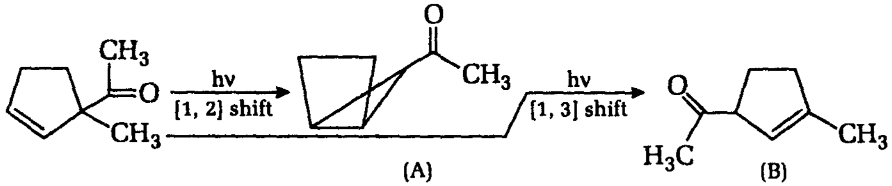
(3)



8. Cyclohexanone on photolysis yields 1, 6- triplet diradical by Norrish type-I cleavage.



9. (1)



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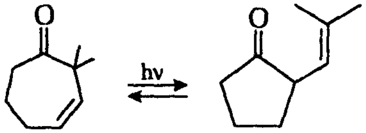
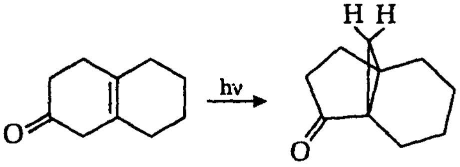
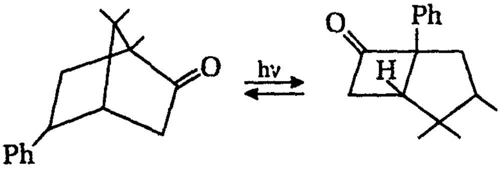


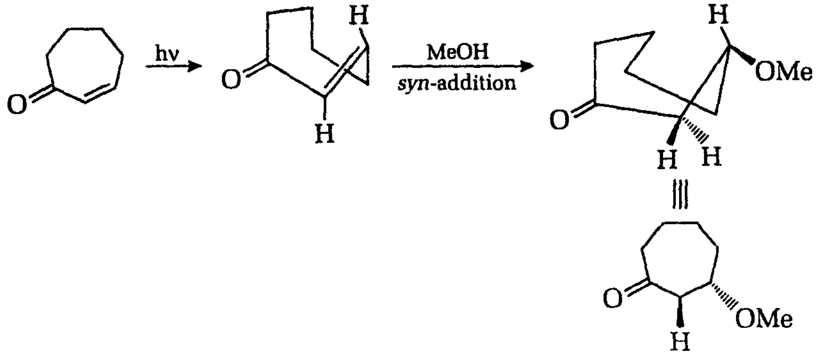
(3)



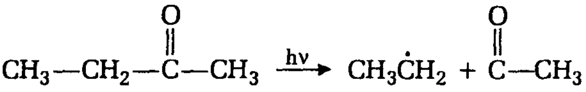
(4)



10.

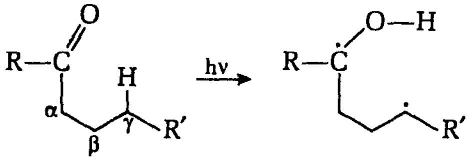


11. (1) Noarish type-I (iii)

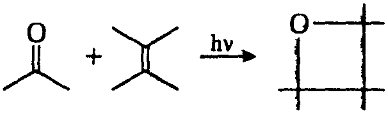


$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{h\nu} CH_3\dot{C}H_2 + \overset{\overset{O}{\|}}{\dot{C}}-CH_3$

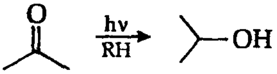
(2) Noarish type-II (i)



(3) Oxetane formation (ii)



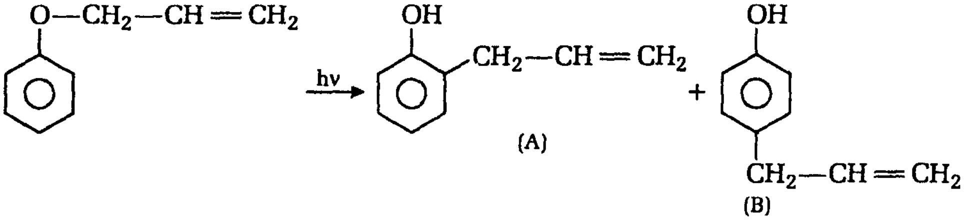
(4) Photooxidation (iv)



8.7 MISCELLANEOUS PHOTOCHEMICAL REACTIONS

PROBLEMS

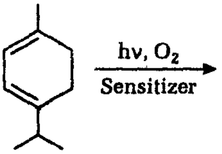
1. Write down the mechanism of the following rearrangement on photolysis?



2. Suggest the mechanism of conversion of Hexan-2-ol nitrite into a mixture of unsaturated alcohols on photolysis?

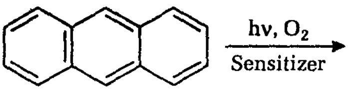
3. Give products?

