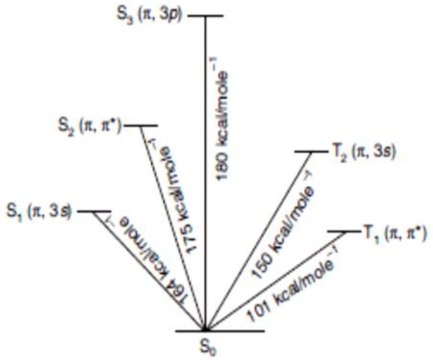
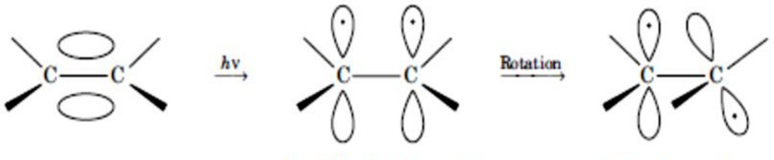
Photochemistry of Alkenes

Electronic absorption spectra of simple alkenes consist of an intense broad band from 140 nm to 190 nm (for ethylene) with absorption threshold of 200 nm (for ethylene) to 240 nm (for 2, 3-dimethyl-2-butene). The diffuse bands in the spectrum of ethylene are attributed to a π → π* transition. The absorption at 174 nm for ethylene is the first singlet Rydberg transition. This Rydberg transition is due to the 2pπ → 3s excitation. The excited states of alkenes are complex because the different electronic states have different electronic configuration. Although the nature of most electronic states of alkenes is not known in detail, some are well understood. Alkenes have two low-lying excited singlet states: The 1[2pπ, 3s] Rydberg state and the 1[π, π*] valence state. Calculation indicates that there is apparently an additional state, i.e., the (2pπ, 3p) Rydberg state. The lowest triplet state is practically pure 3(π, π*) and T2 is essentially a pure Rydberg 3[2pπ, 3s] state.



The singlet-triplet splitting (S-T splitting) is generally large for alkenes (ethylene 70 kcal/mole–1). As a result, ISC is slow and inefficient. Therefore, direct irradiation of alkenes induces singlet excited state reactions, and sensitisation is required for triplet state reactions. Excitation of a planar alkene like ethylene results initially in the formation of planar excited state molecule according to the Franck-Condon principle. The initially formed planarexcited state π, π* species, wherever as a singlet or a triplet relaxes by rotation of the terminal group—methylene in the case of ethylene—through 90° around the central bond to give the lowest energy conformation possible. Thus, the molecule can rotate from the planar configuration, produced by the Frank-Condon excitation, to reach an energy minimum. This energy minimum is arrived at by rotation about the central bond so that the methylene groups are at right angles to each other so relieving the unfavourable interactions between the singly filled orbitals on the carbon atoms.



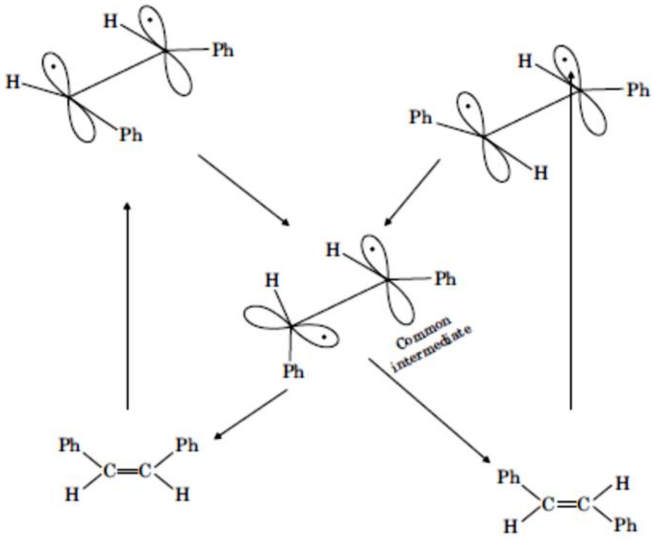
Frank-Condon planar state

Relaxed twisted state

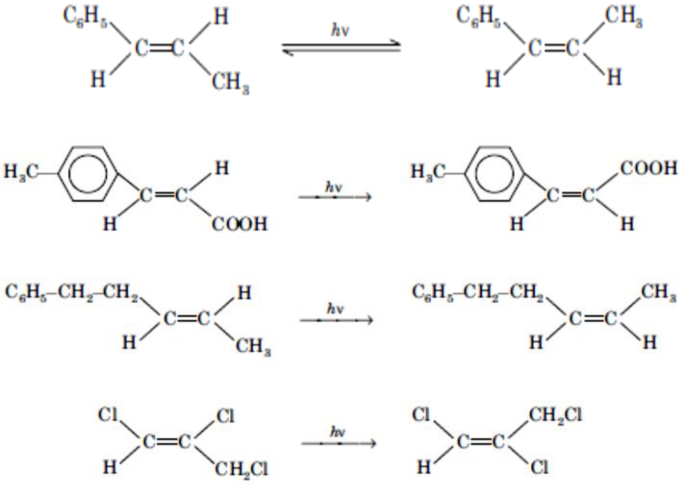
Cis-Trans Isomerization of Alkenes

Direct irradiation for the simplest alkenes (whose λmax is below 200 nm) is difficult to achieve as a result of the high energy absorptions. However, with more substituted alkenes the UV absorptions are pushed above 200 nm and so direct excitation can be more readily achieved. The most common substrate for isomerisation is the stilbenes. The irradiation of either cis- or trans- stilbene at 313 nm results in the formation of 93% cis- and 7% trans- stilbenes. No matter how long, within reason, the irradiation is continued the ratio of products does not alter and such a state is referred to as a photostationary state. The composition of the photostationary state is determined by the excitation co-efficient of the two isomers at the exciting wavelength. For most alkenes (εmax) trans is greater than (εmax) cis. Therefore, in an equilibrium mixture more molecules of trans than cis isomer will reach the excited singlet state, followed by rapid relaxation to S0. At photostationary state the rate of cis → trans and trans → cis isomerisation becomes equal, no change in the composition of the reaction mixture occurs upon further irradiation.

The energy of a π → π* excited species is a function of the angle twist about the carbon carbon σ (sigma) bond, as mentioned earlier, and trans-to cis-isomerisation is believed to be effected by distortion of the trans- excited state initially produced, to an excited state common to both cis- and trans isomers. This excited state is termed as a phantom state. The mechanism by which the cis-trans isomerisation occurs, in terms of the sample model involves the excitation of an electron to a planar excited state which subsequently relaxes to the twisted state. A simple representation is given in the figure. A small activation energy of 2 kcal/mole is required to twist the planar trans singlet to the twisted singlet state. Decay from this twisted state can give either cis or trans stilbene.



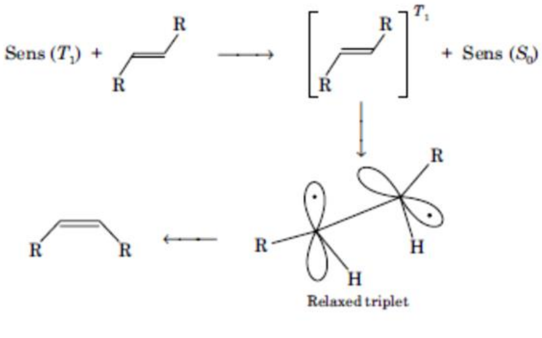
However, as mentioned earlier the trans form absorbs more light at the exciting wavelength (εmax trans = 16300) than does the cis form (εmax cis = 2880) and consequently the trans isomer is converted almost completely into the cis. The synthetic utility value of trans-cis isomerisation lies in the fact that the more stable alkene can be readily converted into the less stable alkene. Some examples of the result of direct irradiation of alkenes are shown below



Sensitised cis-trans isomerisation

Sensitised cis-trans isomerisation of an alkene can be brought about by the use of a triplet sensitiser such as ketone. The sensitised isomerisation of stilbene is a typical example. The composition of the photostationary state of the sensitised isomerisation varies with the energy of the sensitiser employed. In this process if the donor species fulfils the conditions for effective sensitisation and its triplet energy is greater than that of either of the geometrical isomers then triplet energy transfer to both cis and trans isomers and isomerisation takes place. The initially formed cis and trans triplet excited species undergo distortion to a common phantom triplet which, on collapsing to the ground state (S0) affords a mixture of isomers. Because the sensitiser can excite both isomers, the proportion of cis-trans isomer in the photostationary state from a sensitised reaction is lower than that obtained from direct irradiation. This is in contrast to the unsensitised isomerisation. Sensitisers of high energy give photostationary state with approximately the same composition of isomers (55% cis), while direct photolysis results in a higher proportion of cis isomer (93%) in case of stilbene. As the sensitiser energy is reduced anomalous results are observed.

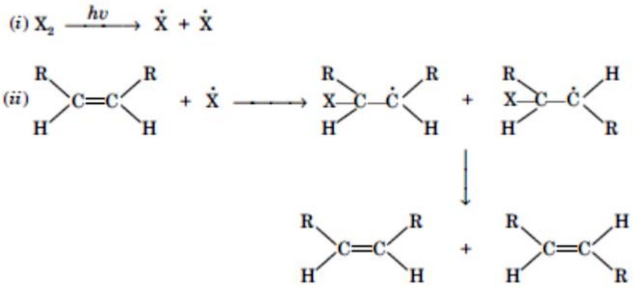
$$\text{Sens}(S_0) \xrightarrow{h\nu} \text{Sens}(S_1) \xrightarrow{\text{ISC}} \text{Sens}(T_1)$$



The composition of photostationary state depends very much on the triplet energy sensitiser. With sensitiser having triplet energy above 60 kcal/mole, cis-trans ratio is slightly more than one but a range of sensitiser having triplet energy of 52 to 58 kcal/mole offered much higher cis-trans ratio in the photostationary state. The higher cis-trans ratio in this region results from the fact that energy required for excitation of trans isomer is less than for excitation of cis isomer. The sensitiser having triplet energies in the range of 52 to 58 kcal/mole, selectively excites the trans isomer. Since the rate of trans-cis conversion is increased, the composition of the photostationary state is then enriched in cis isomer.

Photochemical cis-trans isomerisation in the presence of halogens

Sometimes photochemical cis-trans isomerisation may also take place in the presence of halogens. It appears that under these conditions there is a photochemical product of halogen atoms which adds to the alkene yielding a radical. Elimination of halogen from this radical yield a constant ratio of cis and trans isomers.



Photochemistry of Conjugated Dienes

Conjugated dienes can give the following type of photochemical reactions:

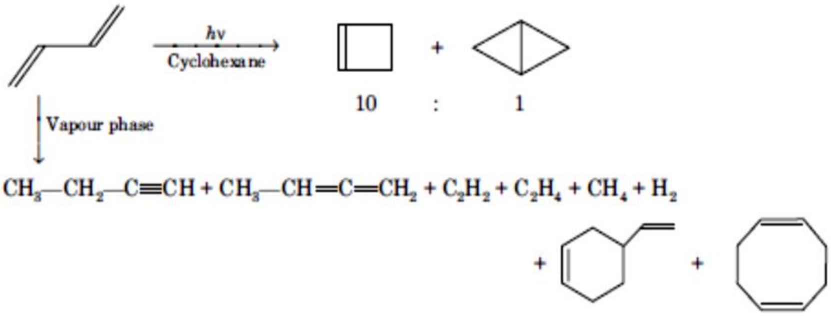
Cis-trans isomerisation

Sigmatropic shift

Disrotatory electrocyclic ring closure

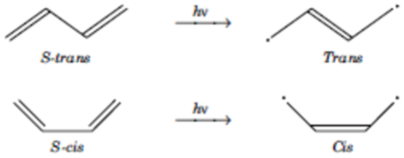
Intramolecular x [2 + 2] cycloaddition

The above photochemical reactions of conjugated dienes depend to a large extend on the excited state population, and on the phase in which reaction is performed. Singlet excitation generally leads to intramolecular process (i.e., disrotatory electrocyclic ring closure and sigmatropic rearrangement) whereas dimerisation and addition reactions are more common from the triplet excited state. Reaction in the gas phase at low pressure often leads to greater fragmentation than in solution. The solution phase photolysis of butadiene leads to cyclobutene and bicyclobutane, whereas in the vapour phase (gas phase) 1-butyne, methylallene, acetylene, ethylene, methane, hydrogen and polymeric materials are produced.

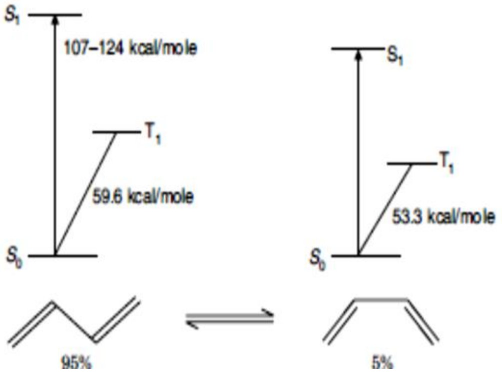


Intramolecular [2 + 2] Cycloaddition Reaction

1, 3-Butadiene exists in solution as a rapidly equilibrating mixture of S-transoid (95%) and S-cisoid (5%) conformers. Irradiation of butadiene promotes an electron from HOMO to LUMO (ψ2 → ψ3*) which results in the increased bonding between C-2 and C-3 at the expense of C-1 and C-2 and C-3 and C-4. Thus, the lower excited states of S-trans and S-cis butadiene should exhibit still larger energy barriers to rotation about the C2—C3 bond because of its double bond character. Thus, conformational character of butadienes are retained in the excited states.

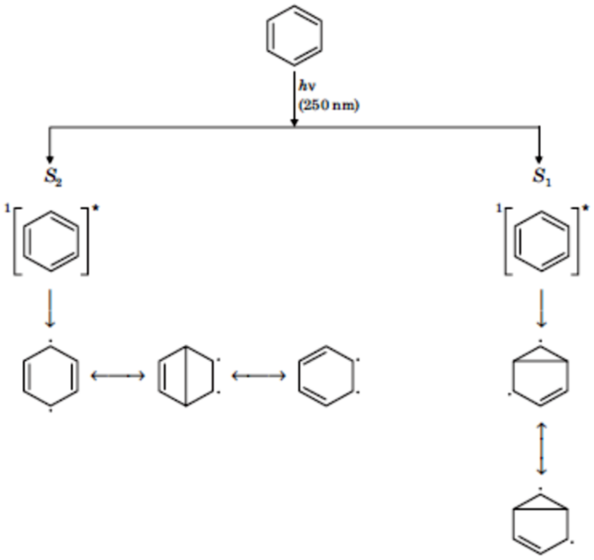


The exact energies of the S1 states are not known, but cisoid S1 probably lies below transoid S1. There is large energy gap between S1 and T1. Also inter system crossing does not take place in this case. The energy gap between S1 and T1 accounts for the fact that inter system crossing does not occur. Direct irradiation of 1, 3-butadiene in solution thus gives rise to chemistry only from the S1 state. The energy of the excited states of butadienes are shown in the Figure.

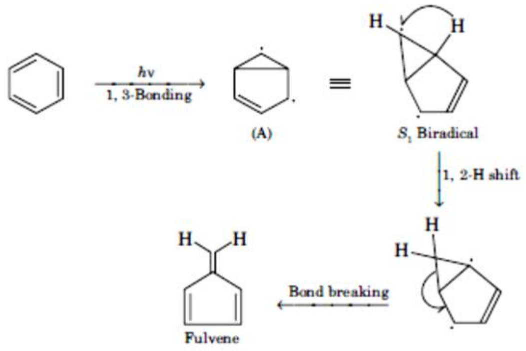


Photoisomerisation of Benzene compounds

Benzene and substituted benzene undergo valence isomerisation by irradiation. Selective excitation into S1 gives preferentially meta and ortho product while excitation into S2 gives para bonded products by valence isomerisation. These processes are described by biradical intermediate for case of visualisation.

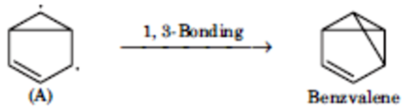


Irradiation of liquid benzene under nitrogen at 254 nm causes excitation to S1 state and the products, benzvalene and fulvene are formed via 1, 3-biradical.

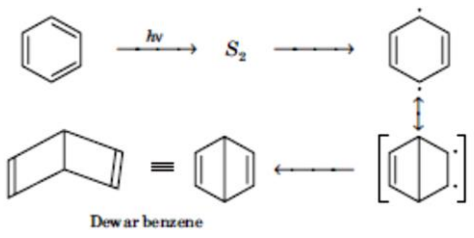


The formation of fulvene can now be considered to arise by reaction of the biradical (A) by a 1, 2-hydrogen migration and bond breaking.

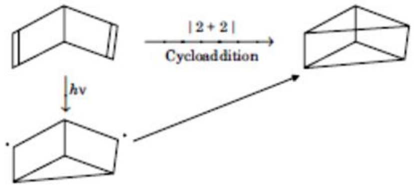
Formation of benzvalene can take place as follows:



Dewar benzene is formed via S2 state upon short wavelength irradiation (205 nm).

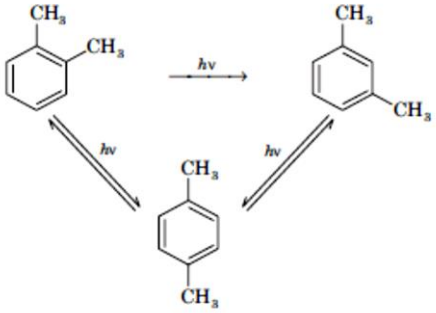


It has been confirmed that Dewar benzene is converted into prismane either by concerted path or by formation of a biradical.



All these strained intermediates are thermally labile and ultimately isomerises into benzenoid compounds.

Monocyclic aromatic compounds undergo remarkable photochemical rearrangements. For example, o-xylene on irradiation gives mixture of o, m and p-xylenes.

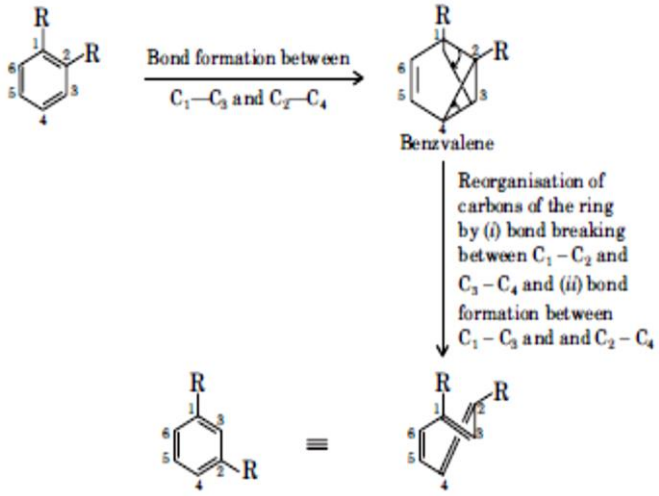


Conversion of o-xylene into m-xylene and m-xylene into p-xylene is due to 1, 2-alkyl group shift. Similarly conversion of o-xylene into p-xylene and vice-versa is due to the 1, 3-alkyl group shift. 1, 2-Alkyl group shift takes place by benzvalene as well as prismane intermediates whereas 1, 3-alkyl group shift takes place only by prismane intermediate.

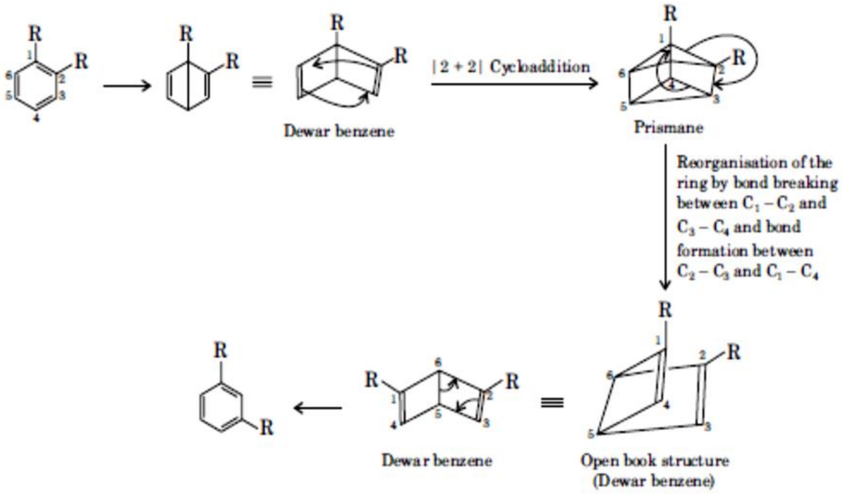
1, 2-Alkyl Shift

1, 2-Alkyl group shift (rearrangement of the atoms in the benzene ring) takes place via formation of benzvalene and prismane as reaction intermediate.

Mechanism of 1, 2-shift via benzvalene intermediate

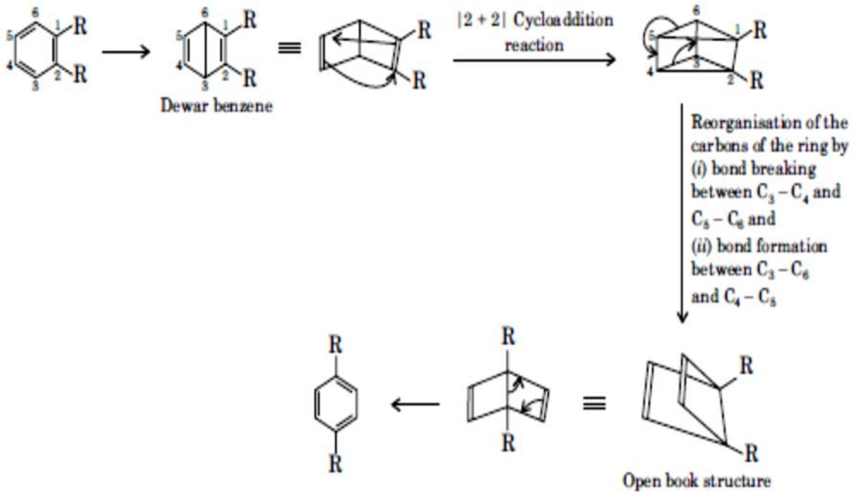


Mechanism of 1, 2-alkyl group shift via prismane intermediate



Mechanism of 1,3 alkyl Shift

1, 3-Alkyl group shift takes place only via formation of prismane as reaction intermediate.



Photoaddition Reactions

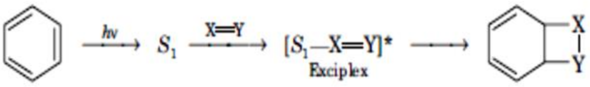
Benzene and its derivatives in the S1 state undergo cycloaddition reactions with various π(pi) systems, specially alkenes, alkynes and dienes. The T1 state of aromatic compounds does not give cycloaddition reactions because the T1 state of aromatic compounds is quenched by the transfer of excitation energy to the alkene. Under certain structural and electronic circumstances, a reverse model, i.e., S1 alkene + S0 arene prevails. Three different modes of cycloaddition reactions have been observed: 1, 2 or ortho, 1, 3 or meta and 1, 4 or para. The 1, 4-addition is the least efficient cycloaddition reaction. These reactions occur either bimolecularly or intramolecularly. Thus, there are atleast four broad mechanistic pathways possible for these reactions. These are as follows:

(i) Interaction of excited aromatic with ground state alkene.
(ii) Interaction of excited alkene with ground state aromatic.

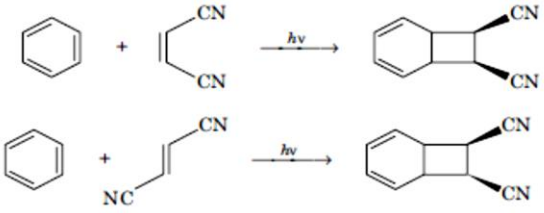
(iii) Formation of biradical intermediate from excited aromatic and reaction of the biradical with alkene to give product. (iv) Involvement of dipolar entities such as (aromatic + • ...... olefin − •) or (aromatic − • ...... olefin + •), obtained either by excitation of charge-transfer complexes pre-existing in the ground state or by electron transfer in an exciplex.

1,2–Cycloaddition Reaction

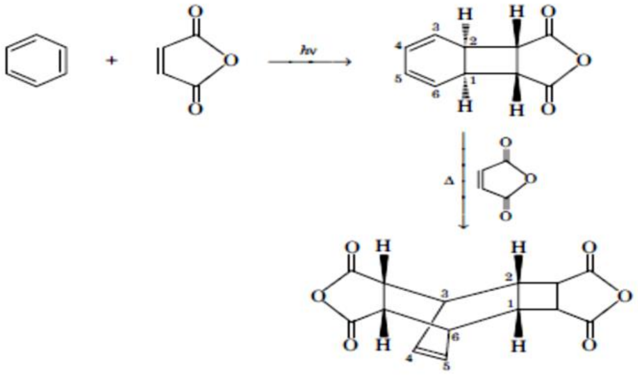
Electron poor alkenes (alkenes having electron withdrawing groups) give 1, 2-addition reaction with arenes in addition to some 1, 4 products. The para product is the secondary product. The formation of the ortho product is generally favoured by donor-acceptor interaction. The more polar the interactions (charge-transfer) in the exciplex, the longer the proportion of ortho and para cycloadditions.



The 1, 2-cycloaddition reactions are concerted reactions. The photocycloaddition of cis and trans-2-butene to benzene in the liquid phase gives the 1, 2-adduct stereospecifically showing that the reaction is concerted reaction. This also confirmed that the product formation is taking place via formation of exciplex.



Irradiation of benzene in the presence of maleic anhydride yields an exo 1, 2-cycloadduct.

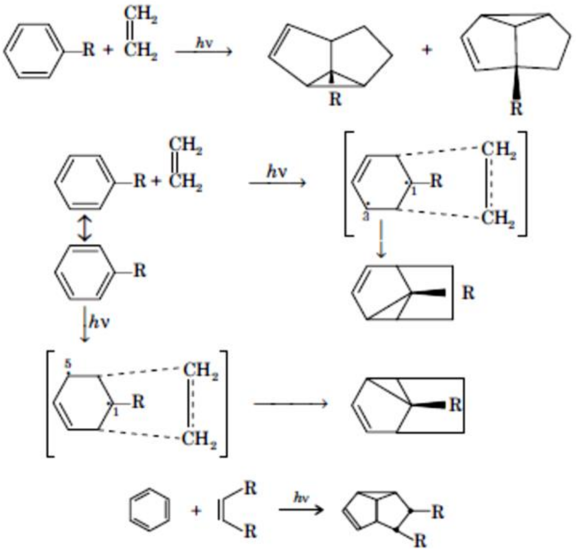


The product formation takes place via S1 state of a charge transfer complex. Exo-1, 2-adduct is a result of a photochemical | 2 + 2 | ortho-cycloaddition reaction followed by a thermal | 4 + 2 | cycloaddition.

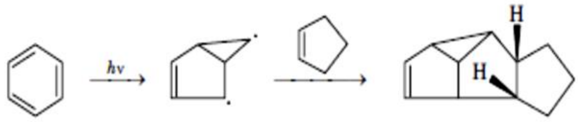
1,3–Photoaddition Reaction

This remarkable process leads to tricyclic system in which an olefinic double bond has added across the meta-positions of a benzene ring.