(1)

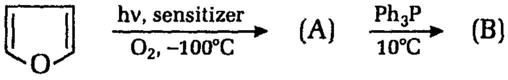


(2)

(3)



4. Detect the product?

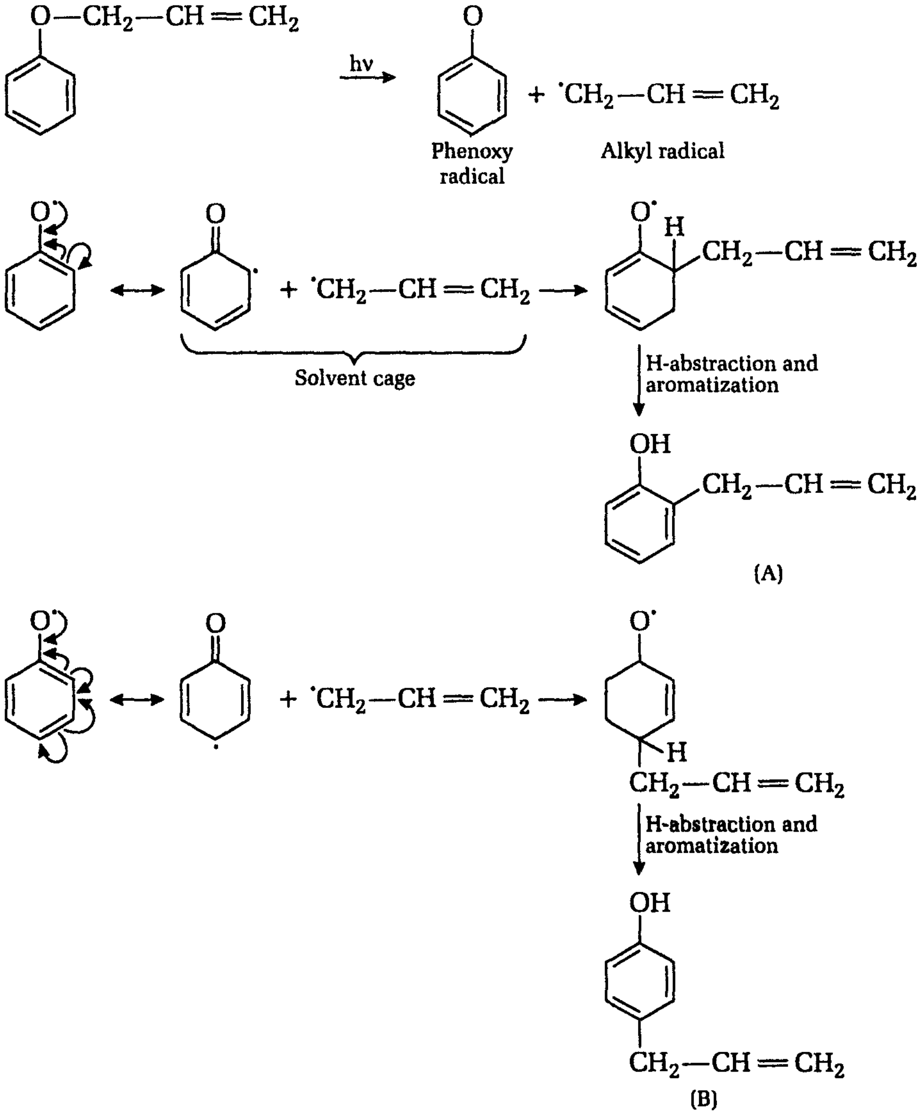


5. "Photochemical degradation of polymers have both good and bad effect on human life". Give example of each in favour of the thought?

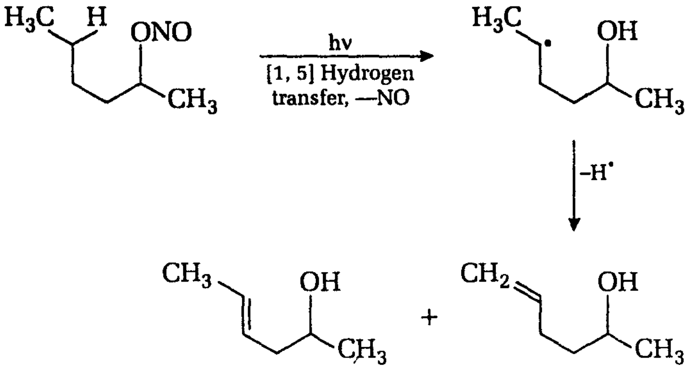
6. Give the structure of all-*trans* retinol and 11-*cis* retinol?

SOLUTIONS

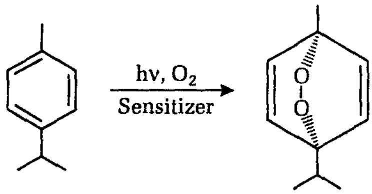
1.



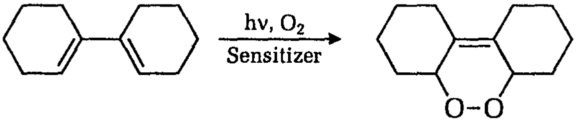
2.



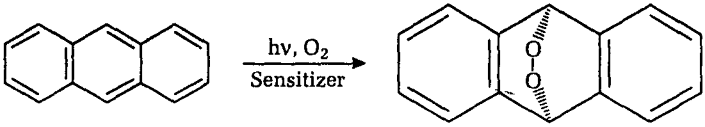
3. (1)



(2)



(3)



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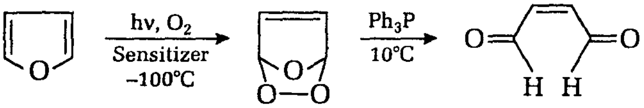
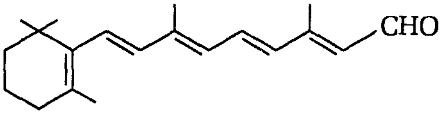
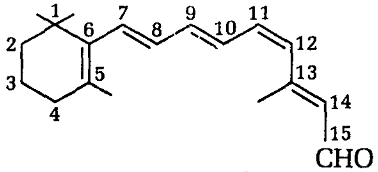


5. The ultra-violet and other short wave-length radiations causes skin cancer in human beings by degrading DNA polymer. While degrading plastic polymer to make them bio-degradable is useful. Thus photochemical degradation is helpful as well as harmful for living beings.

6.



All trans retinol



11-*cis* retinol

* * *

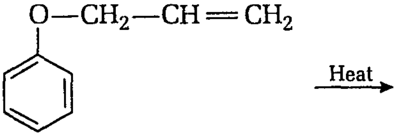
APPENDIX

(FEW QUESTIONS FREQUENTLY ASKED IN EXAMINATIONS)

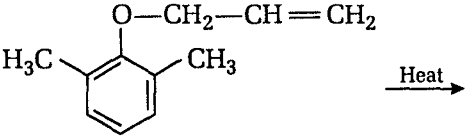
(A) PERICYCLIC REACTIONS

1. Write short note on classification of pericyclic reactions.
2. Discuss Molecular Orbital Symmetry and Classification of Pericyclic Reactions.
3. Discuss Frontier Molecular Orbital (F.M.O.) method for pericyclic reactions. What are electrocyclic reactions? Drawing correlation diagram, describe the conrotatory and disrotatory interconversion of cyclobutene and butadiene.
4. Discuss Frontier Molecular Orbital (F.M.O.) method of analysing electrocyclic reactions. Derive selection rules for electrocyclic reactions.
5. What are electrocyclic reactions? Drawing correlation diagram discuss disrotatory and conrotatory interconversion of cyclobutene and butadiene. Support the results of correlation diagram by F.M.O. theory.
6. Explain 'Conrotatory' and 'Disrotatory' processes in relation to opening of cyclobutane ring.
7. Discuss Frontier Molecular Orbital (F.M.O.) method of analysing cyclic addition reactions. Derive selection rules for cyclic addition reactions.
8. What are suprafacial and antarafacial processes in sigmatropic reactions?
9. Give the products of following reactions and discuss the mechanism involved.

(i)



(ii)

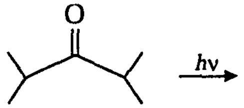


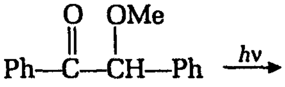
10. Write short note on Claisen rearrangement.
11. Explain mechanism of Claisen rearrangement and give its synthetic importance.
12. Describe Cope or Claisen rearrangement in detail.

(B) ORGANIC PHOTOCHEMISTRY

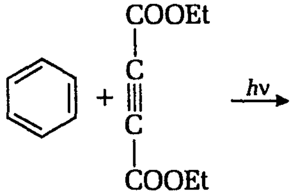
1. Write note on significance of energy transfer in organochemical transformations.
2. Discuss Jablonski diagram.
3. Discuss mode of dissipation of energy in photochemistry.
4. What are photochemical reactions? Describe rate constant of reactions alongwith its determination and types of photochemical reactions.
5. Describe photochemical reactions and discuss the effect of light intensity on the rate of photochemical reactions.
6. What is meant by photochemical reactions. How are they classified? Discuss the effect of light intensity on the rate of photochemical reactions.
7. Write short notes on following :
   (a) Interaction of electromagnetic radiation of matter
   (b) Actinometry
   (c) Quantum yields
8. Write notes on :
   (a) Gas phase photolysis
   (b) Transfer of excitation energy in photochemical reactions
   (c) Fate of excited molecule
9. Describe the rate constant and life times of reactive energy state. Discuss the determination of rate constant of reactions.
10. Discuss photochemistry of , 1, 3-butadiene.
11. Discuss di-π methane rearrangement in 1, 4-pentadiene and 3-phenylalkenes.
12. Define intramolecular cycloaddition reactions with the help of suitable examples.
13. Define 1, 4- and 1, 5-dienes. In addition to it explain the rearrangement of 1, 4- and 1, 5-dienes.
14. Discuss the photochemistry of rearrangements of 1, 4- and 1, 5-dienes with suitable examples.
15. Write the intramolecular reaction of olefinic bond in geometrical isomerism and cyclization reactions.
16. Write notes on :
   (a) Mechanism of Norrish type I and type II reactions.
   (b) Photochemistry of cyclic ketones.
17. Describe intramolecular cycloaddition of carbonyl compounds in dimerization and oxetane formation.
18. Discuss the photochemistry of carbonyl compounds in β, γ- unsaturated and α, β-unsaturated compounds.
19. Discuss photochemistry of carbonyl compounds in cyclic and acyclic compounds.
20. Write notes on :
   (a) Photosensitization (b) Photochemistry of stilbene.

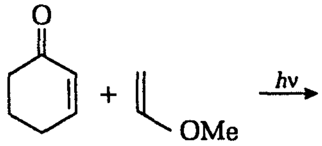
21. Describe the photochemistry of aromatic compounds in isomerizations and substitutions.
22. Describe the photochemistry of aromatic compounds in additions and substitutions.
23. Write short notes on any three of following :
    (a) Photofries rearrangements
    (b) Singlet molecular oxygen reactions
    (c) Photochemical formation of smog
    (d) Barton reaction
24. Write short note on :
    (a) Photofries reactions of anilides
    (b) Photochemistry of vision
    (c) Photodegradation of polymers.
25. Write the products formed in following photochemical transformations :

(a) 

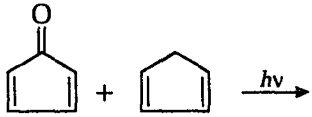
(b) 

$Ph-\overset{\overset{O}{\|}}{C}-\overset{\overset{OMe}{|}}{C}H-Ph \xrightarrow{h\nu}$

(c) 

(d) 

26. Predict with proper discussion the products of following photochemical transformations :

(a) 