The hypothetical presentation for 1, 3 addition can be shown as follows:

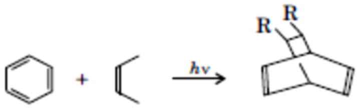


The reaction seems to be restricted to double bonds bearing only alkyl substituents such as 2-butene, norbornene, allene and cyclobutene. It occurs with 254 nm light in both gas phase and liquid phase. It is stereospecific and it involves singlet excited benzene. It is known that neither fulvene nor benzvalene is a precursor. Product formation takes place via formation of prefulvene biradical. In 1, 3-cycloaddition reaction, endo product is the major product

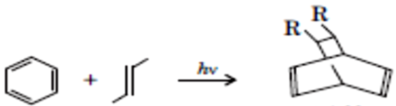


1,4–Photoaddition Reaction

In this reaction olefinic double bond has added across the para-positions of a benzene ring.

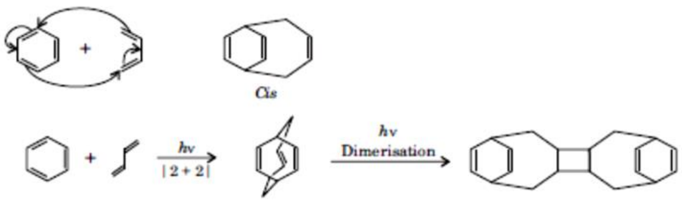


The reaction is concerted and therefore stereospecific and it involves singlet excited state benzene. The reaction is similar to Diels-Alder reaction because benzene behaves as diene in this case.



1, 4-Adduct

Butadiene also gives [4 + 4] cycloaddition reaction with benzene and reaction is stereospecific.



Aromatic Photsubstitution Reaction

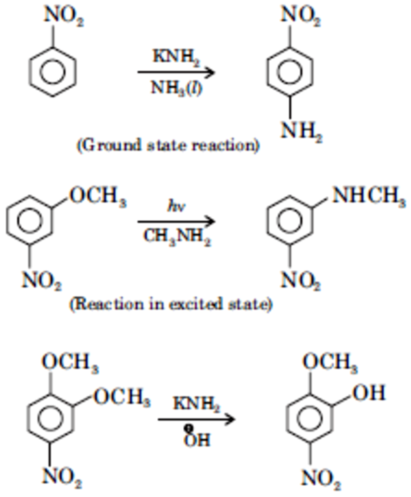
Light-induced substitution in the aromatic compounds can occur either on a ring carbon atom or on an atom of a substituent. These substitution reactions can proceed by heterolytic or radical mechanism. The most common reactions are the heterolytic substitutions which can be classified into two categories:

(i) Type A: In these reactions the orientation rules are different from those obtaining in the ground state.

(ii) (ii) Type B: In these reactions the orientation rules are the same as in the ground state but the process is accelerated by light absorption. All these reactions seem to be functions of the lowest singlet excited state, and many proceed in high quantum yield.

Photonucleophilic Substitution:

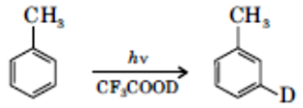
Nitro group is activating group and ortho and para directing group for nucleophilic substitution reactions in the ground state. In the presence of light (i.e., in the excited state) the nitro group is m-directing group.



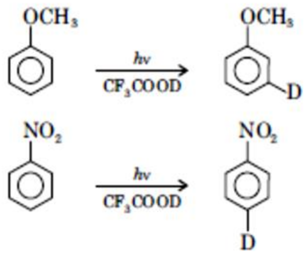
In many cases the cyano group behaves similarly, and analogous reactions are found with substituted naphthalenes.

Photoelectrophilic Substitution:

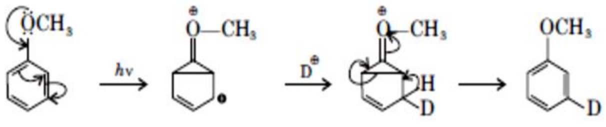
On irradiation in the presence of CF3COOD, toluene gives mainly m-deuterio toluene instead of o-and p-derivatives.



Anisole also gives m-derivative whereas nitrobenzene gives p-derivative



Similarly electron donating group increases electron density at m-position therefore, such groups are m-director for electrophilic substitution reactions.



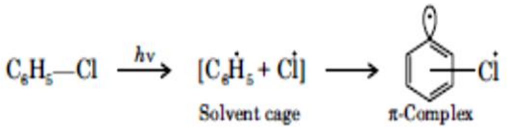
Mechanism of photoelectrophilic substitution

Photoradical Substitution

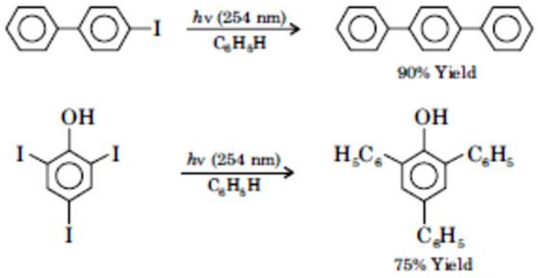
Haloaromatic compounds on irradiation undergo homolysis in ground state to produce radicals which then give rise to products by well-established thermal pathway.

$$Ar + X \xrightarrow{h\nu} \dot{Ar} + \dot{X}$$

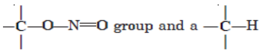
However, when chlorobenzene is excited in the liquid phase, the Ph • and Cl • radicals seems to recombine within the solvent cage generating transient π-chlorobenzene, and isomer of chlorobenzene in which the chlorine atom forms a π complex with phenyl radical.

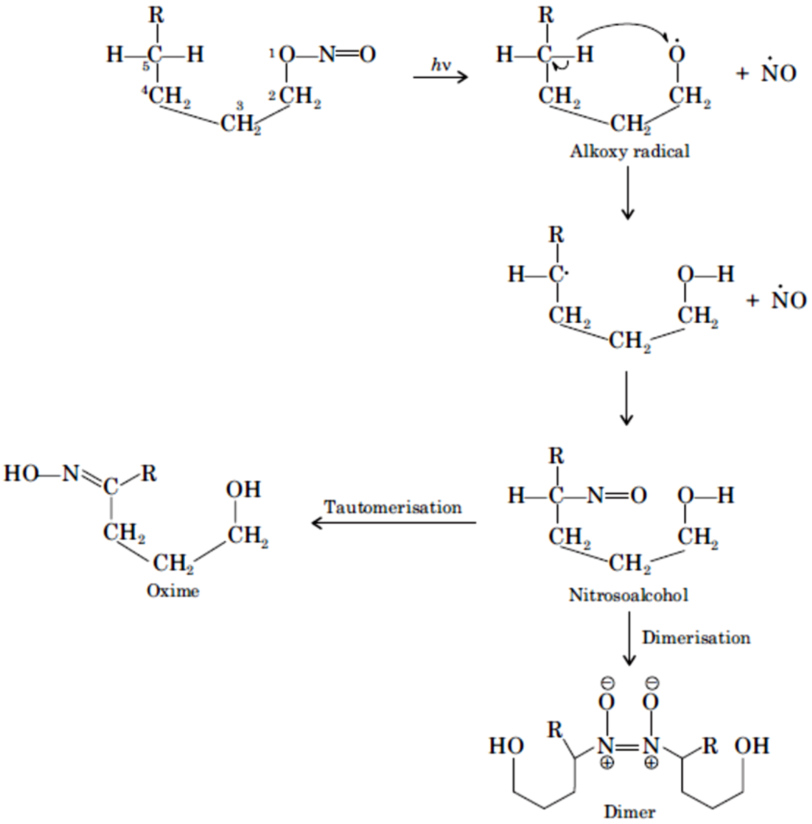


Halogen atom of π complex is more selective than halogen free radical. The light-induced homolysis of aryl-halogen bonds has important synthetic implications. Irradiation of lodinated aromatics in benzene often gives the phenylated aromatic in high yield.



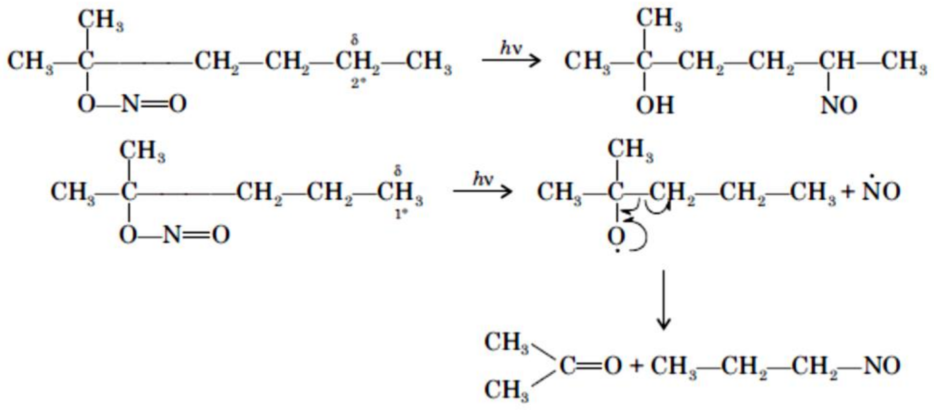
Barton Reaction

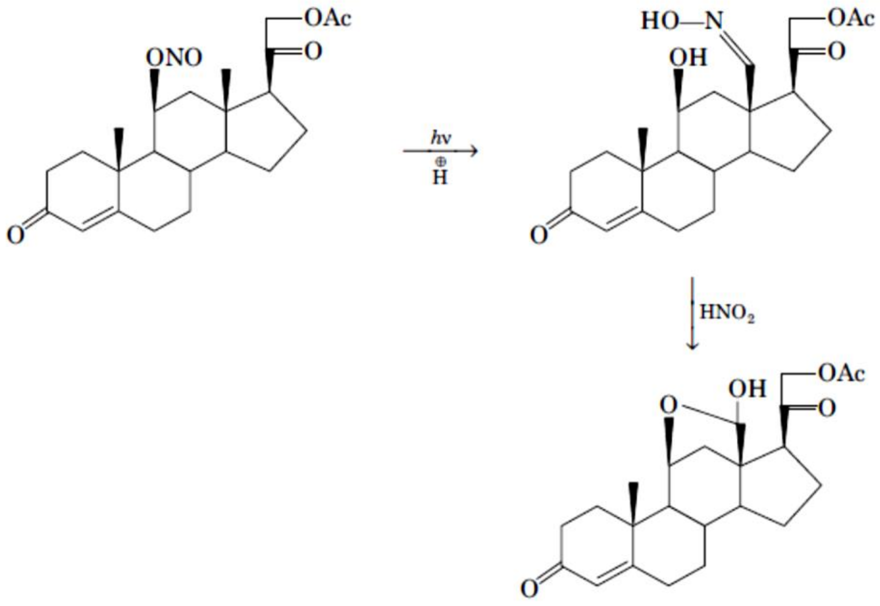
It has been known for many years that vapour phase photolysis or pyrolysis of organic nitrites (X = O, Y = NO) gives alkoxy radicals and nitrogen monoxide. It has been found that when thestructure of the molecule is such as to bring the  $-\overset{|}{\underset{|}{C}}-O-N{=}O$ group and a $-\overset{|}{\underset{|}{C}}-H$ bond into close proximity, or potentially close proximity (generally 1, 5-positions), the alkoxyl radicals produced by photolysis of the nitrites in solution have sufficient energy to bring about selective intramolecular hydrogen abstraction according to the equation to give carbon radical. This carbon radical captures nitrogen monoxide to give nitrosoalcohol. This nitrosoalcohol may be isolated as dimer or may rearrange into oxime. The nitroso and oximo compounds produced may further be transformed into other functional derivatives such as carbonyl compounds, cyano compounds and amino compounds. The photolytic conversion of organic nitrites into nitroalcohols is known as Barton reaction.



Thus, the Barton reaction is an example of the remote functionalisation of an unreactive saturated carbon atom. The reaction starts from the S1 (n π*) state (λ = 310–390 nm) with the cleavage of the R—O—NO bond (Ediss = 150 – 190 kJ) to produce nitric oxide and an activated alkoxy radical (Scheme). This is followed by abstraction of hydrogen via a six-membered cyclic transition state and the formation of hydroxyl group and a carbon radical that combines with nitric oxide (Scheme 1a). The nitroso compound dimerises or preferentially isomerises to the oxime. The reaction is effected by irradiation under nitrogen of a solution of the substrate in a suitable non-hydroxylic solvent with light from a high pressure mercury arc lamp. A pyrex filter is usually employed to limit the radiation of wavelength greater than 300 nm.

Intramolecular hydrogen abstraction by alkoxyl radicals is always accompanied to a greater or lesser extent by disproportionation, radical decomposition and intermolecular reactions. In case of alkoxyl radicals derived from tertiary nitrites the reaction follows the normal course if δ-carbon is secondary or tertiary. But if δ-carbon is primary then Barton reaction is superseded by alkoxyl decomposition.

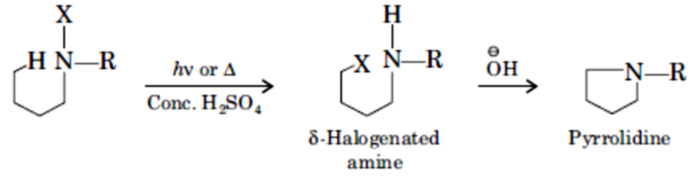




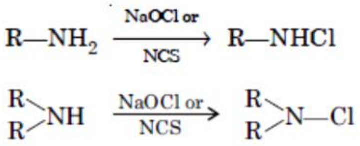
The Barton reaction is potentially useful in the synthesis of natural products, such as hormones and alkaloids. The photolysis of the 11-nitrite of corticosterone acetate has been utilised on an industrial scale in the partial synthesis of aldosterone-21-acetate.

Hoffmann-Loefller-Freytag reaction

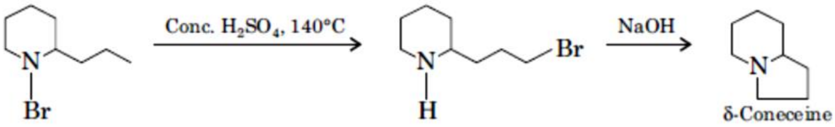
This reaction is given by N-haloamines having hydrogen on δ-carbon. The reaction is affected by warming a solution of the halogenated amine in strong acid (concentrated sulphuric acid or concentrated CF3COOH) or by irradiation of the acid solution with ultraviolet light. The product of the reaction is the δ-halogenated amine. This product is not generally isolated in this reaction. This product on basification gives pyrrolidine and its derivatives.



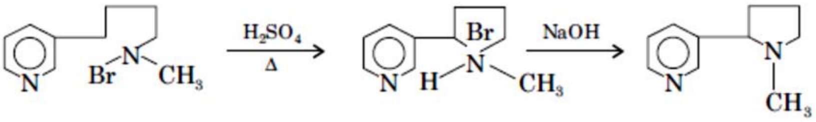
Both N-chloro and N-bromo amines are used as starting material but the N-chloroamines give better result. N-chloroamines are obtained from primary and secondary amines by the action of sodium hypochlorites or N-chlorosuccinamide (NCS).



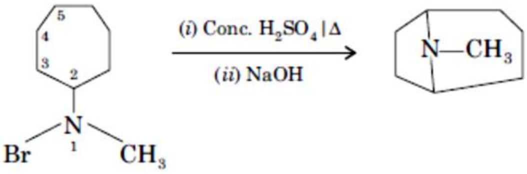
The first example of this reaction was reported by A.W. Hoffmann equation



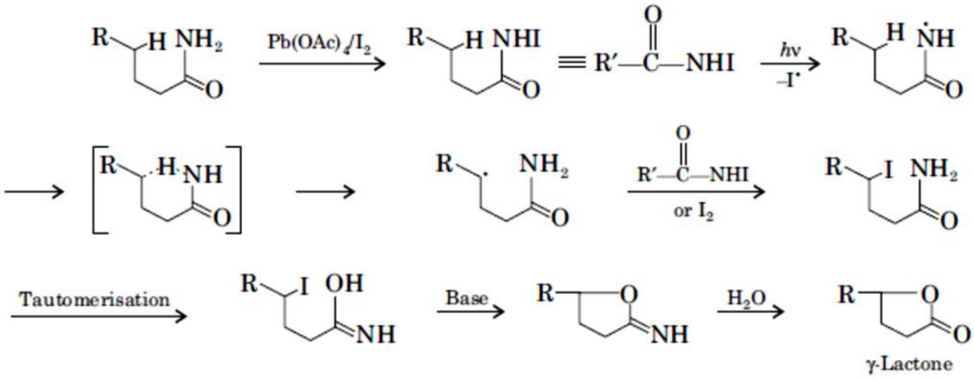
Latter, further examples of this reaction were reported by Loeffler. One of the reactions reported by Loeffler is



With N-halocycloalkylamines cyclisation leads to bridged-ring structures, but in these cases products may not be exclusively pyrrolidine derivatives. In some cases six-membered heterocyclic ring is formed instead of five membered heterocyclic ring. N-Bromo-N-methyl cycloheptylamine gives tropane. In this case pyrrolidine ring is formed.

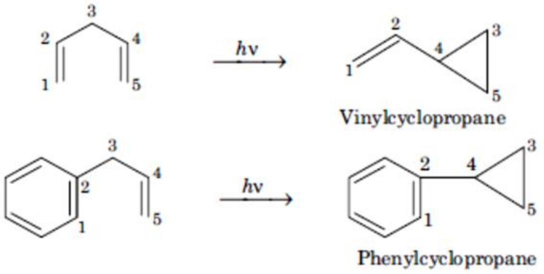


N-Haloamides also give this reaction. In this case N-halogen bond undergoes facile rupture upon photolysis. Barton has made use of this reaction to develope a useful method for the synthesis of γ-lactones. In case of amides the starting material is N-iodoamides prepared either with lead tetraacetate-iodine or by tertiary butyl hypochlorite-iodine mixture

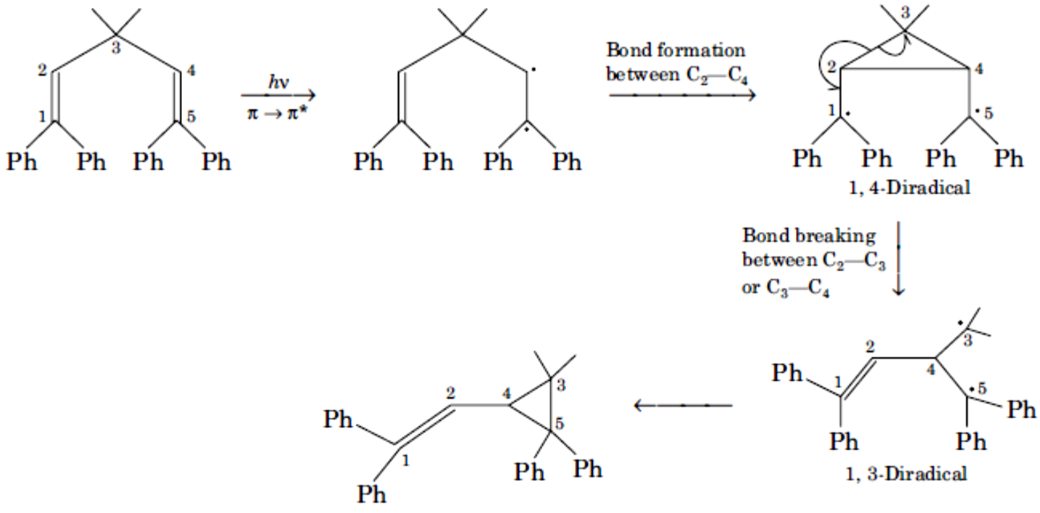


Di-π-methane rearrangement

The most remarkable photochemical reaction of nonconjugated dienes is the di-π-methane rearrangement. This rearrangement is given by dienes having π (pi) system separated by a sp3 hydridised carbon atom i.e., 1, 4-pentadienes. The rearrangement is also given by 3-phenylalkenes in which one of the double bonds is replaced by benzene ring. di-π-methane rearrangement is also known as Zimmerman rearrangement or Zimmerman di-π-methane rearrangement. Irradiation of the substrate induces rearrangement to a vinylcyclopropane or phenylcyclopropane derivative.

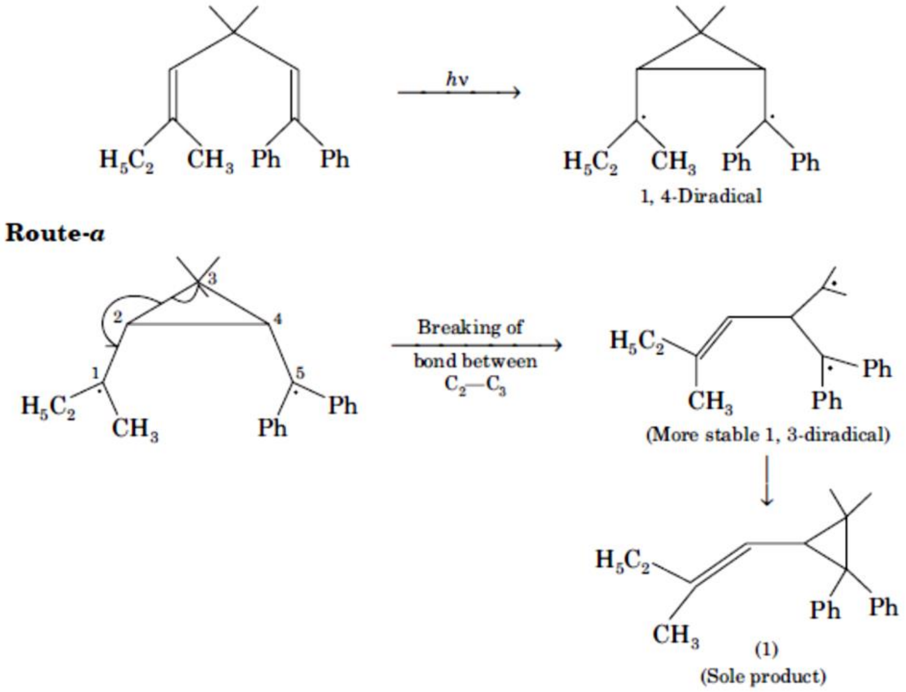


This rearrangement is found in both cyclic and acyclic dienes. The rearrangement of monocyclic and acyclic dienes occurs solely from the singlet state. Sensitised reaction of these substrates lead cis-trans isomerisation or | 2 + 2 | cycloaddition.



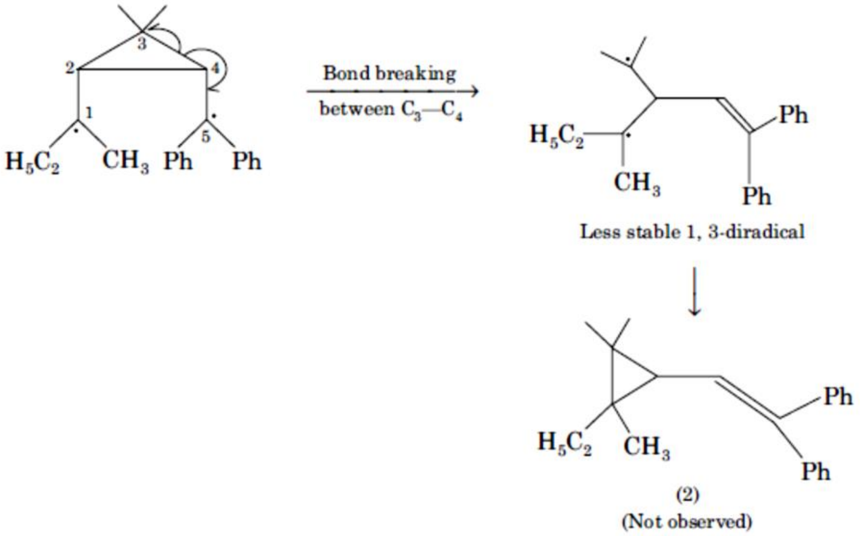
Experimental results show that di-π-methane rearrangement is concerted process, obeys the Woodward-Hoffmann rules, retains configuration on atom-1 and -5 (a result of disrotatory ring closure between C-3 and C-5), and inverts it on atom-3 (conrotatory mode). In actual practice the reaction is represented as one involving a 1, 4 and 1, 3-diradical intermediates in case of 1, 4-pentadiene since it is easier to follow the various steps necessary for the rearrangement

Thus, the di-π-methane rearrangement involves a rearrangement of the pentadiene skeleton with no alkyl or aryl group migration. Nevertheless, the reaction path that would involve the more stable diradical is always followed.

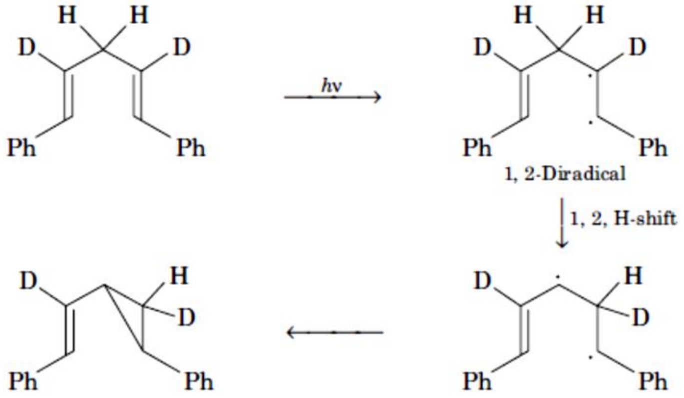


Formation of only one product (1) shows that there is retention of configuration at carbon-1. Thus cis-trans isomerisation of the bond C1—C2 must be slow by comparison with formation of cyclopropane derivative. Similarly, formation of product (1) but not the (2) shows that less stable radical participates in the three membered ring opening which gives more stable 1, 3-diradical. The di-π-methane rearrangement has been studied in a sufficient number of cases to develop some of the patterns regarding the substituent effects.

Route-b

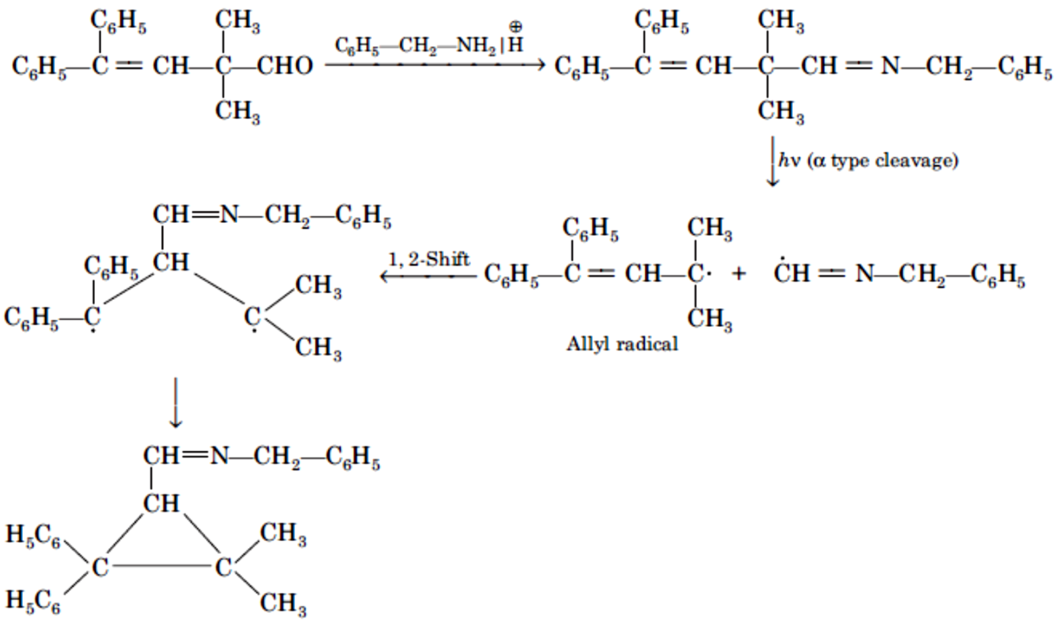


When the central sp3 carbon (C3—carbon) is unsubstituted, the di-π-methane rearrangement mechanism becomes less favourable by mechanism given in Schemes 10 and 11. In such cases the route is the 1, 2-shift and closure to a three membered ring. The case of 1, 5-diphenyl 2, 4-didentero-1, 4-pentadiene is illustrative



Aza di-π-methane rearrangement

1, 2-Acyl shift is given only by β, γ-unsaturated ketones. This rearrangement is not given by aldehydes.