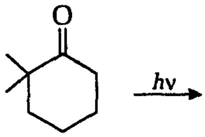
(b) $(C_6H_5)_2-C=O+CH_3-CH=CH-CH_3 \xrightarrow{h\nu}$

(c) $C_6H_5COC_6H_5+CH_3CHOHCH_3 \xrightarrow{h\nu}$

(d) $CH_3COCH_2CH_2CH_3 \xrightarrow{h\nu}$

27. Predict the product of following photochemical transformations. Interpret with proper mechanism :

(a) $C_6H_5CH=CH-C_6H_5 \xrightarrow{h\nu}$

(b) 

(c) $(C_6H_5)_2C=O+(CH_3)_2C=CH_2 \xrightarrow{h\nu}$

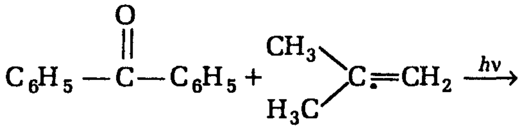
28. Indicate the products that could be formed on the irradiation of following compounds. Give the out line of mechanism of the formation of these products :

(a) $\underset{\text{1, 3-Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} \xrightarrow[\text{Benzophenone}]{h\nu}$

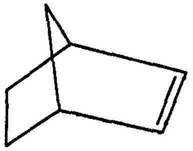
(b) $C_6H_5{-}CH{=}CH{-}C_6H_5 \xrightarrow{h\nu}$

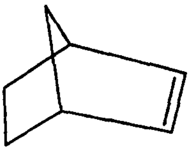
(c) $C_6H_5COC_6H_5 \xrightarrow[\text{Isopropyl alcohol}]{h\nu}$

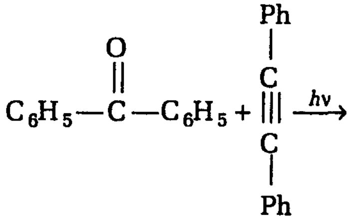
29. Complete the following ıəactions :

(a) 

$$C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5 + \begin{matrix}CH_3\\H_3C\end{matrix}\!\!>C{=}CH_2 \xrightarrow{h\nu}$$

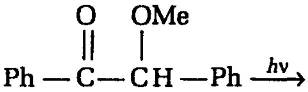
(b)  $+ CH_3COCH_3 \xrightarrow{h\nu}$

(c)  $+ C_6H_5COC_6H_5 \xrightarrow{h\nu}$

(d) 

$$C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5 + \begin{matrix}Ph\\|\\C\\|||\\C\\|\\Ph\end{matrix} \xrightarrow{h\nu}$$

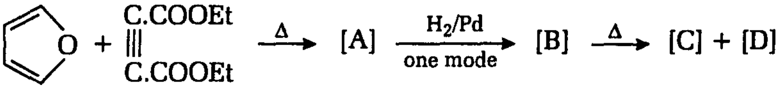
30. Complete the following reactions :

(a) 

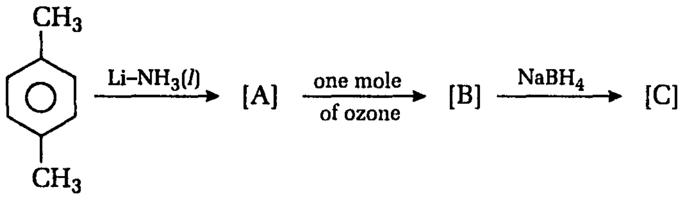
$$Ph-\overset{\overset{O}{\|}}{C}-\overset{\overset{OMe}{|}}{C}H-Ph \xrightarrow{h\nu}$$

(b)  $+H_5C_2OOC{-}C{\equiv}C{-}COOC_2H_5 \xrightarrow{h\nu}$

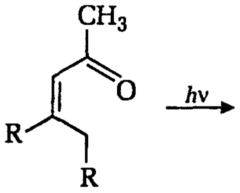
31. Complete the following reactions and name of reaction at each step (where it is possible) :

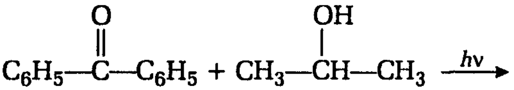
(a) 

$$\text{O} + \begin{matrix}C.COOEt\\|||\\C.COOEt\end{matrix} \xrightarrow{\Delta} [A] \xrightarrow[\text{one mode}]{H_2/Pd} [B] \xrightarrow{\Delta} [C] + [D]$$

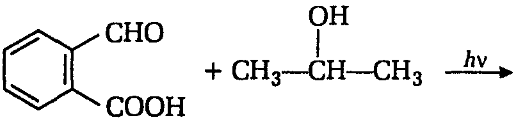
(b) 

32. Complete the following reactions and give their mechanism.

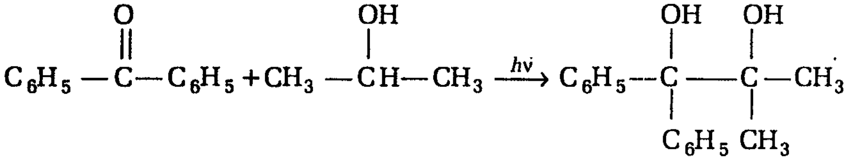
(a) 

(b) 