The failure of aldehydes to undergo 1, 2-acyl shift (i.e., oxa-di-π-methane rearrangement) can be overcome by conversion of the aldehyde to an imine. Thus, when aldehyde is converted to the imine and irradiated under sensitised conditions, the normal cyclopropane forming process takes place. The formation of the cyclopropane by this path is known as azadi-π-methane rearrangement.

A similar path has also been shown to be involved with the oxime acetate.

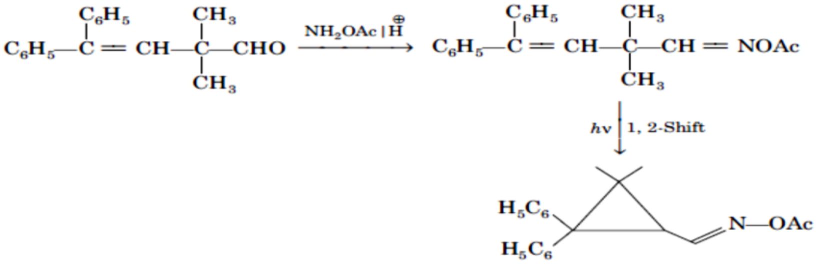
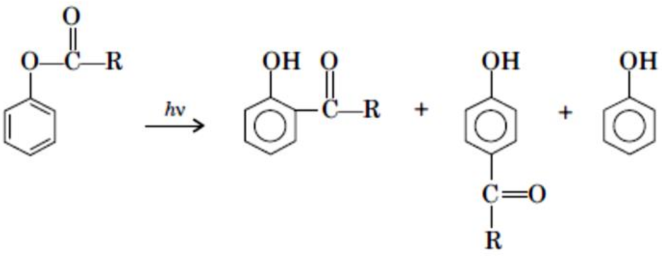
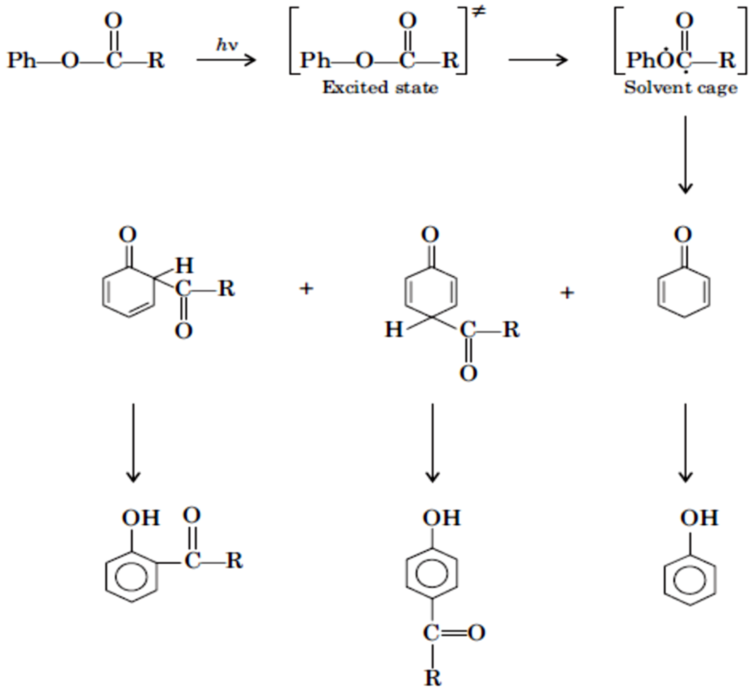


Photo-Fries Rearrangement

The most extensively investigated photo rearrangement is Photo-Fries rearrangement





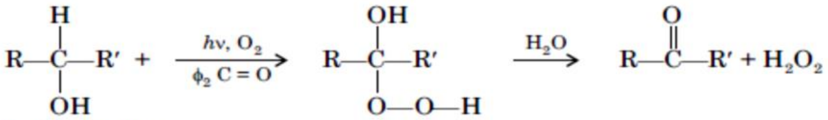
This rearrangement is an intramolecular rearrangement. In this rearrangement substrate undergoes dissociation into phenoxy and acyl radicals which combine within the solvent cage to give intermediates which on aromatisation (or enolisation) give the product. The phenol is produced by phenoxy radicals which escape from the solvent cage. When this reaction is carried out in gaseous phase only phenol is obtained. This confirms the formation of solvent cage.

Photochemical Oxidation

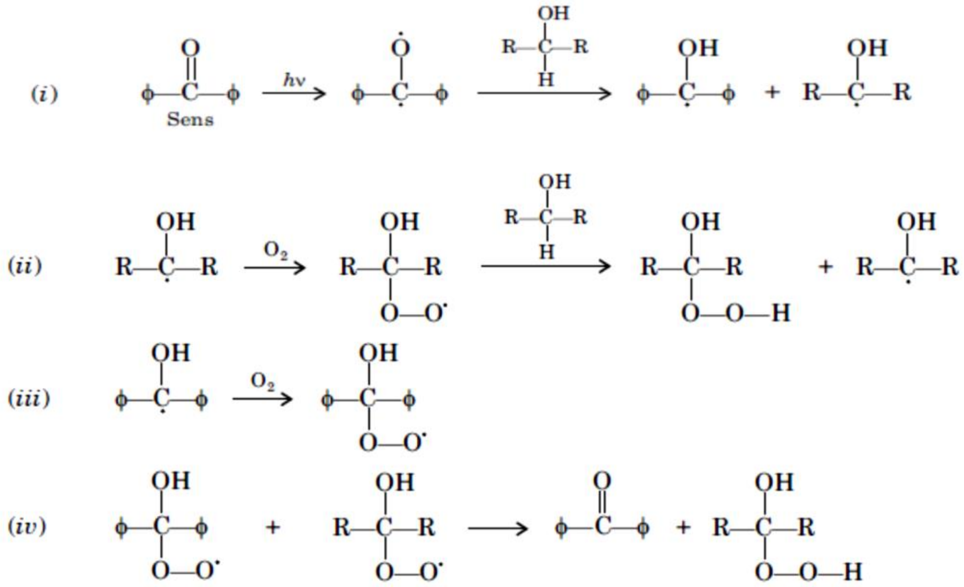
Incorporation of oxygen in the presence of UV light is known as photochemical oxidation. There are two mechanisms by which oxygen is incorporated in photochemical oxidation reactions. The first is the Backstrom mechanism which is also known as photosensitisation oxidation mechanism. Its main characteristic is abstraction of hydrogen by the sensitiser (Sens) in its excited triplet state followed by addition of oxygen to the newly created radical. This type of photooxygenation is known as type I photooxygenation.

$$\begin{aligned}
\text{Sens} + h\nu &\longrightarrow \overset{\uparrow\uparrow}{\text{Sens}} \\
\overset{\uparrow\uparrow}{\text{Sens}} + \text{A}-\text{H} &\longrightarrow \text{Sens}-\dot{\text{H}} + \dot{\text{A}} \\
\dot{\text{A}} + \text{O}_2 &\longrightarrow \text{A}-\text{O}-\dot{\text{O}} \\
\text{A}-\text{O}-\dot{\text{O}} + \text{AH} &\longrightarrow \text{A}-\text{O}-\text{O}-\text{H} + \dot{\text{A}} \\
\text{A}-\text{O}-\dot{\text{O}} + \text{Sens}-\dot{\text{H}} &\longrightarrow \text{A}-\text{O}-\text{O}-\text{H} + \text{Sens}
\end{aligned}$$

Example of photosensitised reactions that take place by this mechanism are found among the oxidation of secondary alcohols to hydroxy hydroperoxides which in aqueous medium decomposes to form ketones and hydrogen peroxide.



Mechanisms:



The second mechanism known as photosensitised oxygen transfer involves the direct combination of the substrate with oxygen. There are two proposals regarding the state of oxygen involved. This type of photooxygenation is known as type II photooxygenation. Schenck's favours an oxygen-transfer step in which the triplet sensitiser forms an adduct with triplet oxygen

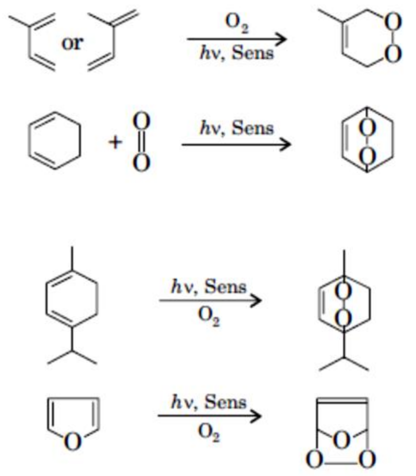
$$\begin{aligned} \text{Sens}^{\bullet} &\xrightarrow{h\nu} {}^{3}\text{Sens} \\ {}^{3}\text{Sens} + \text{O}_2 &\longrightarrow \dot{\text{S}}\text{ens—O—}\dot{\text{O}} \\ \text{A} + \dot{\text{S}}\text{ens—O—}\dot{\text{O}} &\longrightarrow \text{AO}_2 + \text{Sens} \end{aligned}$$

Foote favours the idea of singlet oxygen being the sole agent in the transfer step

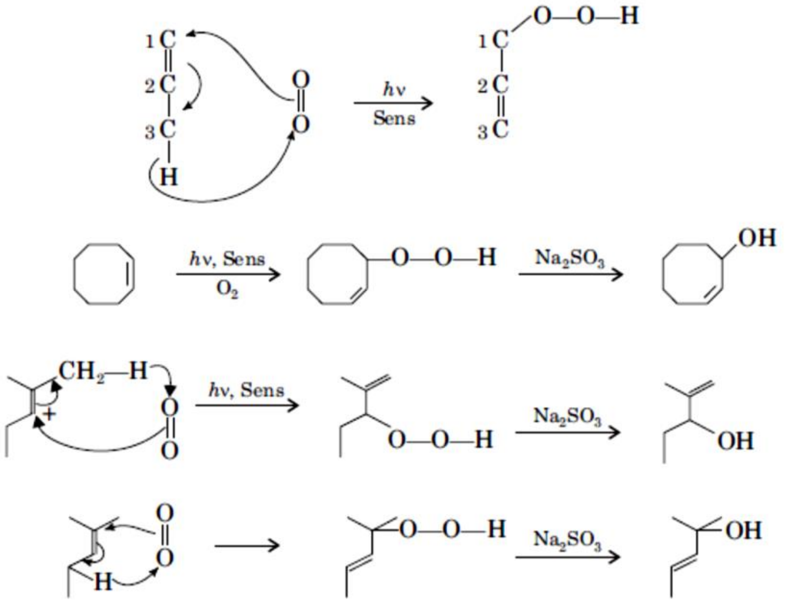
$$\begin{aligned} \text{Sens} &\xrightarrow{h\nu} {}^{3}\text{Sens}^{*} \\ \text{O}_2\ (\text{Triplet}) + \text{Sens}^{*}\ (\text{Triplet}) &\longrightarrow \text{O}_2\ (\text{Singlet}) + \text{Sens} \\ \text{A} + \text{O}_2\ (\text{Singlet}) &\longrightarrow \text{AO}_2 \end{aligned}$$

Photo Oxidation of Alkenes

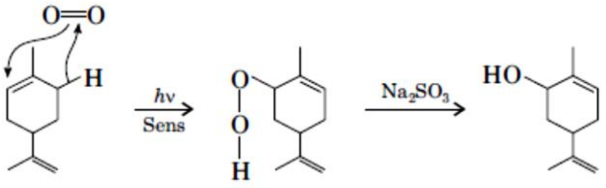
Alkenes, dienes and polyenes are attacked by singlet oxygen. The singlet oxygen may be generated by thermal methods (e.g., by the reaction of hydrogen peroxide with sodium hypochlorite), by excitation of ground state oxygen (triplet oxygen) in a microwave discharge or by the use of visible radiation and photochemical sensitiser such as methylene blue, Rose Bengal, chlorophyll, riboflavin, fluorescein or halo fluorescein. Acyclic or cyclic conjugated dienes gives 1, 4-cycloaddition reaction with singlet oxygen to form six-membered cyclic adduct, i.e., cyclic peroxide.



The formation of hydroperoxides in photosensitised oxygen-transfer reactions that follow the Schenck type of mechanism occurs only when hydrogen is present on allylic carbon. The reaction has, moreover, some definite steric and electronic requirements. Oxygen always becomes attached to one of the double bonded carbon, which then shifts into the allylic position. The reaction is like ene reaction.

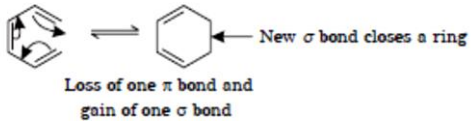


The above reactions do not proceed through free radicals. The oxidation with singlet oxygen occurs by concerted mechanism like the ene reaction

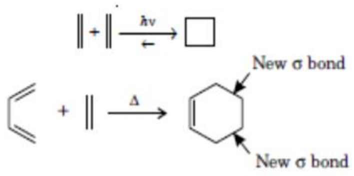


PERICYCLIC REACTIONS

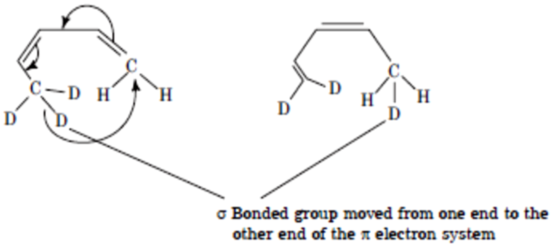
Pericyclic reactions are defined as the reactions that occur by a concerted cyclic shift of electrons. This definition states two key points that characterise a pericyclic reaction. First point is that reaction is concerted. In concerted reaction, reactant bonds are broken and product bonds are formed at the same time, without intermediates. Second key point in pericyclic reactions involves a cyclic shift of electrons. The word pericyclic means around the circle. Pericyclic word comes from cyclic shift of electrons. Pericyclic reactions thus are characterised by a cyclic transition state involving the π bonds. The energy of activation of pericyclic reactions is supplied by heat (Thermal Induction), or by UV light (Photo Induction). Pericyclic reactions are stereospecific and it is not uncommon that the two modes of induction yield products of opposite stereochemistry. We shall concern with four major types of pericyclic reactions. The first type of reaction is the electrocyclic reaction: A reaction in which a ring is closed (or opened) at the expense of a conjugated double (or triple bond) bond.



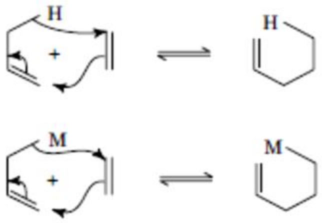
The second type of reaction is the cycloaddition reaction: A reaction in which two or more π electron systems react to form a ring at the expense of one π bond in each of the reacting partners.



In this reaction formation of two new σ (sigma) bonds takes place which close a ring. Overall there is loss of two π (pi) bonds in reactants and gain of two σ (sigma) bonds in a product. The third type of reaction is the sigmatropic rearrangement (or reaction): A reaction in which a σ (sigma) bond formally migrates from one end to the other end of π (pi) electron system and the net number of π bonds remains the same.



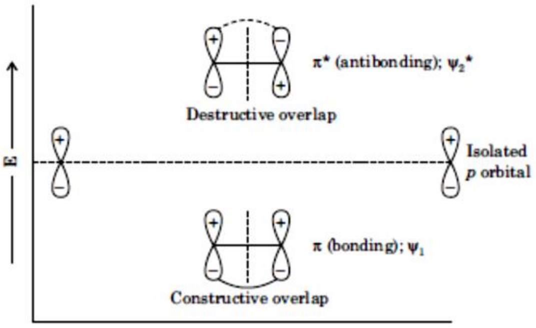
The fourth type of reaction is the group transfer reaction: A reaction in which one or more groups or atoms transfer from one molecule to another molecule. In this reaction both molecules are joined together by σ (sigma) bond.



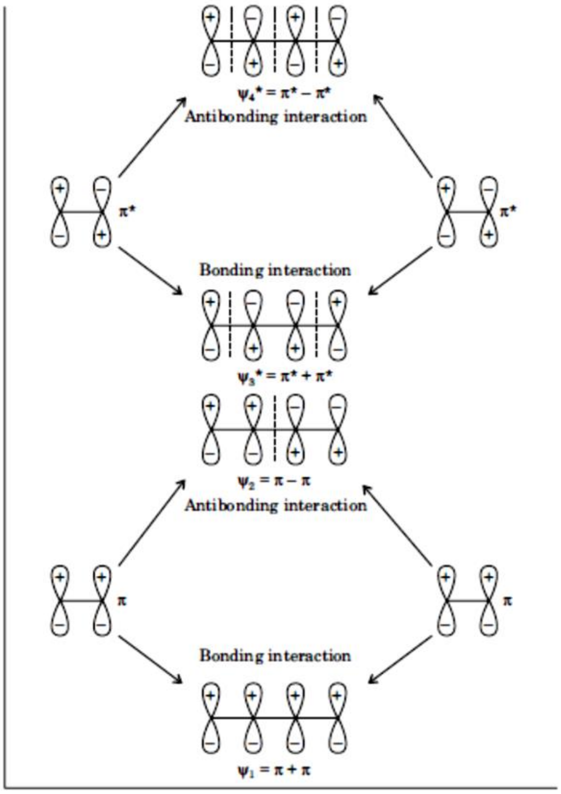
The three features of any pericyclic reaction are intimately interrelated. These are: 1. Activation: Pericyclic reactions are activated either by thermal energy or by UV light. However, many reactions that require heat are not initiated by light and vice-versa. 2. The number of π (pi) bonds involved in the reaction. 3. The stereochemistry of the reaction.

Construction of Molecular Orbitals

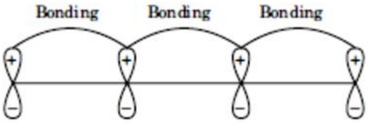
We know that, the number of molecular orbitals is always equal to the number of atomic orbitals that combine to form them. The same principle applies to π molecular orbitals. A π electron system derived from the interaction of number m of p orbitals contain m molecular orbitals, that differ in energy. Half of the molecular orbitals are bonding molecular orbitals and remaining half are antibonding molecular orbitals. π molecular orbitals of ethylene from the two p atomic orbitals of the two carbons can be constructed as follows: Each p orbital consists of two lobes, with opposite phases of the wave function of the two lobes. The plus and minus signs used in drawing these orbitals indicate the phase of the wave function. In the bonding orbital of ethylene, there is overlap of similar signs (+ with + and – with–) in the bonding region between the nuclei. This reinforcement of the wave function is called constructive overlap. In the antibonding orbital there is cancelling of opposite signs (+and –) in the bonding region. This cancelling of the wave function is called destructive overlap.



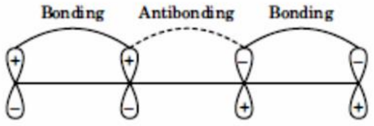
In 1, 3-butadiene, we have a system of four p orbitals on four adjacent carbons. These four p orbitals will overlap to produce four π molecular orbitals. We can get four new MOs in a number of equivalent ways. One of the ways to obtain four new molecular orbitals is by linear combination of two molecular orbitals of ethylene. Linear combination of orbitals is also known as perturbation theory or perturbation molecular orbital (PMO) theory. Linear combination always takes place between two orbitals (two atomic orbitals, two molecular orbitals or one atomic and one molecular orbitals) having minimum energy difference. This means that we need to look only at the results of the π ± π and π* ± π* interactions and do not have to consider π ± π*.



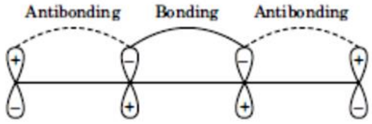
The lowest energy orbital (ψ1) of 1, 3-butadiene is exceptionally stable for two reasons: There are three bonding interactions, and the electrons are delocalised over four nuclei.



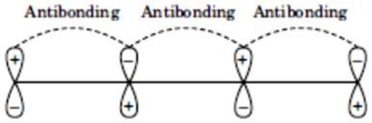
The second molecular orbital ψ2 of 1, 3-butadiene is obtained from the antibonding interaction between two bonding molecular orbitals of ethylene. The ψ2 orbital has two bonding and one antibonding interaction, so we would expect it to be a bonding orbital (two bonding – one antibonding = one bonding). Thus, energy of ψ2 is more than that of ψ1. ψ2 molecular orbital has one node between C2–C3. A node is a plane where the wave function drops to zero.



The third butadiene MO, ψ3* has two nodes. This molecular orbital is obtained from the bonding interaction between π* and π* of two ethylene molecules. There is a bonding interaction of the C2—C3 bond and there are two antibonding interactions: One at C1–C2 bond and the other at the C3—C4 bond. This is an antibonding orbital (one bonding – two antibonding = one antibonding) having two nodes. Thus energy of this ψ3* orbital is more than the energy of ψ2 MO.



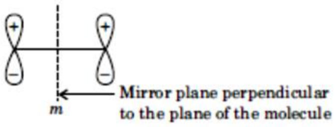
The fourth molecular orbital (ψ4*) is obtained from the antibonding interaction between π* and π* of two ethylene molecules. This molecular orbital has three nodes and is totally antibonding. This MO has the highest energy.



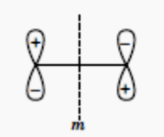
Following generalisations can be made to construct the molecular orbitals of the conjugated polyenes from the π molecular orbitals of ethylene and 1, 3-butadiene: 1. A π electron system derived from the interaction of a number of m of p orbitals contain m molecular orbitals (MOs) that differ in energy. Thus, the number of π MOs are always equal to the number of atomic p orbitals. In 1, 3-butadiene, four p orbitals are used in the formation of the π MOs, thus four π MOs results, which we shall abbreviate as ψ1, ψ2, ψ3 and ψ4 (or π1, π2, π3 and π4). 2. Half of the molecular orbitals (i.e., m/2) have lower energy than the isolated p orbitals. These are called bonding molecular orbitals (BMOs). The other half have energy higher than the isolated p orbitals. These are called antibonding molecular orbitals (ABMOs). To emphasise this distinction, antibonding MOs will be indicated with asterisks. Thus, 1, 3-butadiene has two bonding MOs (ψ1 and ψ2) and two antibonding MOs (ψ3* and ψ4*). 3. The bonding MO of lowest energy ψ1 has no node. Each molecular orbital of increasingly higher energy has one additional node. Thus, in 1, 3-butadiene ψ1 has zero node, ψ2 has one node, ψ3* has two nodes and ψ4* has three nodes. 4. The nodes occur between atoms and are arranged symmetrically with respect to the centre of the π electron system.

Symmetry in π Molecular Orbitals

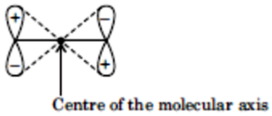
A π molecular orbital possesses either mirror plane symmetry or centre of symmetry. Both symmetries are not present together in a given π molecular orbital. m-Symmetry: Some molecular orbitals have the symmetry about the mirror plane (m) which bisects the molecular orbitals and is perpendicular to the plane of the molecule.



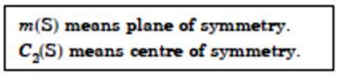
Both orbitals in Figure are mirror images to each other hence in this MO there is mirror plane symmetry, abbreviated as m(S).



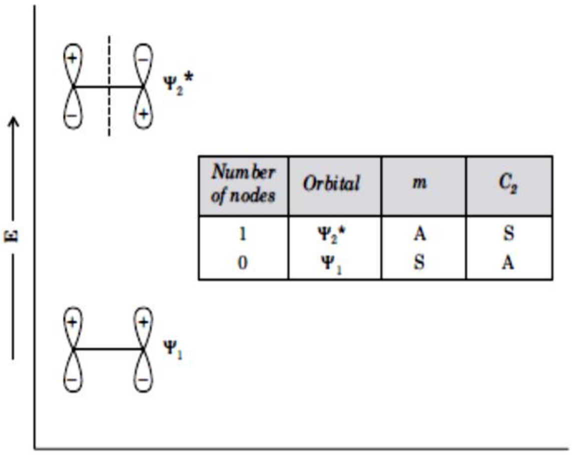
In Figure both orbitals are not mirror images to each other. Thus in this MO there is mirror plane asymmetry, abbreviated as m(A). C2-Symmetry: The centre of symmetry is a point in the molecular axis from which if lines are drawn on one side and extended an equal distance on the other side, will meet the same phases of the orbitals.



Both orbitals in Figure are symmetrical with respect to centre of the molecular axis. Thus in this MO there is centre of symmetry, abbreviated as C2(S).

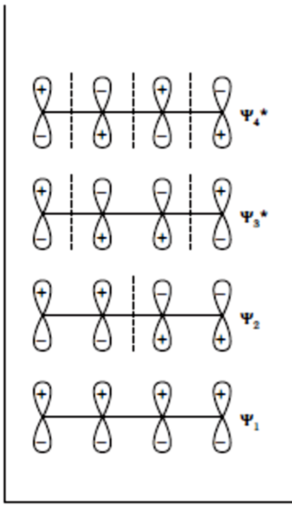

m(S) means plane of symmetry.
C_2(S) means centre of symmetry.

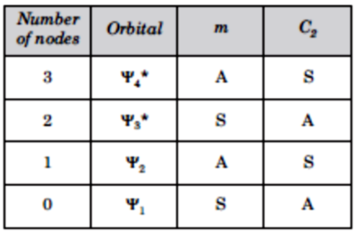
Let us take examples for the purpose of symmetry properties in ethylene and 1, 3-butadiene.



Number of nodes	Orbital	m	C_2
1	Ψ_2^*	A	S
0	Ψ_1	S	A

Symmetries in the MO of Ethylene



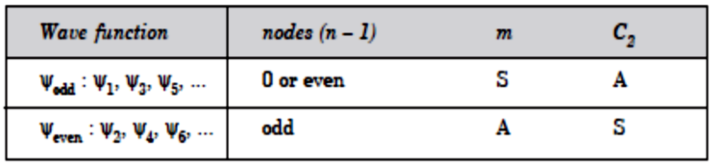


Number of nodes	Orbital	m	C_2
3	Ψ_4^*	A	S
2	Ψ_3^*	S	A
1	Ψ_2	A	S
0	Ψ_1	S	A

Symmetries in the MO of 1,3 – butadiene

On the basis of the above two examples we can conclude the following very important points for linear conjugated π systems: 1. The wave function ψn will have (n – 1) nodes. 2. When n is odd, ψn will be symmetric with m and asymmetric with C2. 3. When n is even, ψn will be symmetric with C2 and asymmetric with m. Table.

Symmetry elements in the orbital ψn of a linear conjugated polyene



Wave function	nodes (n – 1)	m	C_2
Ψ_{odd} : Ψ_1, Ψ_3, Ψ_5, ...	0 or even	S	A
Ψ_{even} : Ψ_2, Ψ_4, Ψ_6, ...	odd	A	S

Filling of electrons in MO of conjugated Polyenes

Conjugated polyenes always contain even number of carbon atoms. These polyenes contain either (4n)π or (4n + 2)π conjugated electrons. The filling of electrons in the π molecular orbitals of a conjugated polyene is summarised below:

1. Number of bonding π MOs and antibonding π MOs are same.

2. Number of electrons in any molecular orbital is maximum two.

3. If a molecular orbital contains two electrons then both electrons are always paired.

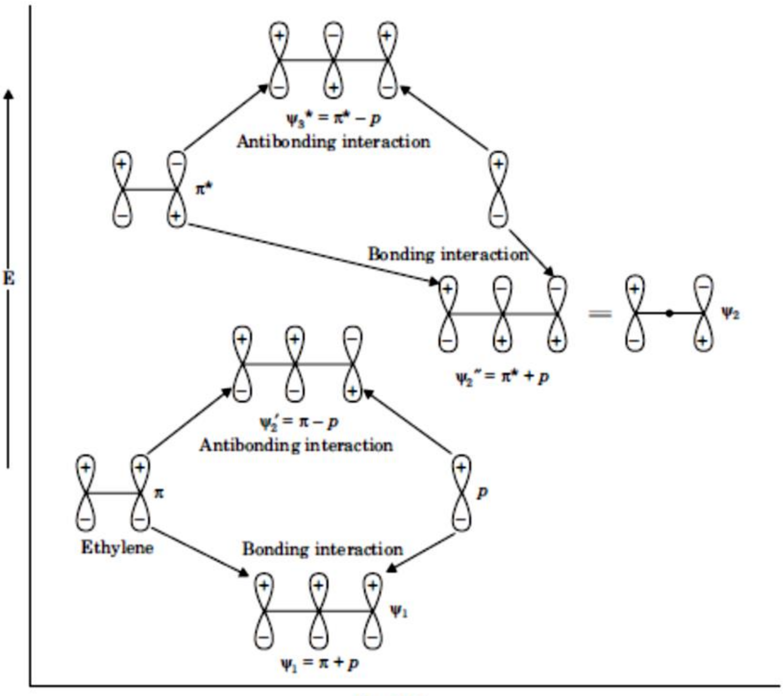
4. Molecular orbitals follow Aufbau principle and Hund’s rule.

5. Energy of the π molecular orbital is directly proportional to the number of the nodal planes.

6. There will be no degenerate molecular orbitals in any energy level, i.e., each and every energy level contains one and only one molecular orbital

Construction of MO in conjugated ions and radicals

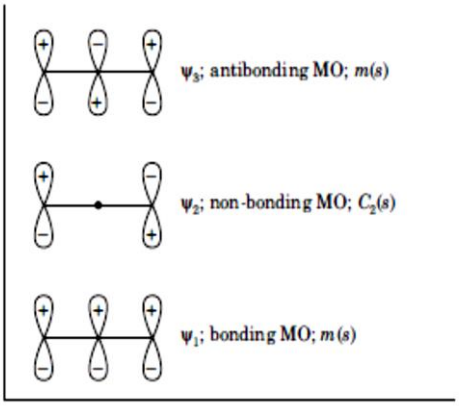
Conjugated unbranched ions and radicals have an odd number of carbon atoms. For example, the allyl system (cation, anion or radical) has three carbons and three p orbitals—hence, three molecular orbitals. We can get three new molecular orbitals by linear combination of one molecular orbital of ethylene and two isolated p orbital. As already mentioned that the linear combination always takes place between two orbitals having minimum energy difference. In allylic system linear combination takes place between one ethylene MO and one p orbital. This means that we need to look at the results of the π ± p and π* ± p interactions



The ethylene bonding orbital, π gives linear combination with the p orbital in a bonding way and moving down in energy to give ψ1.

The ethylene antibonding orbital (π*) gives linear combination with p orbital in an antibonding way and moving up in energy to give ψ3*.

The p orbital mixes with both the bonding and antibonding orbitals of ethylene. Thus, there is double mixing for the p orbital. The lower energy ethylene bonding orbital (π) mixing in an antibonding way to push the p orbital up in the energy (ψ2′ = π – p) but the ethylene antibonding orbital mixing in a bonding way to push to p orbital down in energy (ψ2″ = π* + p). Thus, the net result in the energy change is zero. Under this situation a nodal plane always passes through the central carbon of the chain. This means an electron in ψ2 has no electron density on the central carbon. Thus, the ψ2, i.e., central molecular orbital must be non-bonding molecular orbital. Thus, the molecular orbitals of the allylic system is represented as follows



From the example of allyl system following generalisation can be made to construct the molecular orbitals of the conjugated open chain system (cation, anion and radical) containing odd number of carbon atoms:

1. Number of conjugated atoms (or p orbitals) are always odd. For example, allyl system has three orbitals and 2, 4-pentadienyl system has five orbitals.

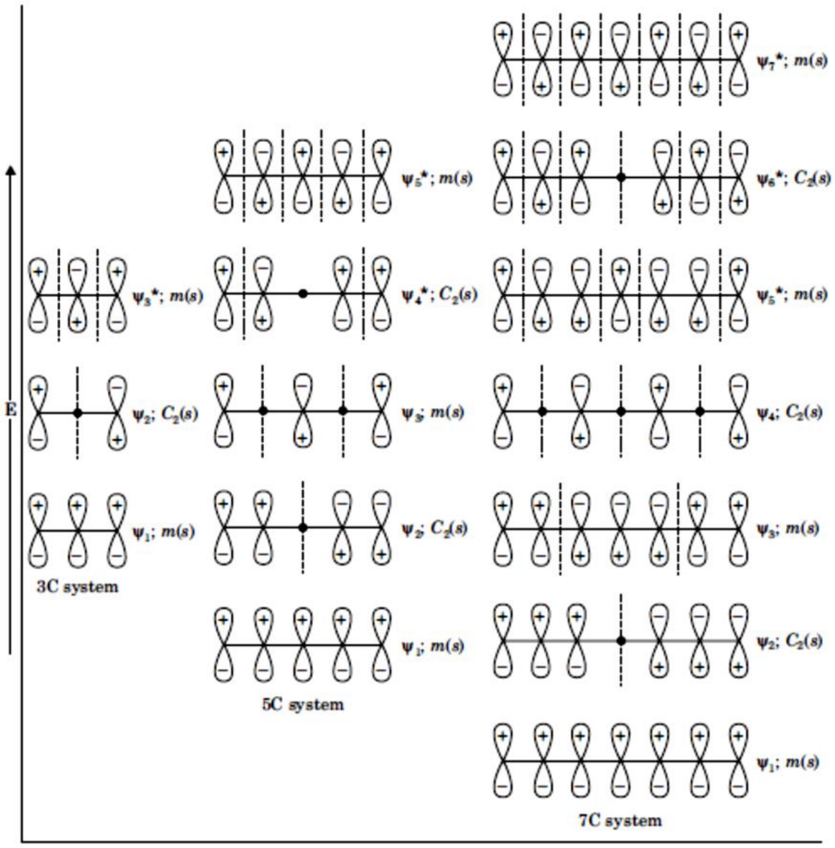
2. These systems have always one non-bonding molecular orbital whose energy is always equal to the unhybrid p orbital. Non-bonding molecular orbital is always central molecular orbital of the system.

3. If system has m (which is always odd) atomic p orbitals then it has: (i) m− 1 2 bonding molecular orbitals, (ii) m− 1 2 antibonding molecular orbitals, and (iii) one non-bonding molecular orbital.

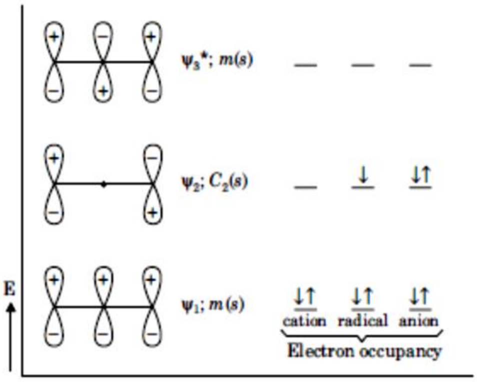
4. In non-bonding molecular orbital all the nodal planes (i.e., n – 1 nodal planes for ψn wave function) pass through the carbon nucleus (or nuclei)

5. For odd ψn (ψ1, ψ3, ψ5, ...), all nodal planes pass between two carbon nuclei.

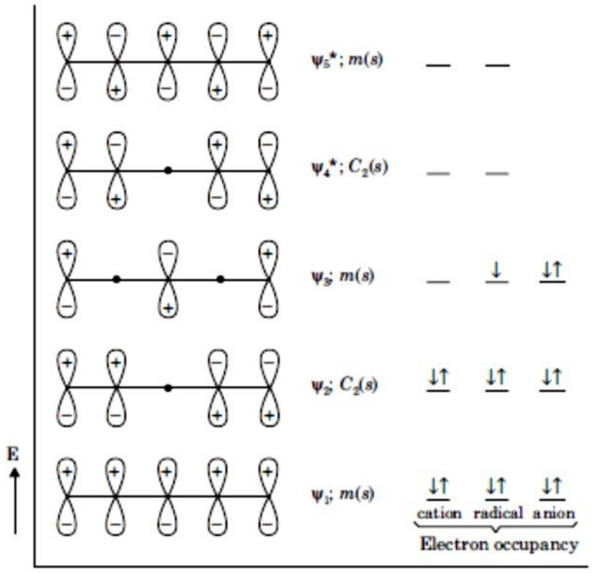
6. For even ψn (ψ2, ψ4, ψ6, ...), one nodal plane passes through the central carbon atom and remaining nodal planes pass between two carbon atoms. Figure illustrates schematically the forms of the molecular orbitals for chains up to seven carbon atoms in length with symmetries and nodal planes.



Electron occupancy of allyl carbocation, allyl free radical and allyl carbanion

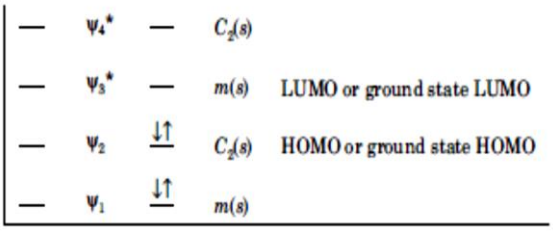


Electron occupancy of 2, 4-pentadienyl systems



Frontier Molecular Orbitals

Two π molecular orbitals are of particular importance in understanding pericyclic reactions. One is the occupied molecular orbital of highest energy, known as highest occupied molecular orbital (HOMO). The other is the unoccupied molecular orbital of lowest energy known as lowest unoccupied molecular orbital (LUMO). HOMO and LUMO of any given compound have opposite symmetries. HOMO and LUMO are referred to as frontier molecular orbitals.

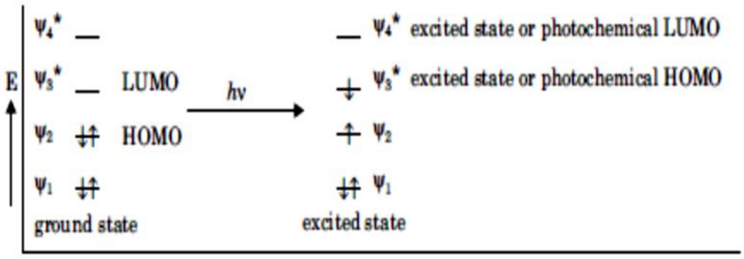


HOMO of the ground state species is also known as ground state HOMO. Similarly, LUMO of the ground state of the species is known as ground state LUMO. Why are the LUMO and HOMO so important in determining the course of a concerted reaction? The electrons in the HOMO of a molecule are like the outer shell electrons of an atom. They can be removed with the least expenditure of energy because they are already in a highest energy level than any of the other electrons in the molecule. The LUMO of a molecule is the orbital to which electrons can be transformed with the least expenditure of energy. The higher is the energy of HOMO of a molecule, the more easily electrons can be removed from it. The lower is the energy of the LUMO of the molecule, the more easily electrons can be transferred into it. Therefore, the interaction between a molecule with a high HOMO and a low LUMO is particularly strong. In general, the smallest the difference in energy between HOMO of one molecule and the

LUMO of another with which it is reacting, the stronger is the interaction between the two molecules.

Excited States

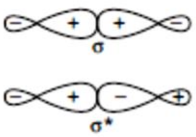
The molecules and ions we have been discussing can absorb energy from electromagnetic radiation of certain wavelengths. This process is shown schematically in Figure for 1, 3-butadiene. Let us refer to the normal electronic configuration of 1, 3-butadiene as the ground state. When 1, 3-butadiene absorbs a photon of proper wavelength an electron is promoted from the HOMO (ψ2) to the LUMO (ψ3*). The species with the promoted electron is an excited state of 1, 3-butadiene. The orbital ψ3* becomes HOMO and ψ4* becomes LUMO of the excited state. HOMO of excited state is termed as excited state HOMO or photochemical HOMO. Similarly, LUMO of the excited state is termed as excited state LUMO or photochemical LUMO.



Notice that the HOMO of ground state and excited state have opposite symmetries. Similarly, LUMO of the ground state and excited state also have opposite symmetries.

Symmetries

The sigma orbital of a carbon-carbon covalent bond has a mirror plane symmetry, and since a rotation of 180° through its midpoint regenerates the same sigma orbital, it also has a C2 symmetry. A sigma antibonding molecular orbital is asymmetric with respect to both m and C2.



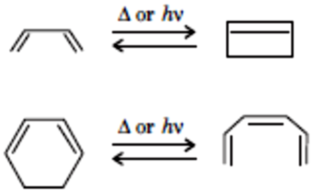
Orbital	m	C_2
σ*	A	A
σ	S	S

Pericyclic Reaction

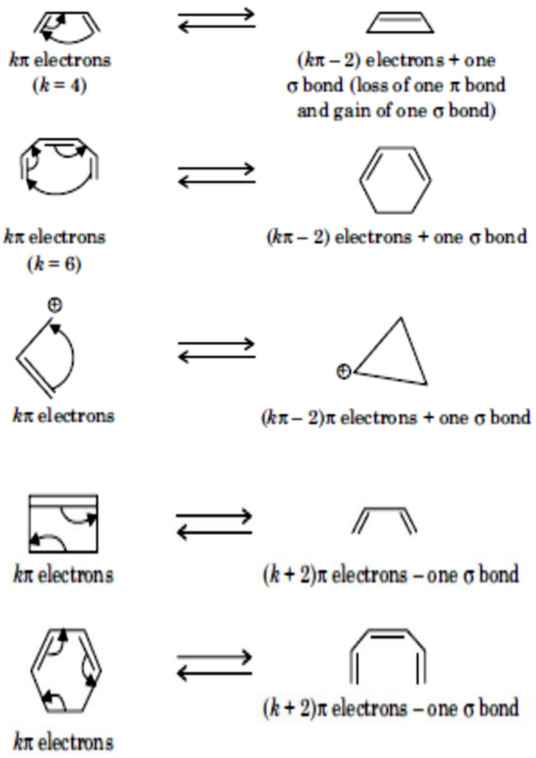
Pericyclic reactions are defined as reactions that occur by concerted cyclic shift of electrons. According to the Woodward and Hoffmann symmetry of the molecular orbitals that participate in the chemical reaction determines the course of the reaction. They proposed what they called the principle of the conservation of orbital symmetry; in the concerted reactions. In the most general terms, the principle means that in concerted pericyclic reactions, the molecular orbitals of the starting materials must be transformed into the molecular orbitals of the product in smooth continuous way. This is possible only if the orbitals have similar symmetry, i.e., orbitals of the reactant and product have similar symmetries. In concerted reaction product formation takes place by formation of cyclic transition state. The transition state of pericyclic reactions should be intermediate between the electronic ground states of the starting material and product. Obviously, the most stable transition state will be one which conserves the symmetry of the reactant orbitals in passing to product orbitals. In other words, a symmetric (S) orbital in the reactant must transform into a symmetric orbital in the product and that an asymmetric (A) orbital must transform into an asymmetric orbital. If the symmetries of the reactants and product orbitals are not the same, the reaction will not take place in a concerted manner. If symmetry is conserved during the course of the reaction then reaction will take place and process is known as **symmetry allowed process**. If symmetry is not conserved during the course of the reaction, the reaction is known as **symmetry-forbidden process**. The energy of the transition state (i.e., energy of activation of the transition state) of symmetry allowed process is always lower than the symmetry-forbidden process.

Electrocyclic Reactions

An electrocyclic reaction is the concerted interconversion of a conjugated polyene and a cycloalkene. Electrocyclic reactions are induced either thermally or photochemically.



All electrocyclic reactions are reversible reactions. Open-chain partner of the reaction is always conjugated system whereas cyclic partner may or may not contain conjugated system. In electrocyclic reactions either a ring is formed with the generation of a new σ bond and the loss of a π bond (i.e., gain of one σ bond and loss of one π bond) or ring is broken with the loss of one σ bond and gain of one π bond.



Thus electrocyclic reactions can be classified into two categories:

Electrocyclic opening of the ring, and

Electrocyclic closure of the conjugated system.

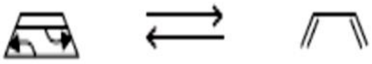
In electrocyclic closure of the ring (or ring closing electrocyclic reaction) if the π system of the open-chain partner contains kπ electrons, the corresponding cyclic partner contains (k – 2)π electrons and one additional σ bond. In ring opening electrocyclic reaction if ring partner contains kπ electrons, the open chain partner will contain (k + 2)π electrons with the loss of one σ bond. There are two possible stereochemistries for the ring-opening and ring-closing of electrocyclic reactions. They are:

1. Conrotatory process (or motion), and

2. Disrotatory process (motion).

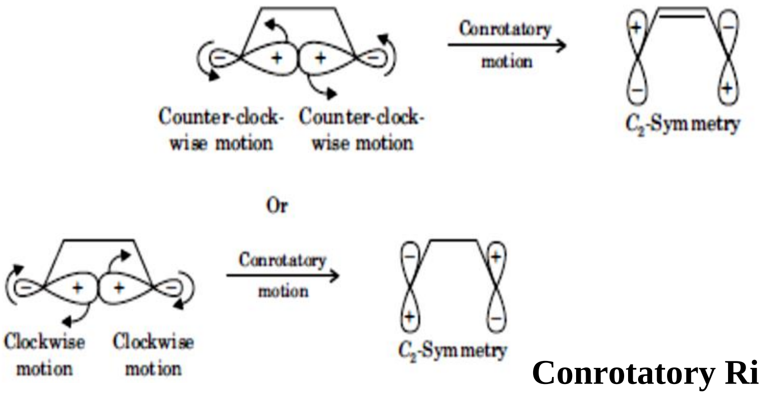
Conrotatory and Disrotatory motions in ring opening reactions

The most common example of the ring opening reaction is the conversion of cyclobutene to 1, 3-butadiene. This conversion can only be possible if a σ (sigma) bond between C3—C4 of cyclobutene must break during the course of the reaction.



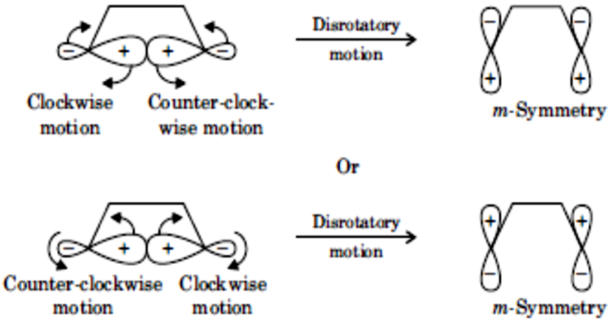
Ring opening reaction

This σ (sigma) bond may break in two ways. First, the two atomic orbital components of the σ (sigma) bond may both rotate in the same direction, clockwise or counter-clockwise. This process is known as conrotatory motion



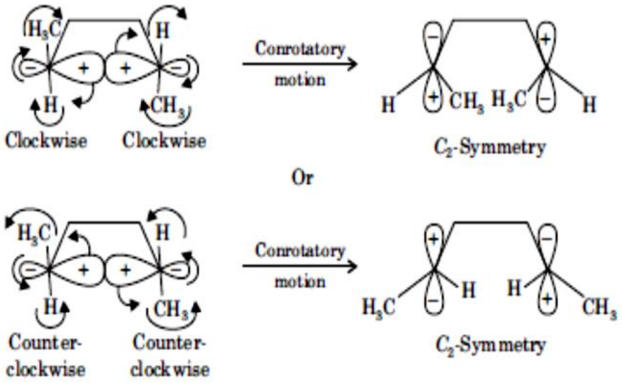
Conrotatory Ring Opening

Second, the atomic orbitals may rotate in opposite directions, one clockwise and the other counter-clockwise. This process of ring-opening is known as disrotatory motion

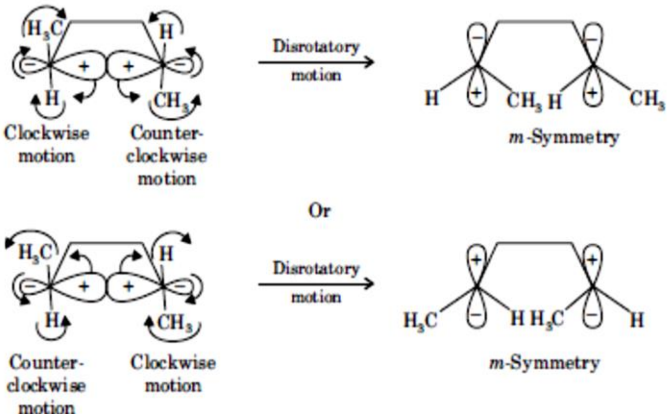


Disrotatory Ring Opening

The substituents present on the carbons of the rotating orbitals may also rotate in the direction of the rotating orbitals. Thus in the conrotatory motion substituents rotate in the same direction and in disrotatory motion substituents rotate in the opposite directions



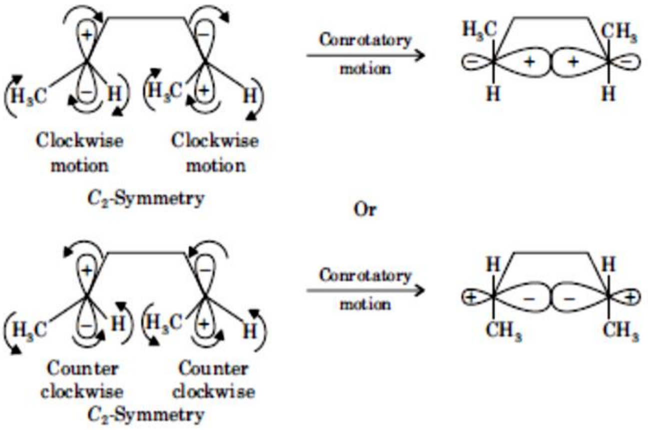
Conrotatory Ring Opening



Disrotatory Ring Opening

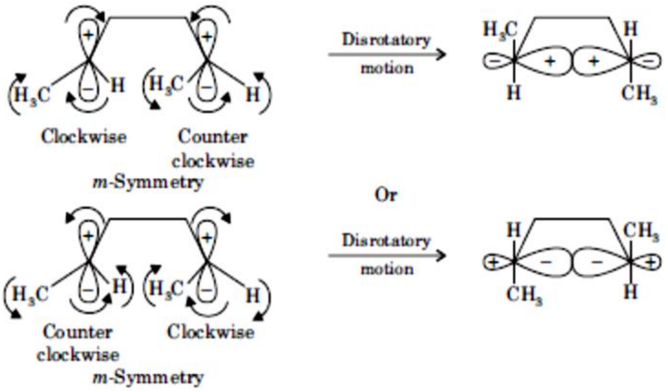
Conrotatory and Disrotatory motions in ring closing reactions

When an electrocyclic reaction takes place, the carbon at each end of the conjugated π system must turn in a concerted fashion so that the p orbitals can overlap (and rehybridised) to form σ bond that closes the ring. This turning can also occur in two stereochemically distinct ways. In a conrotatory closure the orbitals and groups of the two carbon atoms turn in the same direction, clockwise or counter-clockwise.



Conrotatory Ring Closure

In a disrotatory closure the orbitals and groups of the two carbon atoms turn in the opposite direction, one clockwise and other counter-clockwise

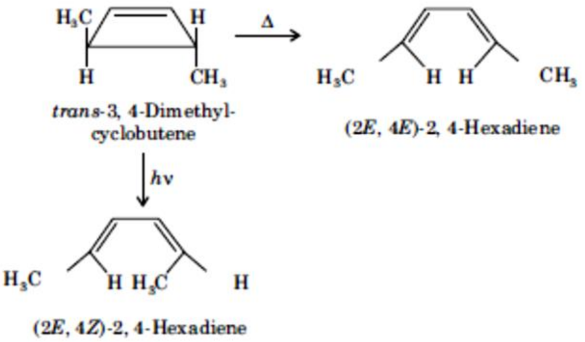


Disrotatory Ring Closure

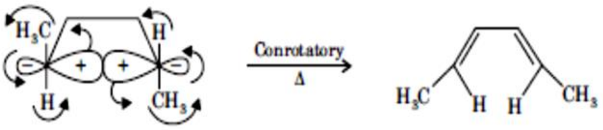
From these examples it is clear that orbitals having m-symmetry always give disrotatory motion. whereas orbitals having C2-symmetry give conrotatory motion. The reason behind this rule can be easily understood by recalling that overlap of wave functions of the same sign is bonding (and symmetry allowed reaction) whereas overlap of wave functions of opposite sign is antibonding (and symmetry forbidden process). Electrocyclic reactions are highly stereospecific. An intriguing feature about electrocyclic reactions is that the stereochemistry of the product is dependent on whether the reaction is thermally induced or photo-induced.

Open chain conjugated system having 4nπ conjugated electrons

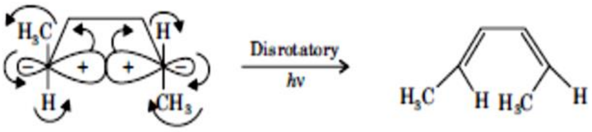
Let us consider the simplest example in which a cyclobutene derivative opens to a 1, 3-butadiene derivative, i.e., open-chain conjugated system has 4n conjugated π electrons. In thermal condition trans-3, 4-dimethylcyclobutene gives (2E, 4E)-2, 4-hexadiene. Thus, this reaction is completely stereospecific. In the photochemical condition the same substrate gives (2E, 4Z)-2, 4-hexadiene. In this case too, the reaction is completely stereospecific. Thus the reaction can be performed thermally or photochemically, and under either condition the reaction is completely stereospecific.



Stereochemistry of the thermal reaction-1 (of the 4nπ system) can only be explained if process should be conrotatory.



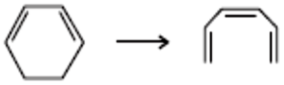
Stereochemistry of the photochemical reaction-2 (of the 4n, π system) can only be explained if process should be disrotatory.