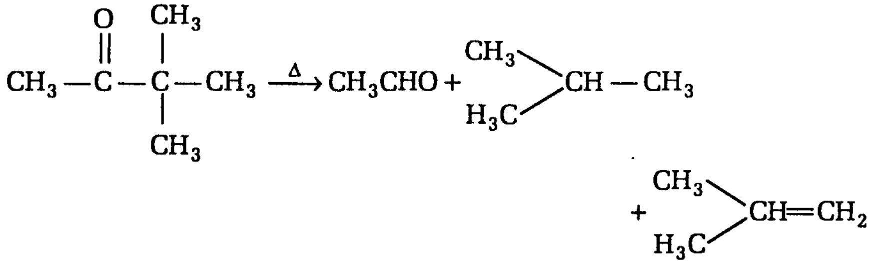
$C_6H_5-\overset{\overset{\large O}{\|}}{C}-C_6H_5 + CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_3 \xrightarrow{h\nu}$

(c) 

33. Discuss the mechanism of following reactions :

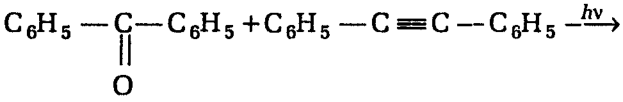
(a) 

$C_6H_5-\overset{\overset{\large O}{\|}}{C}-C_6H_5+CH_3-\overset{\overset{\large OH}{|}}{C}H-CH_3 \xrightarrow{h\nu} C_6H_5-\underset{\underset{\large C_6H_5}{|}}{\overset{\overset{\large OH}{|}}{C}}-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large OH}{|}}{C}}-CH_3$

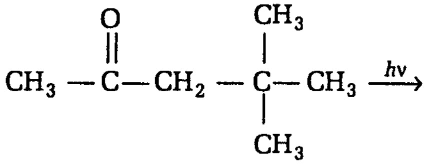
(b) 

$CH_3-\overset{\overset{\large O}{\|}}{C}-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3 \xrightarrow{\Delta} CH_3CHO + (CH_3)(H_3C)CH-CH_3 + (CH_3)(H_3C)CH{=}CH_2$

34. Complete the following reactions and give their mechanism also.

(a) 

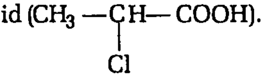
$C_6H_5-\underset{\underset{\large O}{\|}}{C}-C_6H_5+C_6H_5-C\equiv C-C_6H_5 \xrightarrow{h\nu}$

(b) 

$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_2-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3 \xrightarrow{h\nu}$

TABLES

Table 1. Some Common Greek Alphabets

Greek alphabets are generally used to denote physical constants. They are also of use in indicating positions of substituents in trival nomenclature of organic compounds, *e.g.*, α-chloropropionic acid  $(CH_3—\underset{Cl}{\underset{|}{C}}H—COOH)$. Now a days, positions of substituents are preferably indicated by the Arabian numerals 1, 2, 3, ... etc.

Greek name	Greek letter	Greek name	Greek letter
1. Alpha	α	14. Mu	μ
2. Beta	β	15. Nu	ν
3. Chi	χ	16. Omega (small)	ω
4. Gamma	γ, Γ	17. Omega (capital)	Ω
5. Delta (small)	δ	18. Omicron	ο
6. Delta (capital)	Δ	19. Pi	π
7. Epsilon	ε	20. Phi	φ
8. Eta	η	21. Psi	ψ
9. Iota	ι	22. Rho	ρ
10. Kappa (small)	κ	23. Sigma	σ
11. Kappa (capital)	K	24. Tau	τ
12. Lambda (small)	Λ	25. Xi	ξ
13. Lambda (capital)	λ	26. Zeta	ζ

Table 2. Some Basic SI* Units

Quantity	Unit	Symbol
1. Length	meter	m
2. Mass	kilogram	kg
3. Time	second	S
4. Electrical current	ampere	A
5. Temperature	kelvin	K
6. Amount of substance	mole	mol
7. Angle in plane	radian	rad
8. Katalytic amount	katal	kat
9. Luminous intensity	condela	Cd

* **System International *d* Unit** was approved as international system of units by General conference of weight and measures in 1960 and is being used since then all over the world.

Table 3. Some Derived SI Units*

Quantity	Unit	Symbol
1. Temperature	Degree celsius	°C
2. Pressure	Pascal	Pa
3. Energy	Joule	J
4. Frequency	Hertz	Hz
5. Force	Newton	N
6. Electric charge	Coulomb	C
7. Electrical potential	Volt	V
8. Electrical resistance	Ohm	Ω
9. Power	Watt	W

* Derived S.I. units are obtained by appropriate combinations of basic S.I. units.

Table 4. Some Important Submultiples and Multiple*

Quantity	Prefix	Symbol
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a
10^{-21}	zepto	z
10^{-24}	yocto	y
10^{1}	deca	da
10^{2}	hecto	h
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G
10^{12}	tera	T
10^{15}	peta	P
10^{18}	exa	E
10^{21}	zetta	Z
10^{24}	yotta	Y

* Submultiples and multiples are used as prefixes to express too small or too large quantities to avoid writting too many zeros. For example, 0.000015 mol is written as 15 μ mol.

Table 5. Some Non-SI Units in use

Unit	Symbol	Value of unit
1. Angstrom	Å	10^{-10} m or 10^{-8} cm, 10^{-4} μ
2. Atmospheric	atm	760 mm Hg
3. Calorie	cal	4.184 J
4. Dyne	dyn	10^{-5} N
5. Erg	erg	10^{-7} J
6. Gauss	G	10^{-4} T (testa)
7. Litre*	l	10^{-3} m^3 or dm^3
8. Micron	μ	10^{6} m
9. Millimicron	m μ	10^{9} m or nm

* 1 litre = 10^{-3} m^3 = 1 dm^3 (dm^3 = cubic decimetre)

1 milititre = 10^{-6} m^3 = 1 cm^3 (cm^3 = cubic centimeter)

1 microlitre = $10^{-9}m^3$ = 1 mm^3 (mm^3 = cubic mililitre)

A litre is the volume occupied by 1 kg of pure water at 4°C and 760 mm Hg pressure.

Units of mass other than basic kg unit are gram (g), μg and mg.

Unit of time other the second are minute, hour and year.

Unit of pressure other than pascal (Pa) is kilopascal (kPa)

$$1 \text{ Pa} = \text{N/m}^2$$

$$1 \text{ kPa} = 7.5 \text{ mm Hg pressure}$$

Table 6. Conversion Tables

		(A) Lengths		
(i)	1 Centimeter	= 0.3937 inch;	1 inch	= 2.5400 centimeters
(ii)	1 meter	= 3.2808 feet;	1 foot	= 0.30480 meter
(iii)	1 meter	= 1.09361 yards;	1 yard	= 0.91440 meter
(iv)	1 kilometer	= 0.62137 mile;	1 mile	= 1.60934 kilometer
		(B) Area		
(i)	1 sq. centimeter	= 0.1550 sq. inch;	1 sq. in	= 6.4516 sq. cm
(ii)	1 sq. meter	= 10.7638 sq. ft;	1 sq. ft	= 0.9290 sq. m
(iii)	1 sq. meter	= 1.1960 sq. yds;	1 sq. yd.	= 0.83613 sq. m
(iv)	1 sq. km	= 0.38610 sq. miles;	1 sq. mile	= 2.5900 sq. m.
(v)	1 hectare	= 2.47105 acres;	1 acre	= 0.40469 hectare
		(C) Volume		
(i)	1 cubic cm (c.c)	= 0.061024 cubic inch;	1 cubic inch	= 16.387 c.c
(ii)	1 cubic meter	= 35.3144 cubic feet;	1 cubic feet	= 0.028317 m
(iii)	1 cubic meter	= 1.3079 cubic yds	1 cubic yd	= 0.7645 cubic meter

Table 7. Some Mathematical Signs and Symbols

(i)	$=$	Equal to
(ii)	$\cong$	Approximately equal to
(iii)	$\equiv$	Identical to
(iv)	$\neq$	is not equal to
(v)	$>$	Greater than
(vi)	$>>$	Very-very greater than
(vii)	$<$	Lesser than
(viii)	$<<$	Very-very lesser than
(ix)	$\geq$	Greater than or equal to
(x)	$\leq$	Lesser than or equal to
(xi)	Σ	Sigma (sum of)
(xii)	$\pm$	Plus or minus
(xiii)	$\bar{x}$	Average value of x
(xiv)	$\propto$	Directly proportionl to
(xv)	∞	Infinity

SOME MATHEMATICAL OPERATIONS

(A) Exponential Numbers

An exponent indicates that how many times a number is multiplied by itself. In dcimal system, exponential numbers are expressed with powers of 10 *e.g.*,

$$56000 = 56 \times 10^{3}$$

$$0.00056 = 5.6 \times 10^{-4}$$

Some properties of exponents are as decribed below :

(1) When powers of 10 are multiplied, exponents are added :

$$10^2 \times 10^2 = 10^{2+2} = 10^4$$

$$(4.0 \times 10^2)(3.0 \times 10^4) = (4.0 \times 3.0) \times 10^{2+4} = 12 \times 10^6$$

(2) When powers of 10 are divided, exponents are subtracted

$$\frac{10^6}{10^2} = 10^{6-2} = 10^4$$

$$\frac{3.6 \times 10^7}{1.8 \times 10^{-2}} = \frac{3.6}{1.8} \times 10^{7-(-2)} = 2.0 \times 10^9$$

(3) When exponential numbers are added or subtracted, powers of 10 must be same :

(a) $3.26 \times 10^3 + 1.74 \times 10^4 = 3.26 \times 10^3 + 17.4 \times 10^3 = 20.66 \times 10^3$

(b) $5.6 \times 10^5 - 2.2 \times 10^3 = 560 \times 10^3 - 2.2 \times 10^3 = (560 - 2.2) \times 10^3$

$= 557.8 \times 10^3$

(4) To take square root of powers of 10, exponents of 10 are divided by 2 and to take cube root, the exponent is divided by 3. If required, the number is rewritten so that the exponent of 10 is perfectly divisible by 2 (for square root) and by 3 (for cube root) :

Square root of $9.0 \times 10^6 = (9 \times 10^6)^{1/2} = 3 \times 10^3$

Cube root of $8 \times 10^{-12} = (8 \times 10^{-12})^{1/3} = 2 \times 10^{-4}$

Square root of $1.6 \times 10^5 = (16 \times 10^4)^{1/2} = 4 \times 10^2$

Square root of $2.5 \times 10^{-7} = (25 \times 10^{-8})^{1/2} = 5 \times 10^{-4}$

(B) Logarithms

The logarithms of a number is the power to which a base must be raised to the given number. There are two bases which are commonly used in logarithms. These bases are 10 and e ($e = 2.71828$ ...). The logarithms to base 10 are called common logs (abbreviated as log) and the logarithms to base e are known as natural logarithms (abbreviated as log a or ln). Relationship between ln and log is

$$\ln x = 2.303 \log_{10}$$

Common operations with logarithms are :