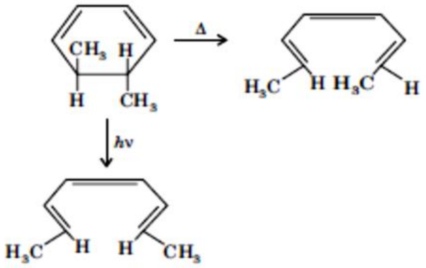
From the above two examples it is clear that thermally induced electrocyclic reaction involving 4nπ conjugated electrons require conrotatory motion and photochemically induced electrocyclic reaction require disrotatory motion.

Open chain conjugated system having (4n+2)π conjugated electrons

The simplest example of this category is the ring-opening of 1, 3-cyclohexadiene into 1, 3, 5-hexatriene.

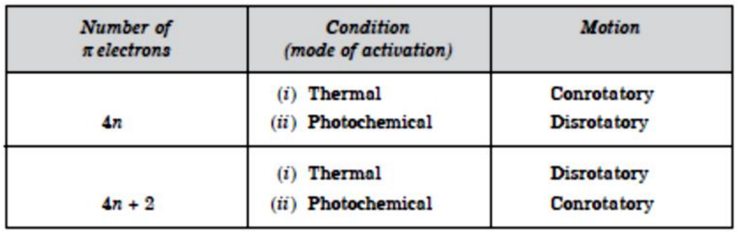


In thermal condition 5, 6-trans-dimethyl-1, 3-cyclohexadiene is converted exclusively to (2E, 4Z, 6Z)-2, 4, 6-octatriene. In the photochemical condition the same substrate is converted exclusively to (2E, 4Z, 6E)-2, 4, 6-octatriene



These two conversions are also highly stereospecific. Stereochemistry of these two reactions (i.e., reaction-3 and 4) can only be explained if process should be disrotatory in thermal condition and conrotatory in photochemical condition.

On the basis of these experimental results the stereochemistry of electrocyclic reactions can be summarised by noting that thermally induced electrocyclic reactions involving 4nπ electrons require conrotatory motion. Under similar conditions, electrocyclic reactions involving (4n + 2)π electrons follow disrotatory motion. Similarly, photo-induced electrocyclic reactions involving 4nπ electrons require disrotatory motion. Under similar conditions, electrocyclic reactions involving (4n + 2)π electrons follow conrotatory motion. A summary of the type of motion to be expected from different polyenes under thermal and photochemical conditions is shown in Table



Number of *π electrons*	*Condition* *(mode of activation)*	*Motion*
$4n$	(*i*) Thermal (*ii*) Photochemical	Conrotatory Disrotatory
$4n + 2$	(*i*) Thermal (*ii*) Photochemical	Disrotatory Conrotatory

The above experimental results can be explained by the four theories given for pericyclic reactions.

Frontier Molecular Orbital (FMO) Method

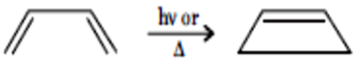
A methodology for quickly predicting whether a given pericyclic reaction is allowed by examining the symmetry of the highest occupied molecular orbital (HOMO) (in case of unimolecular reaction) and, if the reaction is bimolecular, the lowest unoccupied molecular orbital (LUMO) of the second partner. Thus, electrocyclic reaction is analysed by HOMO of the open chain partner because reaction is unimolecular reaction. The stereochemistry of an electrocyclic process is determined by the symmetry of the highest occupied molecular orbital (HOMO) of the open chain partner, regardless of which way the reaction actually runs. In thermal condition HOMO is always ground state HOMO whereas in photochemical condition HOMO is always first excited state HOMO. If the highest occupied molecular orbital has m symmetry, the process will be disrotatory. On the other hand, if HOMO has C2-symmetry then the process will be conrotatory

Symmetry in HOMO	*Mode of rotation*
m-Symmetry	Disrotatory
C_2-Symmetry	Conrotatory

For any electrocyclic reaction there are two conrotatory and two disrotatory modes of ring cleavage and ring closure. The two conrotatory modes can give same or different products. Similarly, the two disrotatory modes can also give the same or different products.

Cyclisation of 4nπ System

Electrocyclic ring-closure reaction given by butadiene: 1, 3-butadiene is the first member of the conjugated polyene having 4nπ electrons.



Thermal-induced cyclisation: When 1, 3-butadiene is heated, reaction takes place from the ground state. The electrons that are used for the σ (sigma) bond formation are in the HOMO (ψ2 in this case). Pertinent p orbitals in ground state HOMO has C2-symmetry. For the new σ (sigma) bond to form, rotation must be conrotatory. Disrotatory motion would not place the in-phase lobes together.

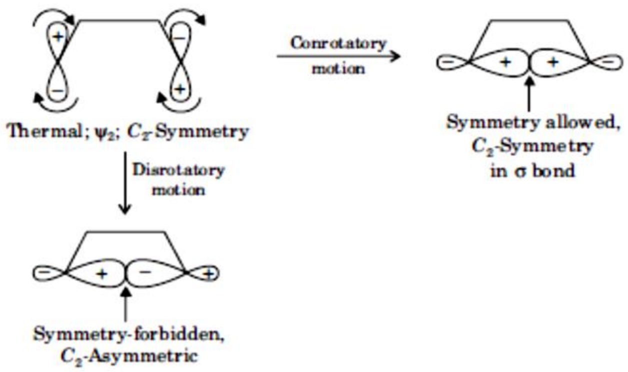
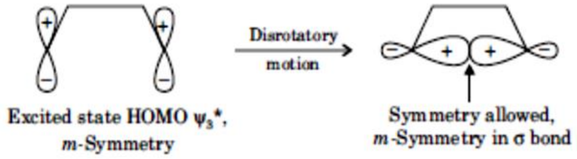
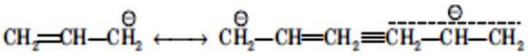


Photo-induced cyclisation: In photo-induced cyclisation, the first excited HOMO of 1, 3-butadiene is ψ3* which has m symmetry. For the new σ (sigma) bond to form, rotation must be disrotatory.

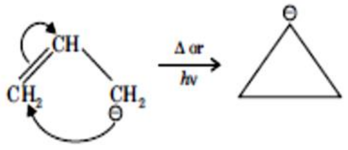


Electrocyclic ring-closure given by allyl carbanion:

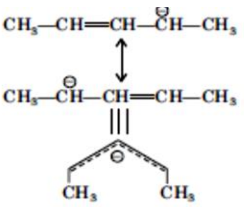
Allyl carbanion is also a 4nπ conjugated system.

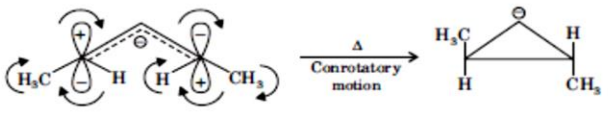


$$CH_2{=}CH{-}\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2{-}CH{=}CH_2 \equiv \overset{\ominus}{\overline{CH_2{-}CH{-}CH_2}}$$

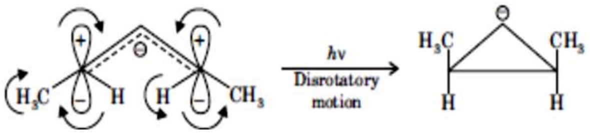


HOMO of the allyl carbanion in the ground state is ψ2 which has C2-symmetry. Therefore, conrotatory motion is the mode of cyclisation in the thermal condition





In case of photocyclisation, the excited HOMO is ψ3* which has m-symmetry. Thus, disrotatory motion is required for σ (sigma) bond formation.

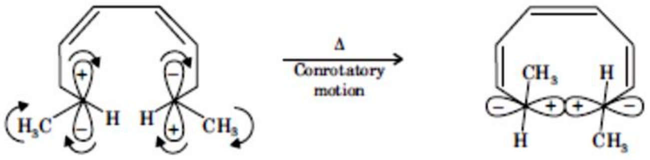


Electrocyclic ring-closure reaction given by 1, 3, 5, 7-octatetraene:

1, 3, 5, 7octatetraene and its derivatives contain 4nπ conjugated electrons. Consider the electrocyclic ring-closure of (2E, 4Z, 6Z, 8E)-2, 4, 6, 8-decatetraene in thermal and photochemical conditions.

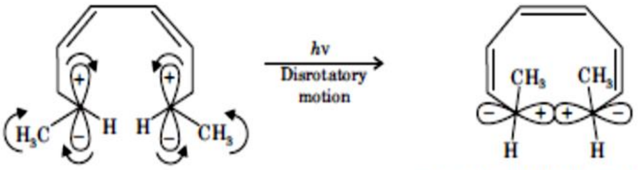
Thermal-induced cyclisation:

The tetraene is a 4n polyene. Its ground state HOMO is ψ4 which has C2-symmetry. Therefore, conrotatory motion is the mode of cyclisation.



trans-7, 8-Dimethyl-1, 3, 5-cyclotriene

Photo-induced cyclisation: In case of photo-induced cyclisation the excited state HOMO is ψ5* which has m-symmetry. Thus disrotatory motion is the mode of cyclisation.



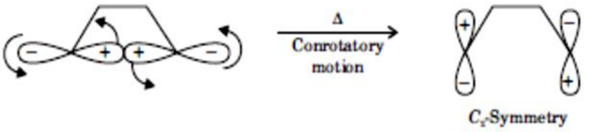
cis-7, 8-Dimethyl-1, 3, 5-cyclooctatriene

Electrocyclic ring-opening reaction of polyene with 4nπ electrons

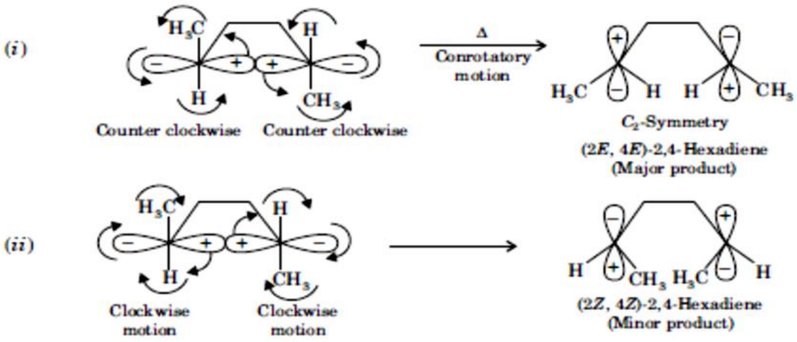
Conversion of cyclobutene to butadiene

Thermal-induced ring opening:

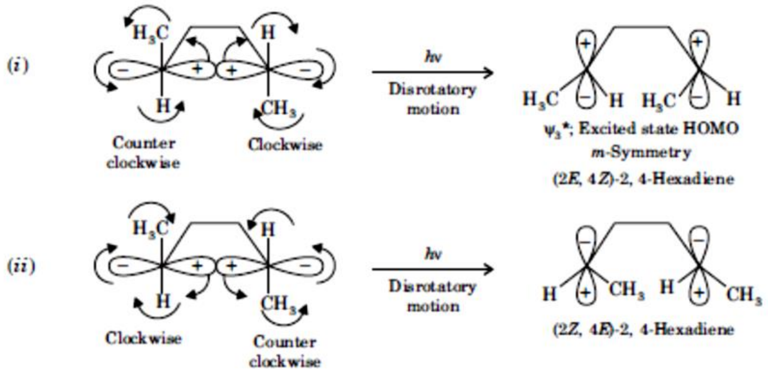
In the ring-opening reactions stereochemistry of the product is determined by the symmetry of the ground state HOMO of the open-chain partner. The ground state HOMO of the butadiene and its derivative will be ψ2 which has C2-symmetry. The cyclobutene ring must open in such a fashion that the σ bond orbitals transform into the HOMO of the product having C2-symmetry. To get C2-symmetry in the product HOMO, motion should be conrotatory in the ring opening of the reaction.



Thus, if the open-chain polyene has 4nπ electrons then the process is always conrotatory in thermal condition whether the reaction is ring-closure or ring opening. Let us take the stereochemistry of the ring opening of trans-3, 4-dimethylcyclobutene. There is possibility of two modes of conrotatory motion, counter clockwise and clockwise motions.



Thus, the thermal process is conrotatory with two products possible in the above case. The conrotation in the second case (clockwise rotation) leads to severe steric interactions between two methyl groups. This interaction is avoided in the first process (rotation is counter clockwise) in which two methyl groups move away from each other, and this is the favoured process. (B) Photo-induced ring opening: The photo state HOMO of the open chain butadiene and its derivative will be ψ3∗ which has m-symmetry. Thus, the cyclobutene ring must be open in such a fashion that the σ bond orbitals transform into the excited state HOMO of the product having m-symmetry. To get m-symmetry in excited state HOMO of the product, motion should be disrotatory in the ring-opening of the reaction. There is also possibility of two modes of disrotatory motion.

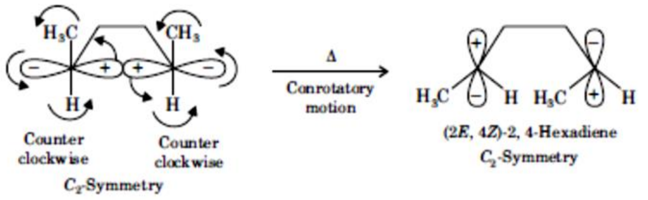


Thus, photo-induced process is disrotatory with either possible disrotation giving same product.

Let us take the conversion of cis-3, 4-dimethylcyclobutene into 2, 4-hexadiene.

Thermal ring-opening

(*i*)



(*ii*)

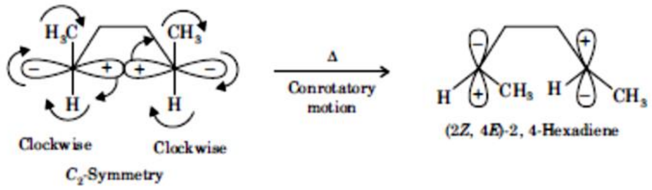
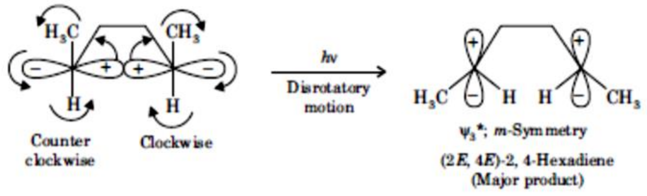
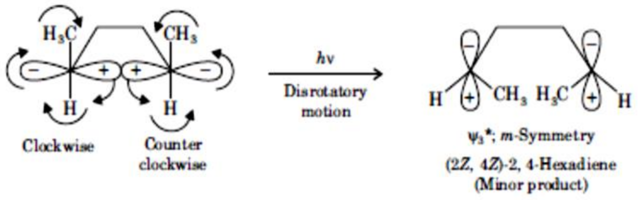


Photo-induced ring-opening

(*i*)



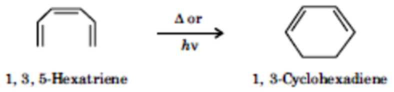
(*ii*)



Cyclisation of (4n+2)π System

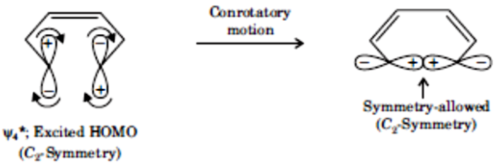
Electrocyclic ring-closure reaction given by 1, 3, 5-hexatriene

1, 3, 5-Hexatriene is the most common example of the polyene having (4n + 2)π conjugated electrons.



Thermal-induced cyclisation: ψ3 is the ground state HOMO of 1, 3, 5-hexatriene which has m-symmetry. Therefore, the thermal cyclisation proceeds by disrotatory motion.

Photo-induced cyclisation: When an electron of 1, 3, 5-hexatriene is promoted by photon absorption, ψ4* becomes the HOMO. This excited state HOMO has C2-symmetry. Therefore, photo-induced cyclisation proceeds by conrotatory motion.



Consider the stereochemistry of the thermal and photo-induced closure of (2E, 4Z, 6E)2, 4, 6-octatriene to 5, 6-dimethyl-1, 3-cyclohexadiene.

Thermal-induced cyclisation: In the case of the thermal induced cyclisation, the ground state HOMO is ψ3 which has m-symmetry. Thus, disrotatory motion is required for sigma bond formation.

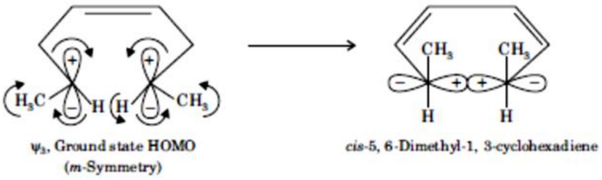
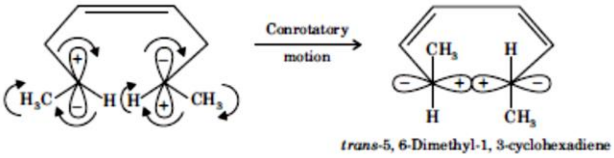


Photo-induced cyclisation: In case of photo-induced cyclisation, the excited state HOMO is ψ4* which has C2-symmetry. Therefore, conrotatory motion is required for σ (sigma) bond formation.

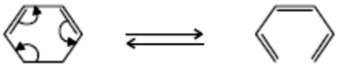


Cyclisation of (4n+2)π System

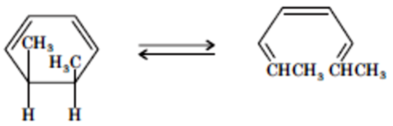
Electrocyclic ring-opening reaction

Conversion of 1, 3-cyclohexadiene to 1, 3, 5-hexatriene system

The most common example of this class is the conversion of 1, 3-cyclohexadiene to 1, 3, 5hexatriene.



Let us take the example of the ring opening of a cis-5, 6-dimethyl-1, 3-cyclohexadiene into 2, 4, 6-octatriene.



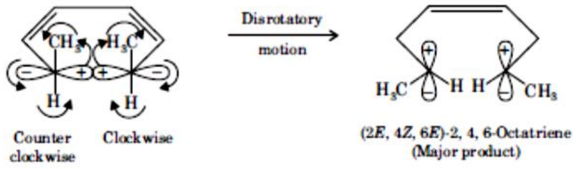
Thermal ring-opening: As mentioned earlier that in the ring opening reactions stereochemistry of product is determined by the symmetry of the ground state HOMO of the open-chain partner. The ground state HOMO of the triene will be ψ3 which has m-symmetry. The cyclohexadiene ring therefore, must open in such a fashion that σ bond orbitals transform into the ground state HOMO of the product having m-symmetry. To get m-symmetry in the HOMO of the product, motion should be disrotatory in the ring opening of the reaction.

The above results can be obtained in short as follows:

Ground state HOMO is ψ_3 which has *m*-symmetry. Therefore, motion is disrotatory

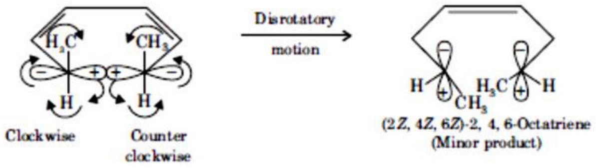
Two modes of disrotatory motions can take place as follows:

(*i*)



(2*E*, 4*Z*, 6*E*)-2, 4, 6-Octatriene (Major product)

(*ii*)



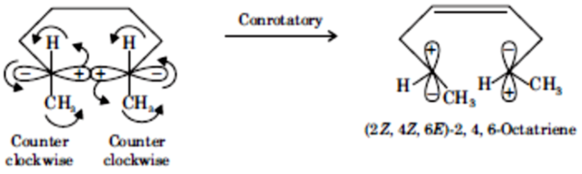
(2*Z*, 4*Z*, 6*Z*)-2, 4, 6-Octatriene (Minor product)

Thus, the thermal process is disrotatory with two possible products, one is major and the other is minor due to the steric reasons.

Photo-induced ring-opening:

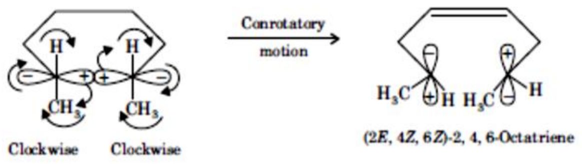
The photo state HOMO of the triene system is ψ4* which has C2-symmetry. To get C2-symmetry in the product, motion should be conrotatory in the ring opening reaction. Consider the two modes of conrotatory motions:

(*i*)



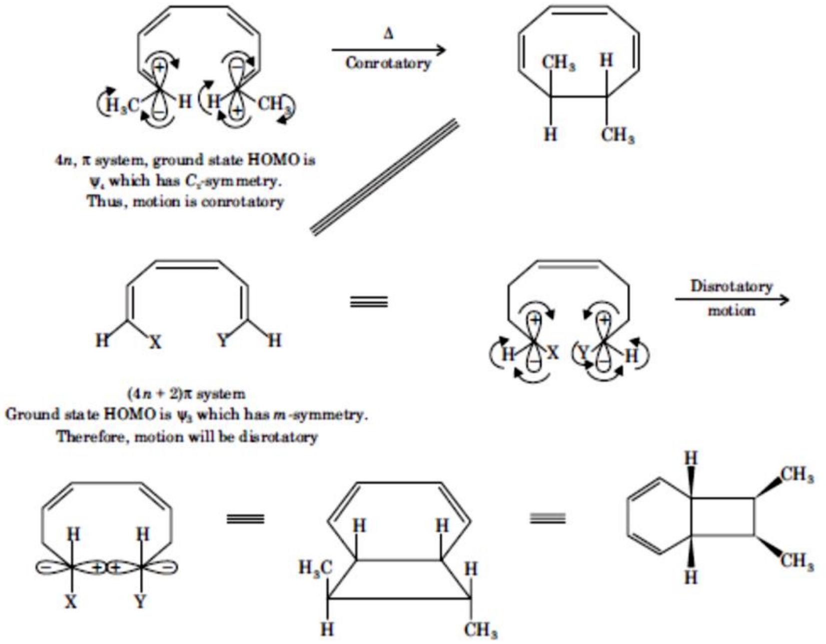
(2*Z*, 4*Z*, 6*E*)-2, 4, 6-Octatriene

(*ii*)



Thermal electrocyclic reaction given by (2E, 4Z, 6Z, 8E)-2, 4, 6, 8-decatetraene

The thermally induced electrocyclic reaction of (2E, 4Z, 6Z, 8E)-2, 4, 6, 8-decatetraene provide elegant examples of electrocyclic reactions. The starting tetraene forms a cyclooctatriene at room temperature. The tetraene is a 4n polyene; therefore, conrotatory motion is the expected mode of cyclisation. Indeed the trans7, 8-dimethyl-1, 3, 5-cyclooctatriene is the product of this initial cyclisation. When this cyclooctatriene is heated above room temperature, another electrocyclic ring closure occurs. However, the cyclooctatriene is a (4n + 2)π polyene; therefore, this thermally induced electrocyclic reaction proceeds with disrotatory motion, and a cis ring junction is formed.

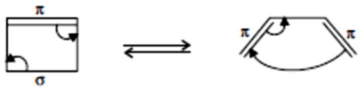


Correlation Diagram

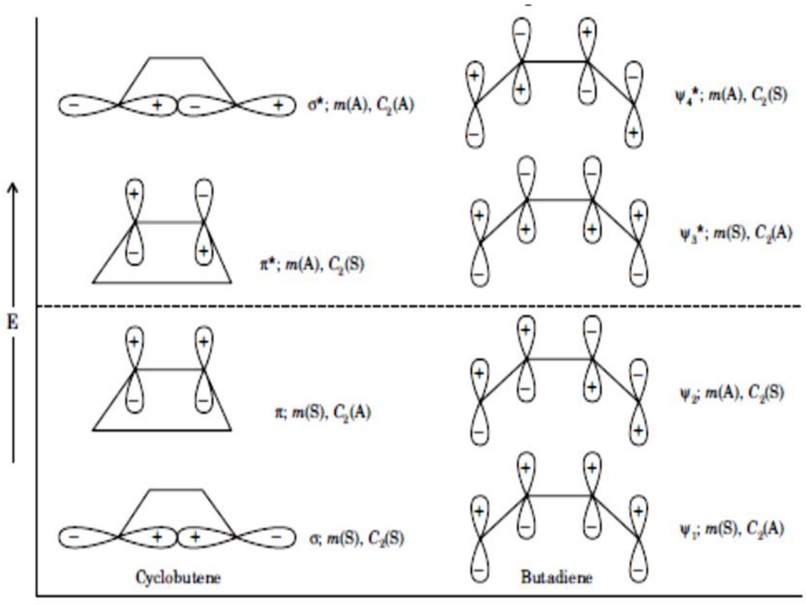
The diagram that shows the correspondence in energy and symmetry between relevant reactant and product orbitals is called orbital correlation diagram or simply correlation diagram. This method can be used for any pericyclic reaction, but is usually utilised only for electrocyclic reactions. The relevant orbitals are those that undergo change during the reaction. Correlation diagram is based on the fundamental rule of the conservation of orbital symmetry as proposed by Woodward and Hoffmann. According to this rule orbital symmetry be conserved throughout the course of reaction in concerted reactions. Thus, as a concerted reaction proceeds it must do so with conservation of orbital symmetry. This means that a symmetric orbital in the starting material must transform into a symmetric orbital in the product and that an asymmetric orbital must transform into an asymmetric orbital. The orbitals that correlate (transform into each other) are connected by lines keeping in view that there is correlation between orbitals of same symmetry having minimum energy difference. The diagram is constructed as follows: in separate columns the relevant orbitals of reactant and product are listed in their order of relative energies; each orbital is classified on the basis of the symmetry elements retained at all points along the reaction coordinate; line are drawn between the reactant and product orbitals connecting the lowest energy orbitals of the same symmetry type. The following two conclusions can be drawn by correlation diagram: (i) Thermal transformation is symmetry allowed reaction when the ground state orbitals of the reactant correlate with ground state orbitals of the product. (ii) Photochemical transformation is symmetry allowed when first excited state orbitals of the reactant correlate with first excited state orbitals of the product.

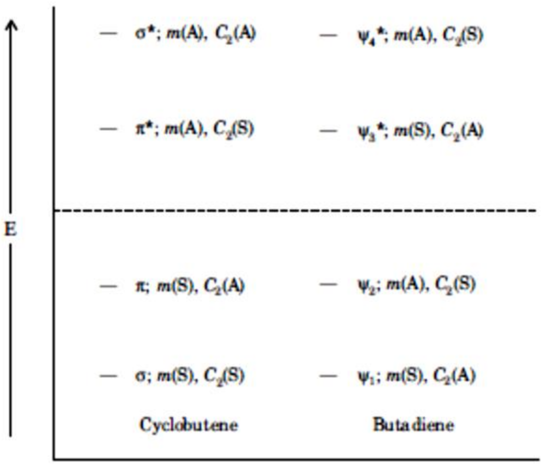
Correlation Diagram for 4nπ System

Let us exemplify the above principle by analysing the cyclobutene-butadiene transformation.

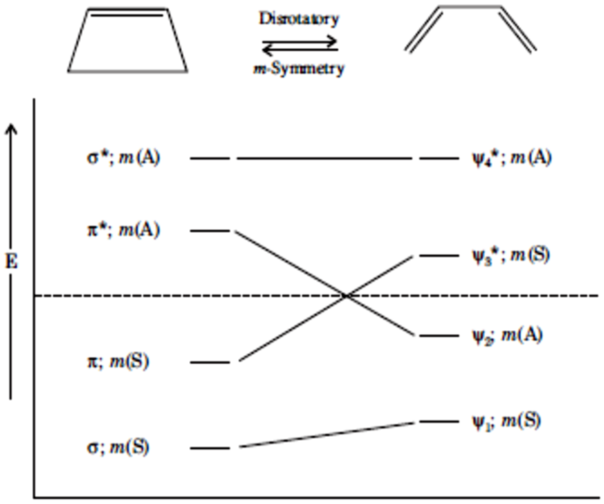


The orbitals that undergo direct changes in cyclobutene are σ, π and the related antibonding orbitals, σ* and π*; these orbitals pass on to the four π molecular orbitals of butadiene, viz., ψ1, ψ2, ψ3* and ψ4*. For correlation diagram, all these orbitals are listed in order of increasing energy alongwith their mirror plane (m) and C2-symmetric properties





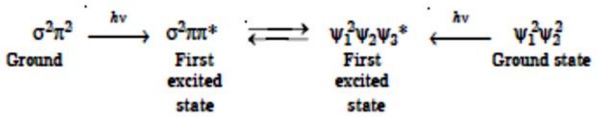
We know that for bonding overlap (i.e., symmetry allowed reaction) disrotatory mode of rotation is needed for orbitals having m-symmetry and conrotatory mode of rotation for C2-symmetry.



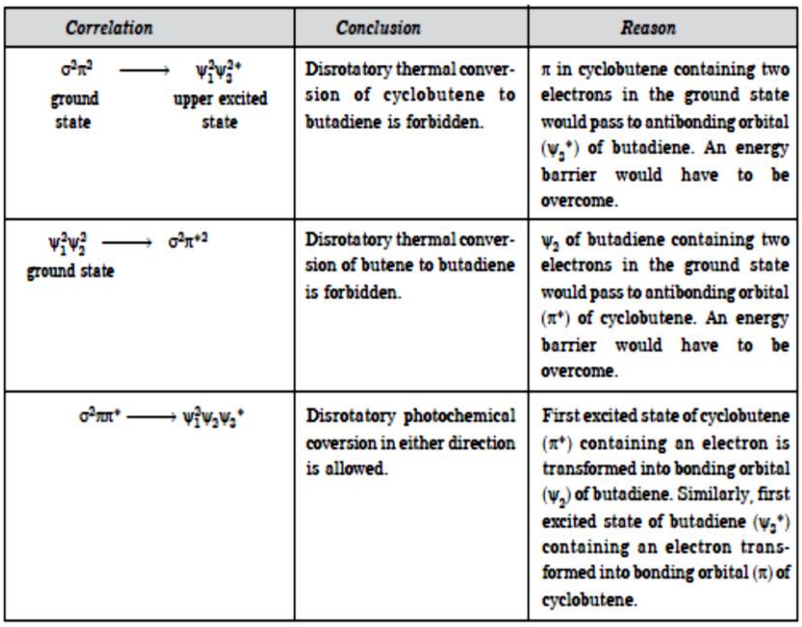
Let us analyse whether disrotatory mode ring-opening of cyclobutene to butadiene is thermal allowed or photochemical allowed process in which m-symmetry is maintained throughout the course of the reaction. Inspection of correlation diagram shows that this process is thermally forbidden because π in cyclobutene containing two electrons would pass to the antibonding orbital (ψ3*) of butadiene. In the correlation diagram the ground state σ orbital of cyclobutene correlate with the ground state ψ1 orbital of butadiene. The ground state π orbital of cyclobutene does not correlate with the ground state ψ2 orbitals of butadiene. Instead it correlates with ψ3* which is an excited state and antibonding orbitals.

$$\sigma^2\pi^2 \; \cancel{\xrightleftharpoons{\Delta \quad \text{dis}}} \; \psi_1^2\psi_2^2$$

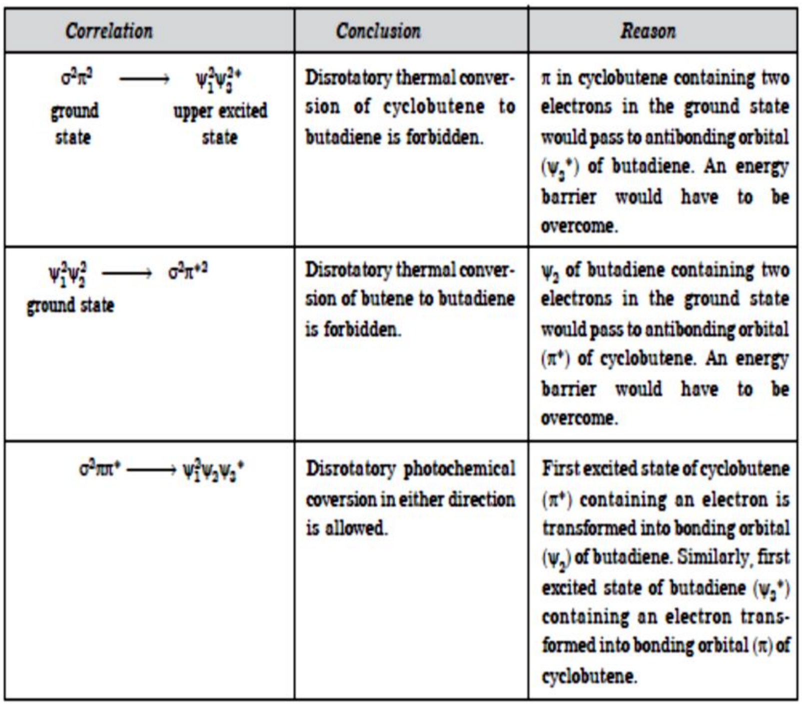
Correlation diagram shows that the first excited state of the cyclobutene σ2, π, π* correlates with the first excited state of butadiene ψ1 2, ψ2ψ3*. Thus, disrotatory process in either direction is photochemically allowed. In the first excited state of cyclobutene π* contains an electron and it is transformed into bonding orbital (ψ2) in butadiene.



conclusions can be drawn from this correlation diagram

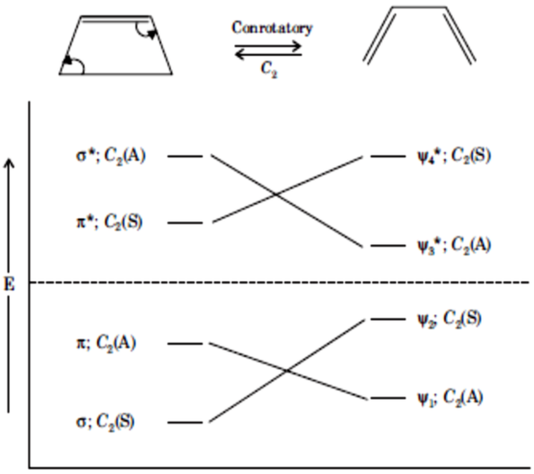


Correlation	*Conclusion*	*Reason*
$\sigma^2\pi^2 \longrightarrow \psi_1^2\psi_3^{2*}$ ground state — upper excited state	Disrotatory thermal conversion of cyclobutene to butadiene is forbidden.	π in cyclobutene containing two electrons in the ground state would pass to antibonding orbital (ψ_3^*) of butadiene. An energy barrier would have to be overcome.
$\psi_1^2\psi_2^2 \longrightarrow \sigma^2\pi^{*2}$ ground state	Disrotatory thermal conversion of butene to butadiene is forbidden.	ψ_2 of butadiene containing two electrons in the ground state would pass to antibonding orbital (π^*) of cyclobutene. An energy barrier would have to be overcome.
$\sigma^2\pi\pi^* \longrightarrow \psi_1^2\psi_2\psi_3^*$	Disrotatory photochemical coversion in either direction is allowed.	First excited state of cyclobutene (π^*) containing an electron is transformed into bonding orbital (ψ_2) of butadiene. Similarly, first excited state of butadiene (ψ_3^*) containing an electron transformed into bonding orbital (π) of cyclobutene.

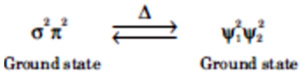


Correlation	*Conclusion*	*Reason*
$\sigma^2\pi^2 \longrightarrow \psi_1^2\psi_3^{2*}$ ground state — upper excited state	Disrotatory thermal conversion of cyclobutene to butadiene is forbidden.	π in cyclobutene containing two electrons in the ground state would pass to antibonding orbital (ψ_3^*) of butadiene. An energy barrier would have to be overcome.
$\psi_1^2\psi_2^2 \longrightarrow \sigma^2\pi^{*2}$ ground state	Disrotatory thermal conversion of butene to butadiene is forbidden.	ψ_2 of butadiene containing two electrons in the ground state would pass to antibonding orbital (π^*) of cyclobutene. An energy barrier would have to be overcome.
$\sigma^2\pi\pi^* \longrightarrow \psi_1^2\psi_2\psi_3^*$	Disrotatory photochemical coversion in either direction is allowed.	First excited state of cyclobutene (π^*) containing an electron is transformed into bonding orbital (ψ_2) of butadiene. Similarly, first excited state of butadiene (ψ_3^*) containing an electron transformed into bonding orbital (π) of cyclobutene.

Now consider the conrotatory conversion of cyclobutene to butadiene in which a C2-symmetry is maintained



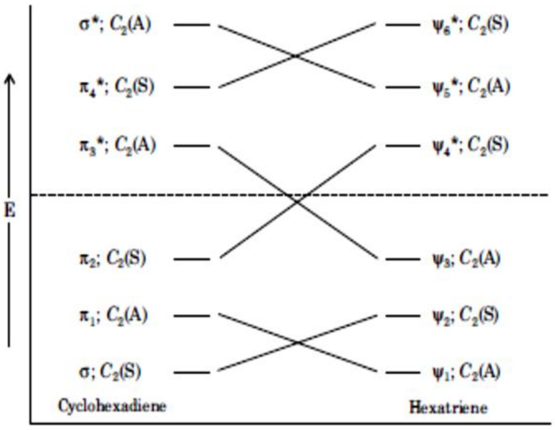
The orbitals now correlate in such a way that the ground state of cyclobutene σ2π2 correlates with the ground state of butadiene ψ1 2ψ2 2. The thermal conrotatory process is thus allowed in either direction.



Inspection of correlation diagram shows that this process is photochemically forbidden. The first excited state of cyclobutene (σ2ππ*) correlates with the upper excited state (ψ1 2ψ2ψ4*) of butadiene thus making it a high energy symmetry-forbidden process. Similarly, the first excited state of butadiene (ψ1 2ψ2ψ3*) correlates with a high energy upper excited state (σ2πσ*) of cyclobutene. In other words, a photochemical conrotatory process in either direction is symmetry-forbidden. Thus, it becomes clear from the correlation diagrams that thermal opening of the cyclobutene proceeds in a conrotatory process while photochemical interconversion involves a disrotatory mode. These generalisations are true for all systems containing 4nπ electrons.

Correlation Diagram for (4n+2)π System

A typical system of this category is the interconversion of 1, 3-cyclohexadiene and 1, 3, 5hexatriene. In this transformation six molecular orbitals (ψ1, ψ2, ψ3, ψ4*, ψ5* and ψ6*) of hexatriene and six molecular orbitals (four π molecular orbitals π1, π2, π3* and π4* and two σ molecular orbitals) of cyclohexadiene are actually involved and, therefore, need to be considered. Consider the conrotatory conversion of cyclohexadiene to hexatriene in which a C2-symmetry is maintained



Inspection of the correlation diagram shows that this process is thermally forbidden because ground state orbitals of the reactant does not correlate with the ground state orbitals of the product.

$$\sigma^2\pi_1^2\pi_2^2 \;\cancel{\rightleftharpoons}\; \psi_1^2\psi_2^2\psi_3^2$$

In the correlation diagram, the ground state σ and π1, orbitals of cyclohexadiene correlate with the ground state ψ1 and ψ2 orbitals of hexatriene. The ground state orbital π2 of cyclohexadiene does not correlate with the ground state orbitals ψ3 of hexatriene. Instead it correlates with ψ4* which is an excited state and antibonding.

$$\sigma^2\pi_1^2\pi_2^2 \longrightarrow \psi_1^2\psi_2^2\psi_4^*$$

Thus, in thermal condition π(π2) in cyclohexadiene containing two electrons would pass to the antibonding orbital (ψ4*) of hexatriene. An energy barrier would have to be overcome in this process and thus process is forbidden.

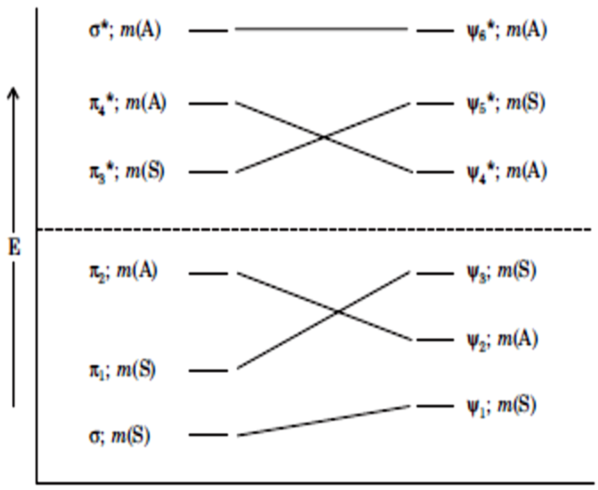
Correlation diagram shows that the first excited state of cyclohexadiene σ2π1 2π2π3* correlates with the first excited state of hexatriene ψ1 2ψ2 2ψ3ψ4*. Thus, conrotatory process in either direction is photochemically allowed.

$$\underset{\substack{\text{Ground}\\\text{state}}}{\sigma^2\pi_1^2\pi_2^2} \xrightarrow{h\nu} \underset{\substack{\text{First excited}\\\text{state}}}{\sigma^2\pi_1^2\pi_2\pi_3^*} \rightleftharpoons \underset{\substack{\text{First excited}\\\text{state}}}{\psi_1^2\psi_2^2\psi_3\psi_4^*} \longleftarrow \underset{\text{Ground state}}{\psi_1^2\psi_2^2\psi_3^2}$$

In this case first excited state of cyclohexadiene π3* containing an electron is transformed into bonding orbital ψ3 of hexatriene. Similarly, first excited state of hexatriene ψ4* containing an electron also transformed into bonding orbital π2 of cyclohexadiene. Thus, process is allowed process.

$$\sigma^2\pi_1^2\pi_2\pi_3^* \rightleftharpoons \psi_1^2\psi_2^2\psi_3\psi_4^*$$

Now consider the disrotatory conversion of cyclohexadiene to hexatriene in which m-symmetry is maintained



Inspection of the correlation diagram shows that the orbitals correlate in such a way that the ground state of cyclohexadiene σ2π1 2π2 2 correlates with the ground state of hexatriene ψ1 2ψ2 2ψ3 2. The thermal disrotatory process is thus allowed in either direction.

$$\sigma^2\pi_1^2\pi_2^2 \underset{}{\overset{\Delta}{\rightleftarrows}} \psi_1^2\psi_2^2\psi_3^2$$

Inspection of the correlation diagram shows that this process is photochemically forbidden. The first excited state of cyclohexadiene π3* correlates with the upper excited state ψ5* of hexatriene. Similarly, the first excited state of hexatriene ψ4* correlates with a high energy upper excited state of cyclohexadiene. An energy barrier would have to be overcome in this process and thus process is forbidden. Thus, it becomes clear from the above considerations that thermal opening of the cyclohexadiene proceeds in a disrotatory process while photochemical interconversion involves a conrotatory mode. There generalisations are true for all conjugated systems containing (4n +2)π electrons. Thus Woodward-Hoffmann rules for electrocyclic reactions on the basis of correlation diagrams may be summed up as in Table

Number of π electrons	*Thermal*	*Photochemical*
$4n$	Conrotatory	Disrotatory
$4n+2$	Disrotatory	Conrotatory

Woodward-Hoffmann Rule for Electrocyclic Reaction

Fortunately, all the conclusions that can be drawn laboriously from correlation diagrams can be drawn more easily from a pair of rules, known as the Woodward-Hoffmann rules. Rules distil the essence of the idea into two statements governing all pericyclic reactions, one rule of thermal reactions and its opposite for photochemical reactions. Correlation diagrams explain why they work, but we no longer depend upon constructing such diagrams.

Woodward-Hoffmann Rule for Thermal Electrocyclic Reaction

A thermal (ground state) electrocyclic reactions is symmetry allowed when the total number of (4q + 2)s and (4r)a components is odd.

Photochemical Electrocyclic Reaction

An electrocyclic reaction in the first electronically excited state is symmetry allowed when the total number of (4q + 2) a and (4r)s is odd. These rules need some explanation.

Component

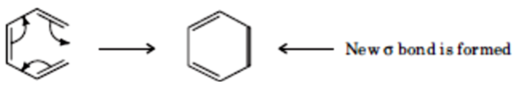
A component is a bond or orbital taking part in a pericyclic reaction as a single unit. A double bond is a π2 component. The number two is the most important part of this designation and simply refers to the number of electrons. The prefix π tells us the type of electrons. A component may have any number of electrons, for example 1, 3-butadiene is a π4 component. Component may not have mixtures of π and σ electrons. Component either contains only σ electrons or contains only π electrons. Designations (4q + 2) and (4r) simply refer to the number of electrons in the component where q and r are integers (0, 1, 2, 3, 4, ..., n). An alkene is a π2 component and so it is of the (4q + 2) kind where q = 0 while diene is a π4 component and so it is of the (4r) kind where r = 1.

Suffix s and a

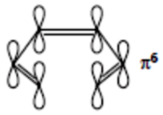
In electrocyclic reaction s means when upper (or lower) lobe of one frontier orbital overlaps with upper (or lower) lobe of other frontier orbital and a means when upper lobe of one orbital overlaps with lower lobe of other.

Let us start with hexatriene ring closure. As a preliminary, we would just note that hexatriene is, of course, a 6π electrons (π6) conjugated system and, on forming cyclohexadiene, the end two orbitals have to form a σ bond. So, now for the Woodward-Hoffmann treatment:

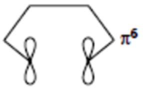
1. Draw the mechanism for the reaction



2. Choose the components. All the bonds taking part in the mechanism must be included and no others.

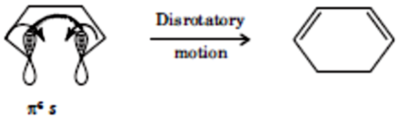


3. Make the three-dimensional drawing of the way the components come together for the reaction putting in orbitals at the ends of the components.



These orbitals are simple p-orbitals and do not make up HOMOs or LUMOs or any particular MOs. Do not attempt to mix frontier orbitals and Woodward-Hoffmann description of correlation of pericyclic reactions. 4. Join up the component(s) where new bond(s) are to be formed. Make sure you join orbitals that are going to form new bonds. In this case formation of new σ bond takes place by two possible cases:

Case I: When component is s. In this case overlapping will be possible if motion is disrotatory.



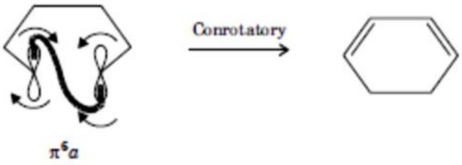
Notice that we call the component ‘s’ because the upper lobes of the two p-orbitals were joining together. If upper lobe of one orbital and lower lobe of another orbital is joined together then component will be ‘a’.

Number of $(4q + 2)$ s component $= 1$
Number of $(4r)$ a component $= 0$
Total $= 1$ (odd)

Thermal: Allowed

Photochemical: Forbidden

Case II: When component is ‘a’. In this case overlapping will be possible if motion is conrotatory.

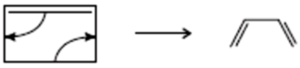


Number of $(4q + 2)a = 1$
Number of $(4r)$ $s = 0$
Total $= 1$ (odd)

Thermal: Forbidden

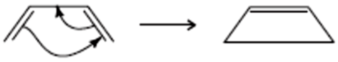
Photochemical: Allowed

Similarly, take the example of conversion of cyclobutene to 1, 3-butadiene.

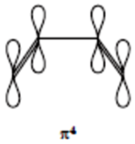


But for the use of Woodward-Hoffmann rule always consider the process in which open system converts into cyclic system.

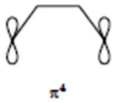
1. Draw the mechanism for the reaction.



2. Choose the components. All the bonds taking part in the mechanism must be included and no others.



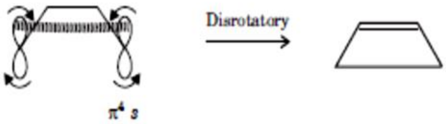
3. Make the three-dimensional drawing of the way in which the component comes together for the reaction, putting the orbitals at the ends of the component.



4. Join up the component(s) where new bond(s) are to be formed.

5. Show bond formation by conrotatory as well as disrotatory motion. Label each component s or a.

(*i*)



Number of $(4q + 2)$ *s* component = 0

Number of $(4r)$ *a* component = 0

Total = 0

Thermally: Disallowed

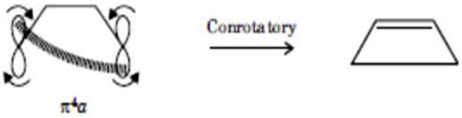
Number of $(4q + 2)$ *a* component = 0

Number of $(4r)$ *s* component = 1

Total = 1 (odd)

Photochemically: Allowed

(*ii*)



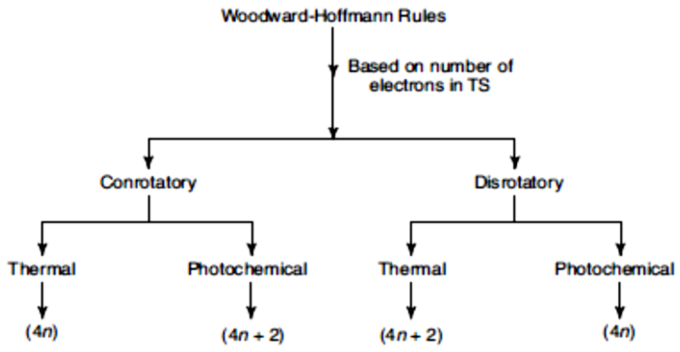
Number of $(4r)a$ = 1

Number of $(4q + 2)$ *s* = 0

Total = 1 (odd)

Thermally: Allowed

Thus, we can conclude the following results from Woodward-Hoffmann rule for electrocyclic reactions:



Huckel-Mobius Method (HM Method) or Perturbation Molecular Orbital (PMO) Method

Another method for quickly assessing whether a given pericyclic process is allowed is to examine the cyclic array of orbitals at the transition state of the pericyclic reaction. This method was popularised by H. Zimmerman and M.J.S. Dewar. Hückel rule of aromaticity states that a monocyclic planar conjugated system is aromatic if it has (4n + 2) π conjugated or delocalised electrons and consequently stable in ground state. Similarly, monocyclic planar conjugated system is anti-aromatic if it has (4n) π conjugated or delocalised electrons. This system is unstable in ground state. However, further calculation shows that these rules are reversed by the presence of a node in the array of atomic orbitals. Thus, system with (4n + 2) π electrons and a node is antiaromatic while system with (4n) π electrons and a node is aromatic.
Thus, system has no node then:

(4n + 2)π electrons → aromatic → stable in ground state.

(4n)π electrons → antiaromatic → unstable in ground state.

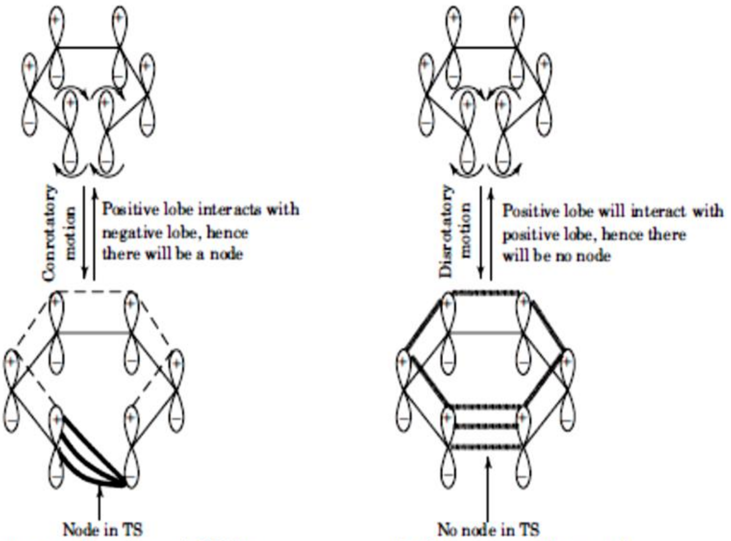
Similarly, system having a node then

(4n) π electron → aromatic → stable in ground state.

(4n + 2) π electrons → antiaromatic → unstable in ground state.

If system has no node then it is called Hückel system and array is called Hückel array. Similarly, if system has node then it is called Mobius system and array is called Mobius array. Application of these rules to pericyclic reactions led to the generalisation that thermal reactions take place via aromatic transition state [i.e., (4n + 2) π electrons having no node or (4n) π electrons having one node] whereas photochemical reactions proceed via antiaromatic transition state [i.e., (4n)π electrons having no node or (4n + 2) π electrons having one node]. A cyclic transition state is said to be aromatic or isoconjugated with the corresponding aromatic system if the number of the conjugated atoms and that of the π (pi) electrons involved are the same as in the corresponding aromatic system. Similarly, a cyclic transition state is said to be antiaromatic or isoconjugated with the corresponding antiaromatic system if the number of conjugated atoms and that of the π (pi) electrons involved are the same as in the corresponding antiaromatic system. We have only to consider a cyclic array of atomic orbitals representing those orbitals which undergo change in the transition state and assign signs to the wave function in the best manner for overlap. Then the number of nodes in the array and number of electrons involved are counted. Let us consider the following electrocyclic reaction.

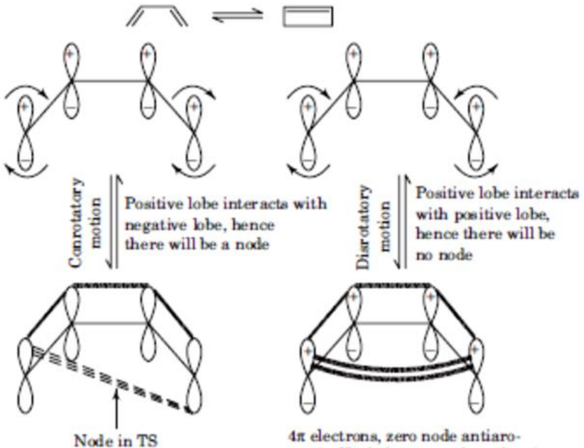
Cis-1, 3, 5-hexatriene ⇌ Cyclohexadiene



Node in TS
6π electrons, one node, antiaromatic Mobius system hence photochemically allowed

No node in TS
6π electrons, zero node, aromatic, Hückel system hence thermally allowed

Similarly for
1, 3-butadiene ⇌ Cyclobutene

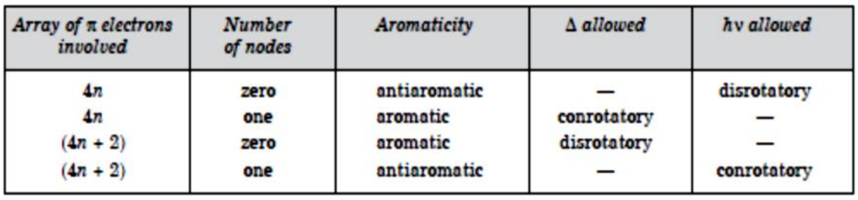


Node in TS
4π electrons, one node, aromatic Mobius system thermally allowed.