(a) Multiplication $\log_{ab} = \log a + \log b$

(b) Division $\log(a/b) = \log a - \log b$

(c) Raising to a power $\log a^n = n(\log a)$

(d) Taking a root $\log(a)^{1/n} = \frac{1}{n}(\log a)$

❑❑❑

SUBJECT INDEX

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COMMON LOGARITHMS $\log_{10} x$

x	0	1	2	3	4	5	6	7	8	9	Δ_m	1	2	3	4	5	6	7	8	9
											++	ADD								
10	.0000	0043	0086	0128	0170	0212					42	4	8	13	17	21	25	29	34	38
						0212	0253	0294	0334	0374	40	4	8	12	16	20	24	28	32	36
11	.0414	0453	0492	0531	0569	0607					39	4	8	12	16	19	23	27	31	35
						0607	0645	0682	0719	0755	37	4	7	11	15	19	22	26	30	33
12	.0792	0828	0864	0899	0934	0969					35	4	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	34	3	7	10	14	17	20	24	27	31
13	.1139	1173	1206	1239	1271	1303					33	3	7	10	13	16	20	23	26	30
						1303	1335	1367	1399	1430	32	3	6	10	13	16	19	22	26	29
14	.1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	30	3	6	9	12	15	18	21	24	27
15	.1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	28	3	6	8	11	14	17	20	22	25
16	.2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	26	3	5	8	10	13	16	18	21	23
17	.2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	25	2	5	7	10	12	15	17	20	22
18	.2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	24	2	5	7	10	12	14	17	19	22
19	.2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	22	2	4	7	9	11	13	15	18	20
20	.3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	21	2	4	6	8	11	13	15	17	19
21	.3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	20	2	4	6	8	10	12	14	16	18
22	.3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	19	2	4	6	8	10	11	13	15	17
23	.3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	18	2	4	5	7	9	11	13	14	16
24	.3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	18	2	4	5	7	9	11	13	14	16
25	.3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	17	2	3	5	7	9	10	12	14	15
26	.4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	16	2	3	5	6	8	10	11	13	14
27	.4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	16	2	3	5	6	8	10	11	13	14
28	.4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	15	2	3	5	6	8	9	11	12	14
29	.4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	15	1	3	4	6	7	9	10	12	13
30	.4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	14	1	3	4	6	7	8	10	11	13
31	.4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	14	1	3	4	6	7	8	10	11	13
32	.5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	13	1	3	4	5	7	8	9	10	12
33	.5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	13	1	3	4	5	6	8	9	10	12
34	.5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	13	1	3	4	5	6	8	9	10	12
35	.5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	12	1	2	4	5	6	7	8	10	11
36	.5563	5573	5587	5599	5611	5623	5635	5647	5668	5670	12	1	2	4	5	6	7	8	10	11
37	.5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	12	1	2	4	5	6	7	8	10	11
38	.5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	11	1	2	3	4	6	7	8	9	10
39	.5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	11	1	2	3	4	6	7	8	9	10
40	.6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	11	1	2	3	4	8	7	8	9	10
41	.6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	10	1	2	3	4	8	6	7	8	9
42	.6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	10	1	2	3	4	8	6	7	8	9
43	.6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	10	1	2	3	4	8	6	7	8	9
44	.6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	10	1	2	3	4	8	6	7	8	9
45	.6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	10	1	2	3	4	8	6	7	8	9
46	.6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	9	1	2	3	4	8	5	6	7	8
47	.6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	9	1	2	3	4	8	5	6	7	8
48	.6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	9	1	2	3	4	4	5	6	7	8
49	.6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	9	1	2	3	4	4	5	6	7	8

COMMON LOGARITHMS $\log_{10} x$

x	0	1	2	3	4	5	6	7	8	9	Δ_m	1	2	3	4	5	6	7	8	9
											++	ADD								
50	.6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	9	1	2	3	4	4	5	6	7	8
51	.7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	8	1	2	2	3	4	5	6	6	7
52	.7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	8	1	2	2	3	4	5	6	6	7
53	.7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	8	1	2	2	3	4	5	6	6	7
54	.7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	8	1	2	2	3	4	5	6	6	7
55	.7404	7412	7419	7427	7433	7443	7451	7459	7466	7474	8	1	2	2	3	4	5	6	6	7
56	.7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	8	1	2	2	3	4	5	6	6	7
57	.7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	8	1	2	2	3	4	5	6	6	7
58	.7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	8	1	2	2	3	4	5	6	6	7
59	.7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	7	1	1	2	3	4	4	5	6	6
60	.7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	7	1	1	2	3	4	4	5	6	6
61	.7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	7	1	1	2	3	4	4	5	6	6
62	.7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	7	1	1	2	3	3	4	5	6	6
63	.7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	7	1	1	2	3	3	4	5	6	6
64	.8062	8069	8075	8082	8089	8096	8101	8109	8116	8182	7	1	1	2	3	3	4	5	6	6
65	.8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	7	1	1	2	3	3	4	5	6	6
66	.8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	7	1	1	2	3	3	4	5	6	6
67	.8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	6	1	1	2	2	3	4	4	5	5
68	.8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	6	1	1	2	2	3	4	4	5	5
69	.8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	6	1	1	2	2	3	4	4	5	5
70	.8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	6	1	1	2	2	3	4	4	5	5
71	.8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	6	1	1	2	2	3	4	4	5	5
72	.8573	8579	8585	8691	8597	8603	8609	8615	8621	8627	6	1	1	2	2	3	4	4	5	5
73	.8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	6	1	1	2	2	3	4	4	5	5
74	.8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	6	1	1	2	2	3	4	4	5	5
75	.8751	8756	8762	9768	8774	8779	8785	8791	8797	8802	6	1	1	2	2	3	4	4	5	5
76	.8808	8814	8820	8825	8831	8837	8842	8843	8854	8859	6	1	1	2	2	3	4	4	5	5
77	.8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	6	1	1	2	2	3	4	4	5	5
78	.8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	6	1	1	2	2	3	4	4	5	5
79	.8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	6	1	1	2	2	3	4	4	5	5
80	.9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	5	1	1	2	2	3	3	4	4	5
81	.9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	5	1	1	2	2	3	3	4	4	5
82	.9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	5	1	1	2	2	3	3	4	4	5
83	.9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	5	1	1	2	2	3	3	4	4	5
84	.9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	5	1	1	2	2	3	3	4	4	5
85	.9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	5	1	1	2	2	3	3	4	4	5
86	.9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	5	1	1	2	2	3	3	4	4	5
87	.9395	9400	9305	9410	9415	9420	9425	9430	9435	9440	5	0	1	1	2	2	3	3	4	4
88	.9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	5	0	1	1	2	2	3	3	4	4
89	.9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	5	0	1	1	2	2	3	3	4	4
90	.9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	5	0	1	1	2	2	3	3	4	4
91	.9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	5	0	1	1	2	2	3	3	4	4
92	.9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	5	0	1	1	2	2	3	3	4	4
93	.9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	5	0	1	1	2	2	3	3	4	4
94	.9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	5	0	1	1	2	2	3	3	4	4
95	.9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	5	0	1	1	2	2	3	3	4	4
96	.9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	4	0	1	1	2	2	2	3	3	4
97	.9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	4	0	1	1	2	2	2	3	3	4
98	.9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	4	0	1	1	2	2	2	3	3	4
99	.9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	4	0	1	1	2	2	2	3	3	4

ANTILOGARITHMS 10^x

x	0	1	2	3	4	5	6	7	8	9	Δ_m	1	2	3	4	5	6	7	8	9
											++	ADD								
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	2	0	0	1	1	1	1	1	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	2	0	0	1	1	1	1	1	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	2	0	0	1	1	1	1	1	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	2	0	0	1	1	1	1	1	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	3	0	1	1	1	1	2	2	2	3
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	3	0	1	1	1	1	2	2	2	3
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	3	0	1	1	1	1	2	2	2	3
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	3	0	1	1	1	1	2	2	2	3
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	3	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	3	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	3	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	3	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	3	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	3	0	1	1	1	2	2	2	2	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	3	0	1	1	1	2	2	2	2	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	3	0	1	1	1	2	2	2	2	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	3	0	1	1	1	2	2	2	2	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	4	0	1	1	2	2	2	3	3	4
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	4	0	1	1	2	2	2	3	3	4
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	4	0	1	1	2	2	2	3	3	4
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	4	0	1	1	2	2	2	3	3	4
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	4	0	1	1	2	2	2	3	3	4
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	4	0	1	1	2	2	2	3	3	4
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	4	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	4	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	4	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	4	0	1	1	2	2	2	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	4	0	1	1	2	2	2	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	4	0	1	1	2	2	2	3	3	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	4	0	1	1	2	2	2	3	3	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	5	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	5	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	5	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	5	1	1	2	2	3	3	4	4	5
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	5	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	5	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	5	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	6	1	1	2	2	3	4	4	5	5
.38	2399	2404	2410	2415	2421	2427	2432	2338	2443	2449	6	1	1	2	2	3	4	4	5	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	6	1	1	2	2	3	4	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	6	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	6	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	6	1	1	2	2	3	4	4	5	5
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	6	1	1	2	2	3	4	4	5	5
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	6	1	1	2	2	3	4	4	5	5
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	7	1	1	2	3	3	4	5	6	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	7	1	1	2	3	3	4	5	6	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	7	1	1	2	3	3	4	5	6	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	7	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	7	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS 10^x

x	0	1	2	3	4	5	6	7	8	9	Δ_m	1	2	3	4	5	6	7	8	9
											++	ADD								
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	7	1	1	2	3	4	4	5	6	6
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	8	1	2	2	3	4	5	6	6	7
.52	3311	3319	3327	3334	3342	3550	3357	3365	3373	3381	8	1	2	2	3	4	5	6	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	8	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	8	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	8	1	2	2	3	4	5	6	6	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	8	1	2	2	3	4	5	6	6	7
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	9	1	2	3	4	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	9	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3926	3945	3954	3863	3972	9	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	9	1	2	3	4	5	5	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	10	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	10	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	10	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	10	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	10	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	11	1	2	3	4	5	7	8	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	11	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4883	11	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	11	1	2	3	4	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	12	1	2	4	5	6	7	8	10	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	12	1	2	4	5	6	7	8	10	11
.72	5248	560	5272	5284	5297	5309	5321	5335	5346	5358	12	1	2	4	5	6	7	8	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	12	1	2	4	5	6	7	8	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	13	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	13	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	13	1	3	4	5	7	8	9	10	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	14	1	3	4	6	7	8	10	11	13
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	14	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	14	1	3	4	6	7	8	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	15	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	15	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	15	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	16	2	3	5	6	8	10	11	13	14
.84	6918	6934	6950	6996	6982	6998	7015	7731	7047	7063	16	2	3	5	6	8	10	11	13	14
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	16	2	3	5	6	8	10	11	13	14
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	17	2	3	5	7	8	10	12	14	15
.87	7413	7430	7447	7564	7482	7499	7516	7534	7551	7568	17	2	3	5	7	9	10	12	14	15
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	18	2	4	5	7	9	11	13	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	18	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	18	2	4	5	7	9	11	13	14	16
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	19	2	4	6	8	10	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	19	2	4	6	8	10	11	13	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	20	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	20	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	21	2	4	6	8	10	13	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	21	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	22	2	4	7	9	11	13	15	18	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	22	2	4	7	9	11	13	15	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	23	2	5	7	9	11	14	16	18	21