4π electrons, zero node antiaromatic, Hückel system photochemically allowed.

Thus, for the thermal reactions involving (4n + 2)π electrons will be disrotatory and involved Hückel type transition whereas those having (4n) π electrons will be conrotatory and the orbital array will be of the Mobius type. Similarly, for photochemical reactions involving (4n + 2) π electrons will be conrotatory and involved Mobius type transition whereas those involving (4n) π electrons will be disrotatory and the orbital array will be Hückel type. Thus for convenience, the selection rules by this approach to electrocyclic reactions are given in Table

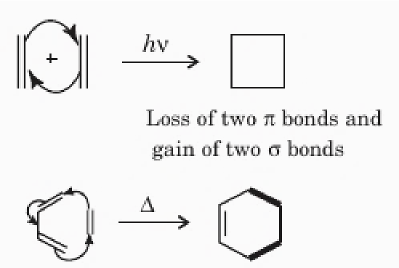
Selection rules for electrocyclic reactions by H.M. method



Array of π electrons involved	*Number of nodes*	*Aromaticity*	*Δ allowed*	*hν allowed*
$4n$	zero	antiaromatic	—	disrotatory
$4n$	one	aromatic	conrotatory	—
$(4n + 2)$	zero	aromatic	disrotatory	—
$(4n + 2)$	one	antiaromatic	—	conrotatory

Cycloaddition Reactions

A cycloaddition is a reaction in which two unsaturated molecules undergo an addition reaction to yield a cyclic product. Formation of cyclic product takes place at the expense of one π (pi) bond in each of the reacting partner and gain of two σ (sigma) bonds at the end of the both components having π (pi) bonds. Thus, in this reaction there is loss of two π (pi) bonds of the reactants and gain of two σ (sigma) bonds in the product.



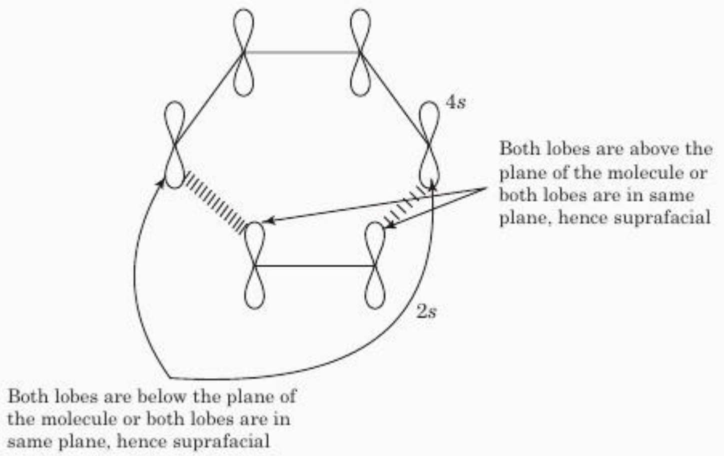
Loss of two π bonds and gain of two σ bonds. Formation of σ bonds at the end of the two components.

The cycloaddition reactions are classified with respect to three facts of the reaction:

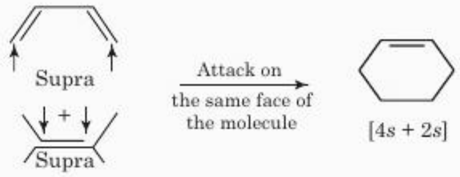
(i)The number of electrons of each unit participating in cycloaddition.

(ii) The nature of orbitals undergoing change (π or σ).

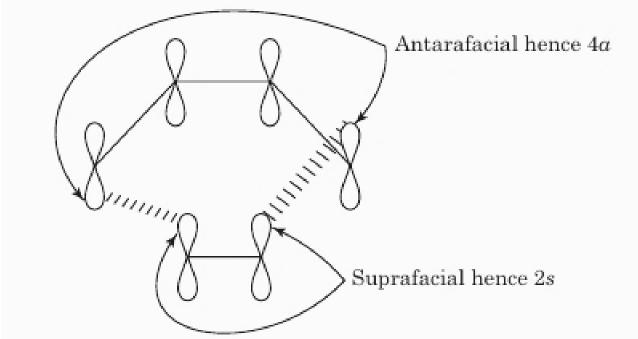
(iii) The stereochemical mode of cycloaddition (supra, syn or antara, anti). The reaction in equation is a [2 + 2] cycloaddition reaction because the reaction involves two electrons from one reacting component and also two electrons from the other. The reaction in equation is a [4 + 2] cycloaddition. The stereochemical mode is given by a subscript s or a which indicates whether the addition occurs in a supra or antara mode on each unit. A cycloaddition may in principle occur either across the same face or across the opposite faces of the planes in each reacting component. If reaction occurs across the same face of a π system, the reaction is said to be suprafacial with respect to that π system. The suprafacial is nothing more than a syn addition.



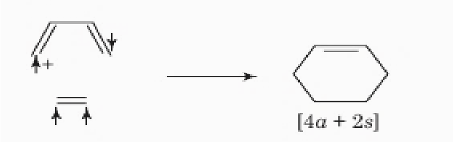
This addition reaction is thus [4s + 2s] cycloaddition reaction. This can also be represented as follows:

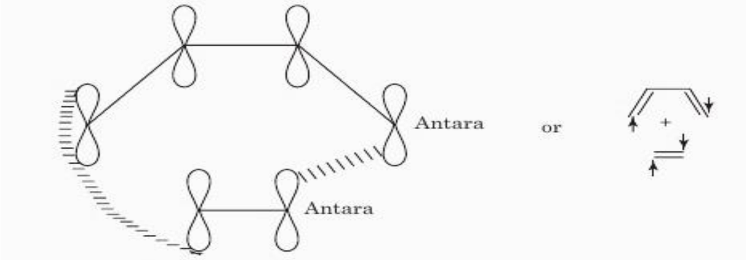


If the reaction bridges opposite faces of a π system, it is said to be antarafacial. An antarafacial is just an anti addition.



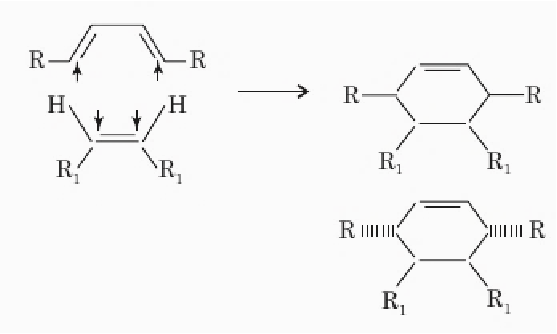
This mode of addition reaction is thus [4a + 2s] cycloaddition reaction. This can be represented as:





[4a + 2a] Cycloaddition reaction

In antarafacial, attack takes place with one bond forming to one surface but other bond forming to other surface. It is rare, it does not occur in any reaction. Almost all cycloaddition reactions are suprafacial on both components.



Cycloaddition: FMO Method

In order, for a cycloaddition to occur, there must be bonding overlap between p-orbitals at the terminal carbons of each π-electron system, this is where the new σ bonds are formed. Let us explain this point with a [4 + 2] cycloaddition. Let us suppose that diene (4π component) behaves as electron donor and the dienophile (2π component) as the electron acceptor (or vice-versa). What electrons will the 4π component donate? Obviously there will be its valence electrons—the electrons in its HOMO (ψ2). The 2π component will accept these electrons to form the new bonds. The molecular orbital used to accept these electrons must be empty since molecular orbital cannot contain more than two electrons. Therefore, the molecular orbital which accepts electron should be LUMO of the 2π component. Thus, one component used its HOMO and the other component used its LUMO for overlapping. Simultaneously with the merging of the π orbitals, these orbitals also undergo hybridisation to yield the new sp3 σ bonds.

[2+2] Cycloaddition

Thermal Induced [2 + 2] Cycloaddition Reactions

Thermal induced [2 + 2] cycloaddition reactions are symmetry forbidden reactions. When ethylene is heated, its π electrons are not promoted, but remain in the ground state ψ1. If we examine the phase of the ground state HOMO of one ethylene molecule and the LUMO of another ethylene molecule we can see why cyclisation does not occur by the thermal induction.

For bonding to occur, the phase of the overlapping orbitals must be same. This is not the case for the ground state HOMO and LUMO of two ethylene molecule or any other [2 + 2] system. Because the phase of the orbitals are incorrect for bonding, a thermally induced [2 + 2] cycloaddition is said to a symmetry forbidden reaction.

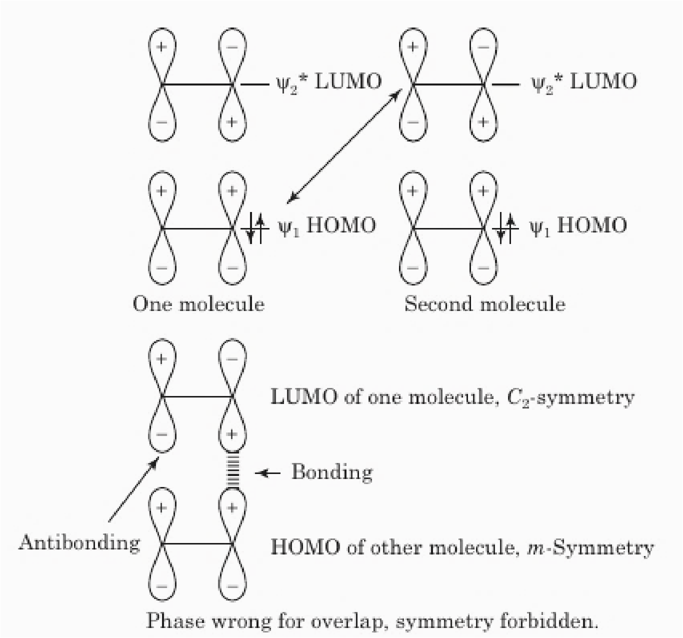
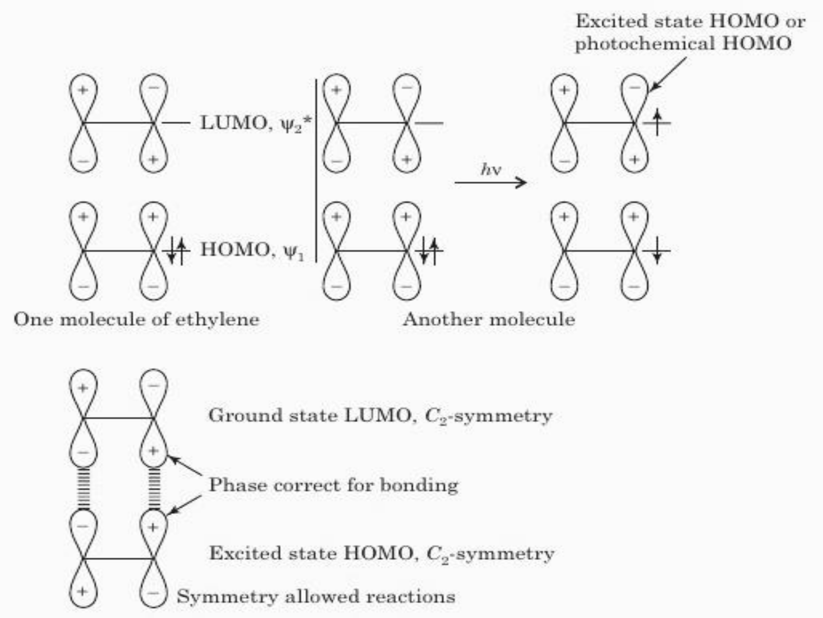


Photo-Induced [2 + 2] Cycloaddition Reactions

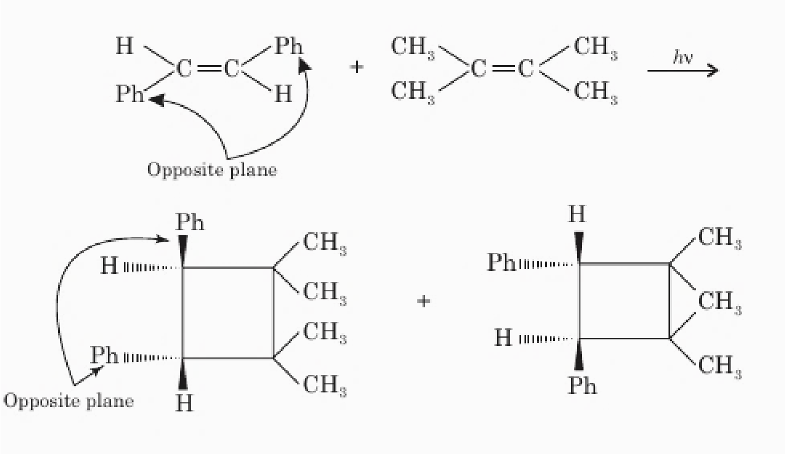
When ethylene is irradiated with photon of UV light, a π electron is promoted from ψ1 to ψ2* orbital in some, but not all, of the molecules. The result is a mixture of ground state and excited state ethylene molecules. Thus photo-induced cycloaddition takes place between photochemical HOMO of one molecule and ground state LUMO of other molecule.

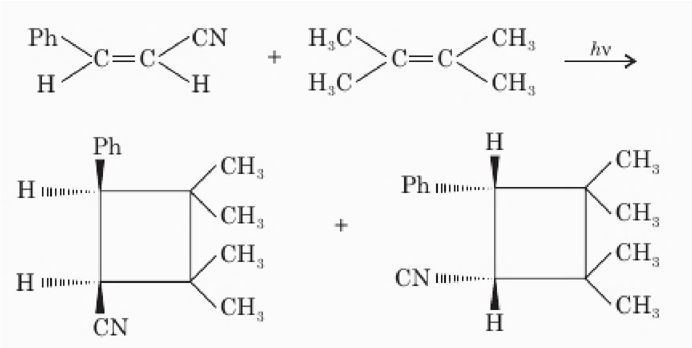


From the example it is clear that for cycloaddition reaction both HOMO and LUMO should have same symmetry otherwise reaction will be symmetry forbidden. For symmetry allowed reaction if HOMO has m-symmetry then LUMO should also have m-symmetry. Similarly, if HOMO has C2-symmetry then LUMO should also have C2-symmetry.

Stereochemistry

Stereochemical integrity is maintained in cycloaddition reaction because reaction is concerted reaction,



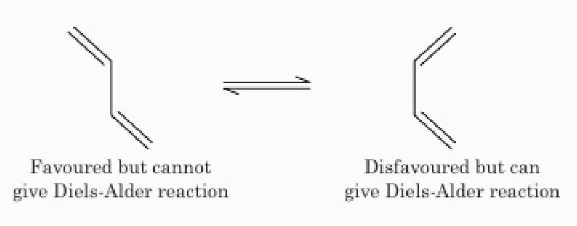


[4+2] Cycloaddition Reactions

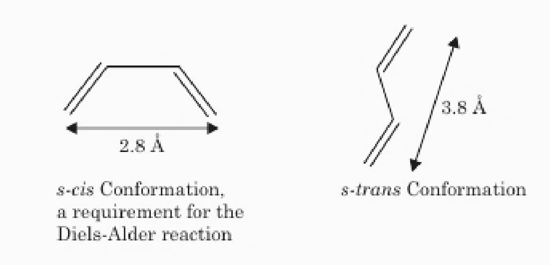
Diels-Alder reaction is the best known [4 + 2] cycloaddition reaction. This reaction is thermally allowed reaction. Diels-Alder reaction is photochemically forbidden. Since Diels-Alder reaction is the most common [4 + 2] cycloaddition reaction, let us first discuss the general description of this reaction. Diels-Alder reactions occur between a conjugated diene and an alkene (or alkyne), usually called the dienophile.

The Dienes

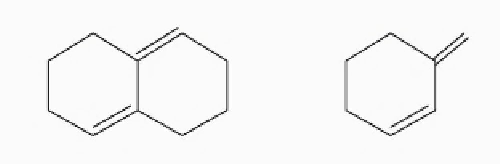
The diene of the Diels-Alder reaction is electron rich, while the dienophile is electron poor. Some Diels-Alder reactions with electron-poor dienes and electron-rich dienophiles are also known, but these are relatively rare. Simple dienes such as 1, 3-butadiene are sufficiently electron-rich to be effective dienes for Diels-Alder reaction. The presence of electron releasing groups such as alkyl groups, phenyl groups or alkoxy groups may further enhance the reactivity of dienes. The diene component of the Diels-Alder reaction can be open-chain or cyclic but it must have s-cis conformation. Butadiene normally prefers the s-trans conformation with the two double bonds as far away from each other as possible for steric reasons. The barrier to rotation about the central σ bond is small (about 30 kJ/mole at 25°C) and rotation to the less favourable but reactive s-cis conformation is rapid.



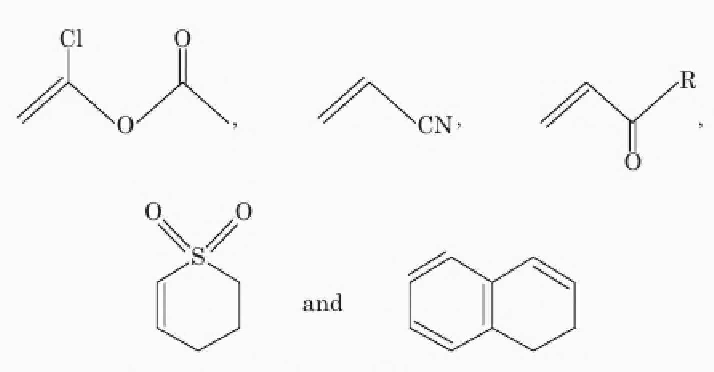
Cyclic dienes that are permanently in the s-cis conformation are exceptionally good for Diels-Alder reaction. On the other hand, cyclic dienes that are permanently in the s-trans conformation and cannot adopt the s-cis conformation will not give the Diels-Alder reaction at all. If the diene is in the s-trans conformation, the dienophile could not 'reach' both ends of the diene at the same time.



This explains why dienes such as those given below will not serve as dienes in the DielsAlder reaction.



(B) The Dienophile The most common dienophiles are the electron-poor alkenes and alkynes. Since electron-poor alkenes and alkynes are prone to react with a diene, these are called dienophiles (lover of dienes).

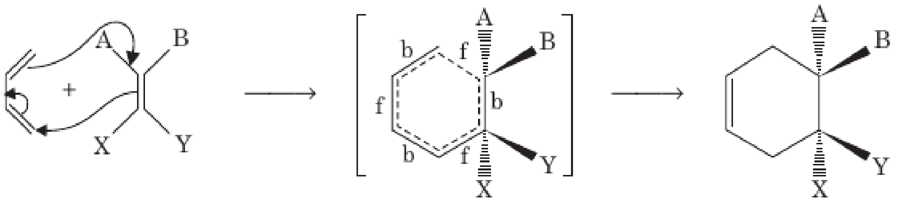


Some dienophiles for the Diels-Alder reaction

Thus the simple alkenes and alkynes such as ethylene and acetylene are not good dienophiles. A good dienophile generally has one or more electron-withdrawing groups pulling electron density away from the π bond. Dienophiles that do undergo the Diels-Alder reaction include conjugated carbonyl compounds, nitro compounds, nitriles, sulphones, arylalkenes, arylalkynes, vinyl ethers, vinyl esters, haloalkenes and dienes.

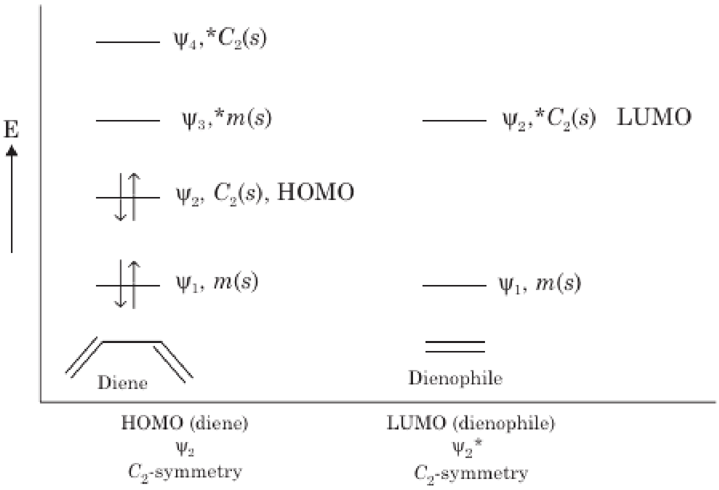
Mechanism of Diels-Alder Reaction

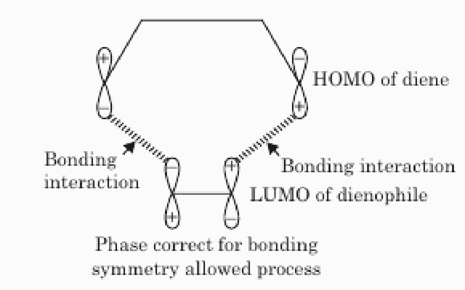
The mechanism of the Diels-Alder reaction is a simultaneous cyclic movement of six electrons: four in the diene and two in the dienophile. The simple representation of the mechanism shown below is fairly accurate. This is called a concerted reaction because all the bond making and bond breaking occurs simultaneously. For these three pairs of electrons to move simultaneously, however, the transition state must have a geometry that allows overlap of the two end p-orbitals of the diene with those of the dienophile.



The Frontier Orbital Description of [4 + 2] Cycloadditions

The reaction condition of [4 + 2] cycloaddition reactions are different from [2 + 2] cycloaddition reactions. [4 + 2] cycloaddition reaction is thermally allowed whereas [2 + 2] cycloaddition reaction is photochemically allowed. To see why this is so, we will examine the HOMO-LUMO interactions of only the p-orbital components that will form the new σ (sigma) bonds in a [4 + 2] cycloaddition. We will compare the HOMO-LUMO interactions for the ground state (for a thermal induced reaction) and those for the excited state (for photo induced reaction).

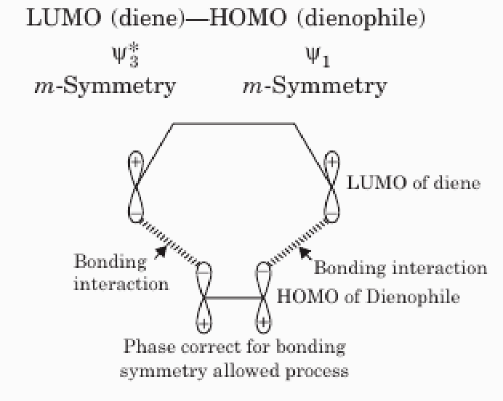




Thermal induced reaction: There are two possible interactions, HOMO (diene)LUMO (dienophile) and HOMO (dienophile)-LUMO (diene).

Case I: HOMO of diene and LUMO of dienophile

Case II: LUMO of diene and HOMO of dienophile



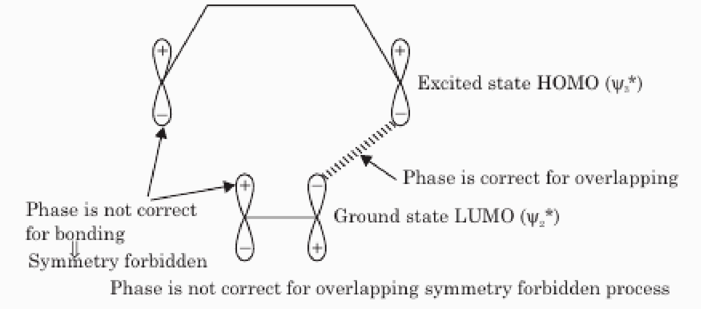
The stronger of these two interactions will control the reaction. In this case, the stronger interaction is between the HOMO and LUMO pair closer in energy. The strength of the orbital overlap and the magnitude of the resulting stabilisation, depends on the relative energies of the two orbitals. The closer the two are in energy, the stronger the interaction. In the Diels-Alder reaction of ethylene and butadiene, the two HOMO-LUMO interactions are of equal energy and orbital symmetry is same in both reactions. Both interactions involve bonding overlap at the point of formation of the two new σ (sigma) bonds. Accordingly this reaction is symmetry allowed reaction.

Photo induced reaction:

In photo-induced cycloaddition reaction, interaction always takes place between excited state HOMO(HOMO*) of diene and ground state LUMO of dienophile and vice-versa. Thus, there are two possible interactions.

(i) Excited state HOMO (diene) and ground state LUMO (dienophile), and

(ii) Excited state HOMO (dienophile) and ground state LUMO (diene). Let us take the example of excited state HOMO of diene and ground state LUMO of dienophile. When butadiene is excited by light its HOMO becomes ψ3* which has m-symmetry. This MO cannot overlap with ground state LUMO of the ethylene which has C2-symmetry.



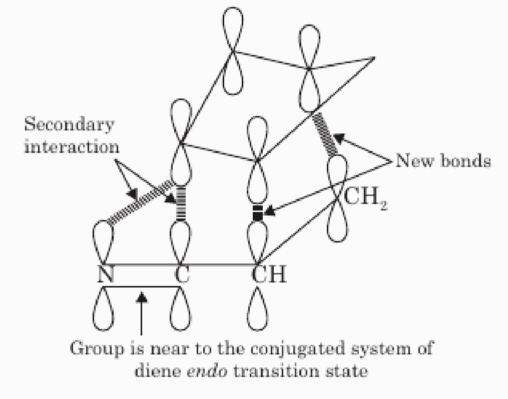
Thus, photochemical cycloaddition of [4 + 2] system is symmetry forbidden reaction. On the basis of the results we can obtain the following selection rules for the cycloaddition reactions.

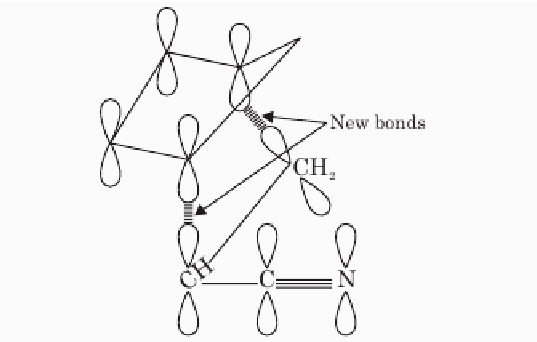
Selection rules for cycloaddition reactions

Number of electrons	*Mode of activation*	*Allowed stereochemistry*
$(4n)\pi$	Photochemical	Supra-Supra
$(4n + 2)\pi$	Thermal	Supra-Supra

Endo orientation in bicyclic compounds:

As mentioned earlier that the exo product is more stable (i.e., it is thermodynamic product) than the endo product (i.e., it is kinetically controlled product) in Diels-Alder reaction. Diels-Alder reaction always gives endo product as a major product when dienophile has a π bond in its electron-withdrawing group. This clearly confirms that transition state of endo product in this case is more stable than the transition state of exo product due to some other factor, which overwhelms steric considerations. In endo orientation the electron-withdrawing group having a π bond of a dienophile is directed to the inside of the cyclic ring, i.e., electron-withdrawing group is nearer to the conjugated system of diene in the formation of transition state. In this orientation the p-orbital of the electron-withdrawing group approach the central carbon atoms (C-2 and C-3) of the diene.



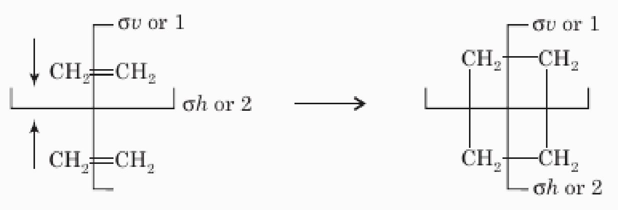


Exo transition state has no possible secondary interactions

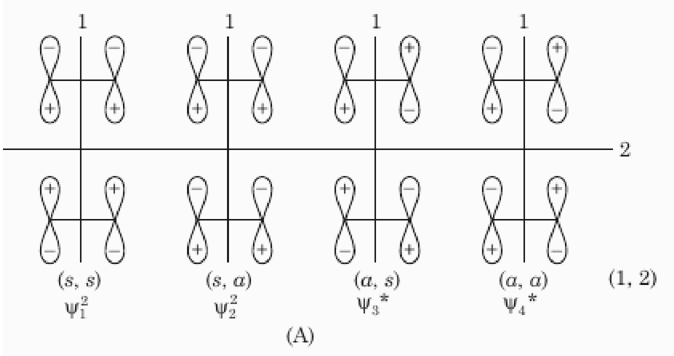
This proximity results in a weak secondary overlap: An overlap of the p-orbitals of the electron-withdrawing group with the p-orbitals of C-2 and C-3 of the diene. This fancy-phrase simply means that there can be interaction between the back diene orbitals and orbitals on the substituent only in the endo transition state. In exo orientation the electron-withdrawing group of the dienophile is directed away from the cyclic diene conjugated system.

Correlation Diagram for Cycloaddition Reactions

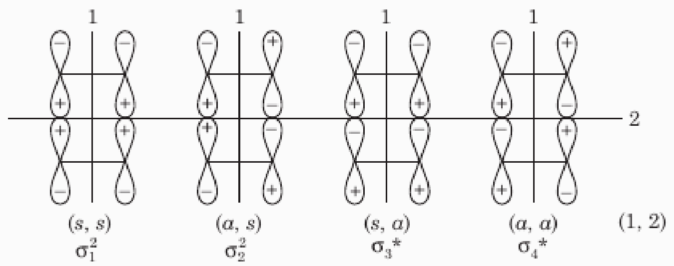
Orbital Symmetry in Cycloaddition Orbital symmetry arguments make useful predictions about concerted cycloaddition reaction which is suprafacial-suprafacial. Consider the [π2s + π2s] cycloaddition of ethylene molecules in parallel planes approaching each other vertically



This system contains vertical and horizontal plane of symmetry (i.e., mirror plane of symmetry) denoted by σv (or 1) and σh (or 2) which are useful in characterising the orbitals. In the transformation of ethylene molecules to cyclobutane we are mainly concerned with the four π (pi) orbitals of two ethylene molecules and the four σ (sigma) orbitals of cyclobutane. Let us first take the σv and σh in two ethylene molecules.



Now let us take the σv and σh in cyclobutene



(B)

Note that more will be symmetry in the system less will be energy of the system for π as well as σ orbitals. Energy of π (pi) system is as follows in increasing order:

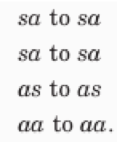
ss sa as aa

Energy of σ (sigma) system is as follow in increasing order:

ss as sa aa

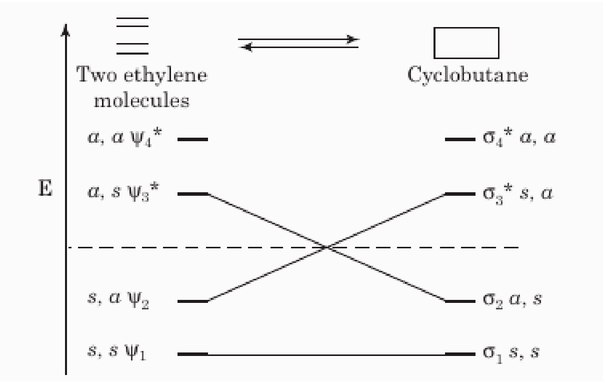
We can now construct the orbital correlation diagram. But before this we must classify the symmetry of the orbitals twice over once for the plane bisecting the π bonds represented by the vertical line, i.e., σv (or 1) and then for the plane between the two ethylene molecules, the horizontal line, i.e., σh (or 2). Thus, the lowest energy orbital in the starting materials is the bonding combination ψ1 (both ψ1 has mirror symmetry) of the bonding π orbitals. This orbital has both symmetry (and hence represented as s, s). The next orbital up is the antibonding combination of ψ2 (both ψ2 has m-symmetry) of the two bonding π orbitals. This orbital has σv symmetry and σh asymmetry so it is classified as sa. The next orbital up is the bonding combination of ψ* 3 (both ψ* 3 has C2-symmetry) of the two antibonding π orbitals. This orbital has σv asymmetry and σh symmetry so it is classified as as. The next orbital up is the antibonding combination of ψ4* (both ψ4* has C2-symmetry) of the two antibonding π orbitals. This orbital has σv as well as σh asymmetry so it is classified as aa. Thus, the orbitals of the interacting ethylenes are the result of forming bonding and antibonding combination of π and π* orbitals of two ethylene molecules. The interacting σ orbitals are similar combination of the σ (σ1, s, s and σ2, a, s) and σ* (σ3*, sa and σ4*, aa).

We can now complete by correlating the energy levels, feeding the orbitals in the starting materials into orbitals of the same symmetry in the product, ss to ss.



sa to *sa*
sa to *sa*
as to *as*
aa to *aa*.

On the basis of the above information, a correlation diagram may be drawn in which the levels of like symmetry are connected by lines.



A close examination of the diagram leads us to the following two conclusions:

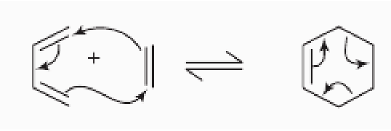
1. The ground state orbitals of ethylene correlate with an excited state of cyclobutane, ψ1 2ψ2 2 σ1 2σ3 *2. Consequently, the combination of two ground state ethylene molecules cannot result in the formation of ground state cyclobutane while conserving the orbital symmetry. Hence the thermal process is symmetry-forbidden.

2. As there is correlation between the first excited state of the ethylene and cyclobutane, ψ12ψ2ψ3* σ12σ2σ3* the photochemical process is symmetry allowed.

Correlation Diagram of [4 + 2] Cycloaddition Reaction

As mentioned earlier correlation diagrams provide a complete explanation of concerted reaction in which symmetry is preserved throughout the reaction. For correlation diagram of [4 + 2] cycloaddition this can be done by the following steps:

1. Draw the concerted reaction and indicate the migration of electrons by curly arrows for the backward and forward reaction.

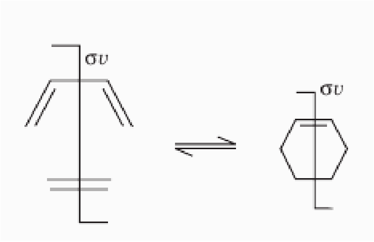


Any substituent(s) present in any reactant (in this case diene and dienophile) symmetrical or unsymmetrical do not disturb the symmetry of the orbitals directly involved.

2. Identify the orbitals undergoing change. The curly arrow helps to focus on what they are, i.e., which orbitals are undergoing change. For the starting materials, they are the π (pi) orbitals (ψ1, ψ2, ψ3* and ψ4*) of diene unit and π (pi) orbitals (π and π*) of the dienophile. For the product, they are the π bond (π and π* orbitals) and two newly formed σ bonds (σ1, σ2, σ3* and σ4*).

3. Identify any symmetry elements maintained throughout the reaction, i.e., the same symmetry should be present in reactants, cyclic transition state and product. The symmetry may be of one or two types (σv and σh).

In Diels-Alder reaction there is only one symmetry and that is vertical plane of symmetry bisecting the bond between C-2 and C-3 of the diene and the double bond of the dienophile.



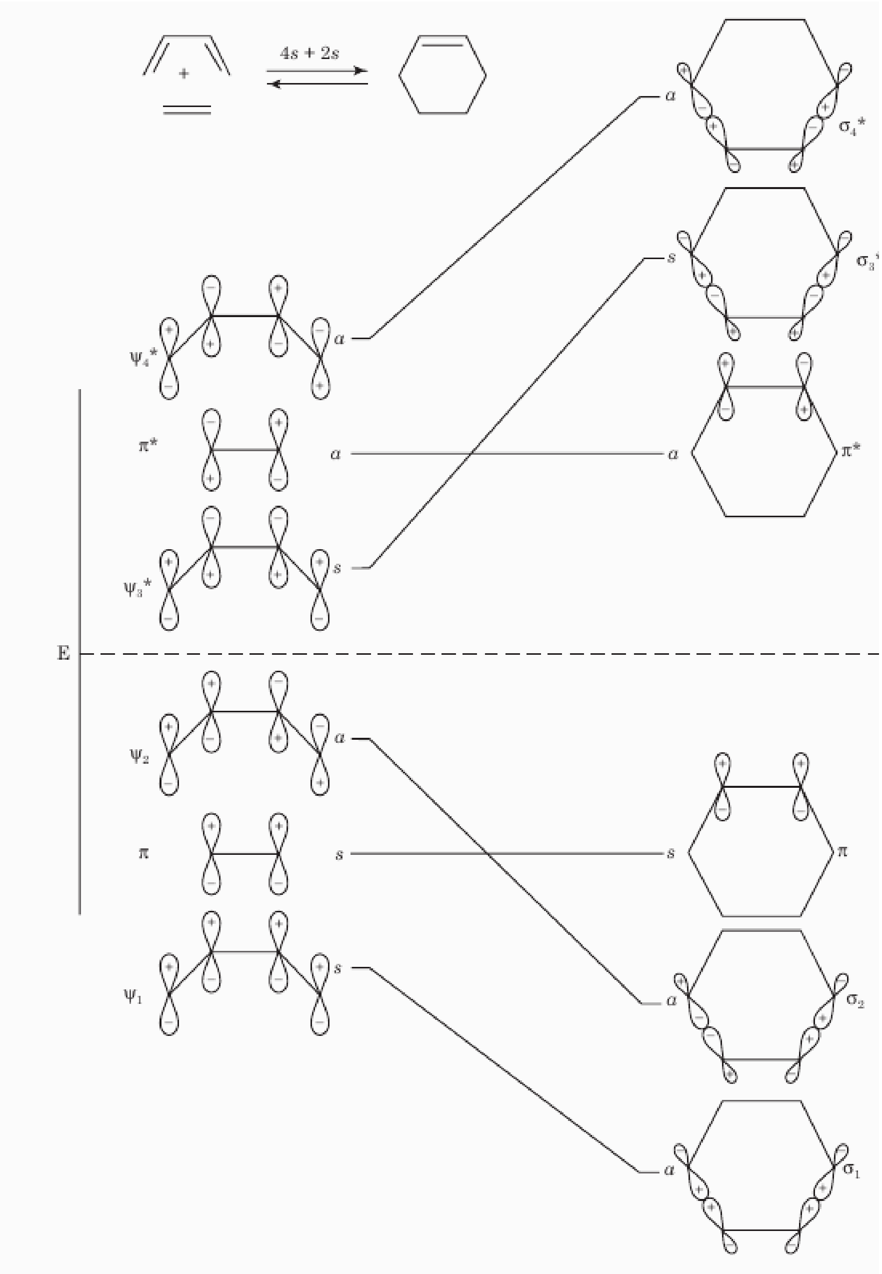
4. Rank the orbitals in increasing order of energy (vertical on the paper) with the reactants on the left and the product(s) on the right. Besides each energy level, draw the orbitals showing signs of the lobes of atomic orbitals. 6. Identify the symmetry of the orbitals with respect to σv or σh or both (which one is possible) of reactant and product. In this case symmetry is σv. 7. Construct an orbital correlation diagram. Following the assumption that an orbital in the starting material must feed into an orbital of same symmetry in the product, draw lines connecting the orbitals of the starting materials to those of the products nearest in energy (i.e., energy difference between correlating orbitals of reactant and product should be minimum and of the same symmetry. Thus ψ1(s) connects to σ1 (s), π(s) to π(s) and ψ2(a) connect to σ2(a) and similarly with unoccupied orbitals ψ3*(s) connects to σ3*, π* (a) connects to π* (a) and ψ4* (a) connects to σ4* (a).

Since ground state orbitals of reactants correlate with the ground state orbitals of the product therefore Diels-Alder reaction is thermally allowed.

$$\psi_1^2\pi^2\psi_2^2 \longrightarrow \sigma_1^2\sigma_2^2\pi^2$$

On the other hand, photochemical transformation is not possible as the first excited state of the reactant does not correlate with the first excited state of the product. Rather it correlates with the upper excited state of the product.

$$\psi_1^2\pi^2\psi_2\psi_3^* \not\longrightarrow \sigma_1^2\sigma_2^2\pi\sigma_3^*$$



The Woodward-Hoffmann Rule for Cycloaddition Reactions

Thermal Reactions

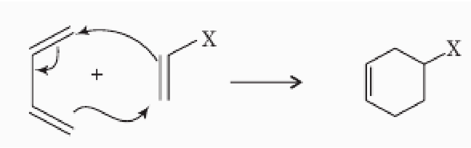
A thermal (ground state) pericyclic change is symmetry-allowed when the total number of (4q + 2)s and (4r) a components is odd.

Photo Chemical Reactions

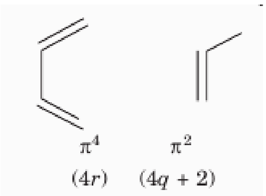
A pericyclic change in the first electronically excited state is symmetry-allowed when the total number of (4q + 2) s and (4r) a component is even.

The Woodward-Hoffmann Rule in | 4 + 2 | Cycloadditions

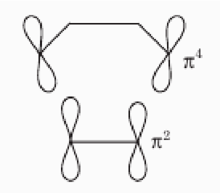
1. Draw the general mechanism of the reaction



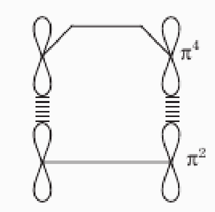
2. Choose the components. All the bonds taking part in the mechanism must be included and ignore all substituents which are not directly involved.



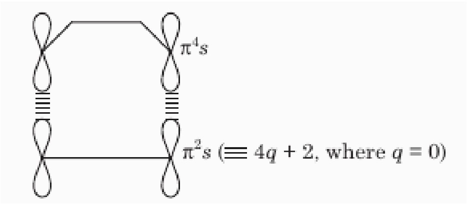
3. Make a three-dimensional drawing of the way the components come together for the reaction putting the orbitals at the ends of the components.



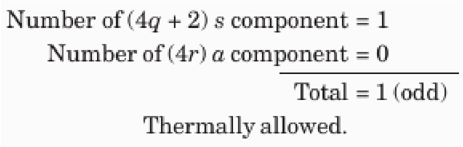
4. Join the components where new bonds are to be formed.



5. Label each component s or a depending on whether new bonds are formed on the same side or opposite sides.



6. Count the number of (4q + 2) s and (4r) a components.



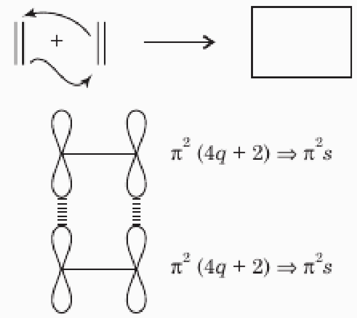
Number of $(4q + 2)$ *s* component = 1

Number of $(4r)$ *a* component = 0

Total = 1 (odd)

Thermally allowed.

Woodward-Hoffmann Rule in |2 + 2| Cycloadditions



Number of $(4q + 2)$ s component = 2
Number of $(4r)$ a component = 0
Total = 2 (even)
Photochemically allowed.

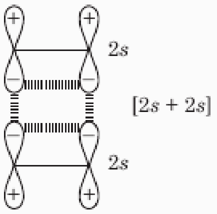
Huckel-Mobius Method for Cycloaddition Reaction

Hückel rule of aromaticity states that a monocyclic planar conjugated system is aromatic if it has (4n + 2)π conjugated or delocalised electrons and consequently stable in ground state. Similarly, monocyclic planar conjugated system is anti-aromatic if it has (4n)π conjugated or delocalised electrons. This system is unstable in ground state. However, further calculation shows that these rules are reversed by the presence of a node in the array of atomic orbitals.

Thus system with (4n + 2)π electrons and a node is anti-aromatic while system with (4n)π electrons and a node is aromatic. If system has no node then it is called Hückel system and array is called Hückel array. Similarly, if system has node then it is called Mobius system and array is called Mobius array. Application of above rules to cycloaddition reactions led to the generalisation that thermal reactions take place via aromatic transition state whereas photochemical reactions proceed via antiaromatic transition state.

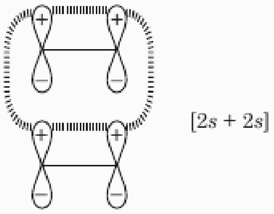
Consider the [2 + 2] cycloaddition reaction:

(*i*)



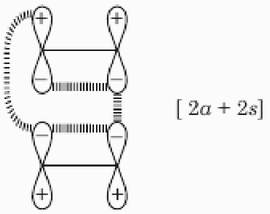
4 Electrons, zero node.
Hückel system, antiaromatic, *h*ν allowed.

(*ii*)



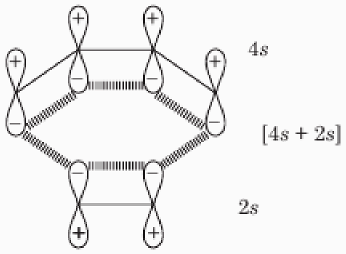
4 Electrons, zero node.
Hückel system, antiaromatic *h*ν allowed.

(*iii*)

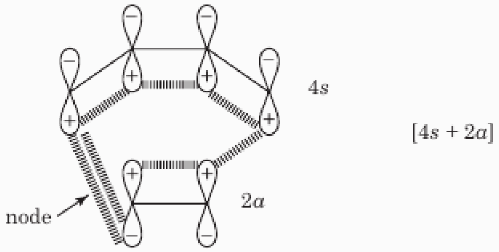


4 Electrons, one node.
Mobius system, aromatic Δ allowed.

Now consider the [4 + 2] cycloadditions:



6 Electrons, zero node.
Hückel system, aromatic, Δ allowed.



6 Electrons, one node.
Antiaromatic, Mobius system, *h*ν allowed.

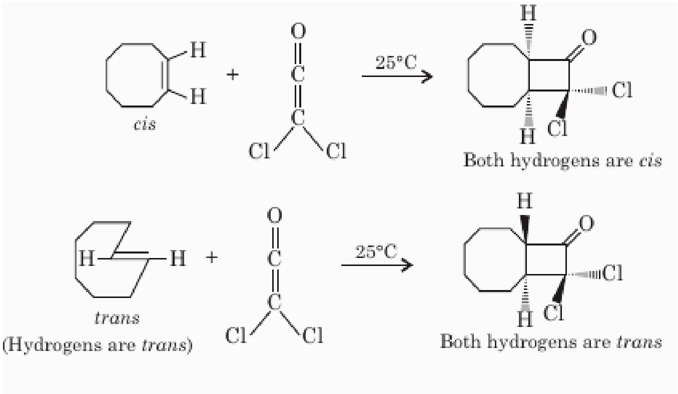
On the basis of the results we can obtain the following selection rules for the cycloaddition reactions:

Selection rules for cycloaddition reactions

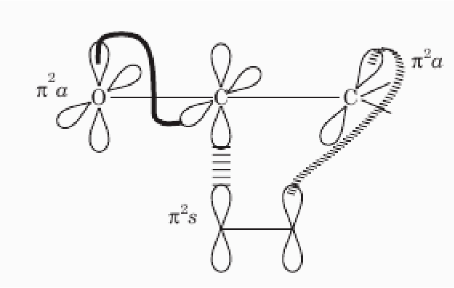
m + *n* electrons	*Number of nodes*	*Aromaticity*	*Thermally allowed*	*Photochemically allowed*
$4n$	0	antiaromatic		supra-supra antara-antara
$4n$	1	aromatic	supra-antara antara-supra	
$4n + 2$	0	aromatic	supra-supra antara-antara	
$4n + 2$	1	antiaromatic		supra-antara antara-supra

[2+2] Cycloaddition Reactions

Let us first take some addition reactions of ketene with alkenes. The reaction has some characteristics of pericyclic cycloaddition. The reaction is syn addition and geometry of reactant is maintained in the product.

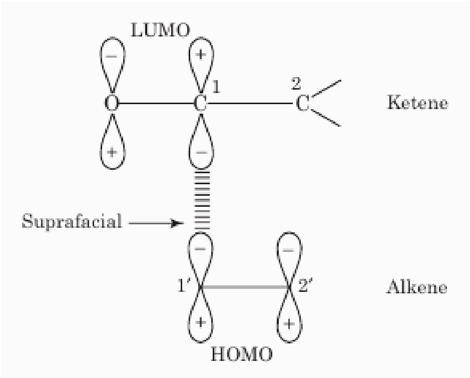


In the given two examples stereochemistry of reactant is maintained in the product. These two reactions are pericyclic [2 + 2] cycloaddition reaction and thermally allowed reactions. We know very well that [2 + 2] cycloaddition is photochemical reaction and suprafacial-suprafacial. If reaction is thermally allowed then reaction should be suprafacial-antarafacial reaction, i.e., [π2s + π2a] cycloaddition. If this is [2πs + 2πa] than how does it overcome the symmetryimposed barrier? One suggestion is that two molecules approach each other at right angles for overlapping in an antarafacial sense of the ketene. Making the reaction the allowed [π2s + 2πa] cycloaddition that we have dismissed as being unreasonable. This is the most simplest explanation. The [2+ 2] cycloadditions of ketenes being concerted is more likely to be a consequence of the fact that ketenes have two sets of π orbitals at right angle to each other and overlap can be developed to orthogonal orbitals (dashed lines) and in addition there is transmission of information from one orbital to its orthogonal neighbour (heavyline)

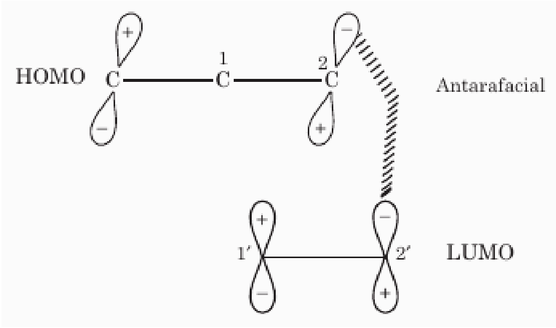


Overlapping orbitals of ketene and alkene

The vision identifies the reaction as an allowed [π2s + π2a + π2s] cycloaddition reaction. The FMO treatment shows that the bond formation between C-1 and C-1′ develops mainly from the interaction of the LUMO of ketene (π* of C O) and HOMO of alkene and that the bond between C-2 and C-2′ develops mainly from the interaction of HOMO ketene [(ψ2) the three atom linear set of orbitals analogous to the allyl anion] and LUMO of the alkene.

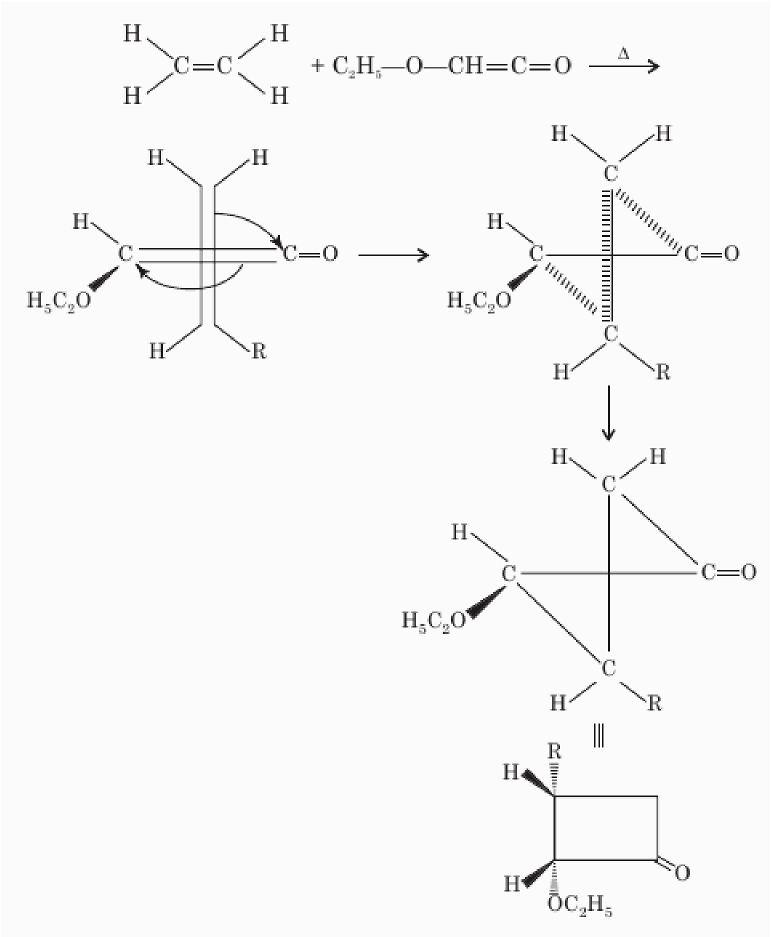


Bond formation between C-1 of ketene and C-1′ of alkene



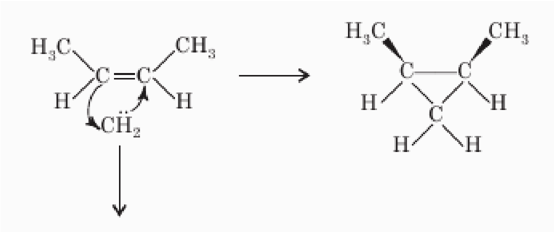
Bond formation between C-2 of ketene and C-2′ of alkene

The reaction can be represented as follows:

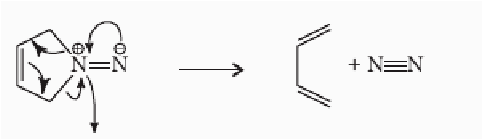


Chelotropic Reactions

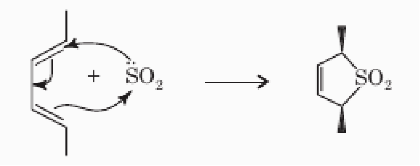
Chelotropic reactions are those reactions in which two σ bonds are formed on same atom or two σ bonds are broken on same atom.



Two σ bonds are formed on this carbon in the product.



Two σ bonds are broken on nitrogen

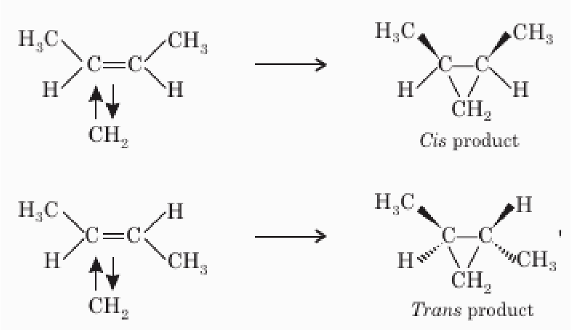


Two σ bonds are formed on sulphur

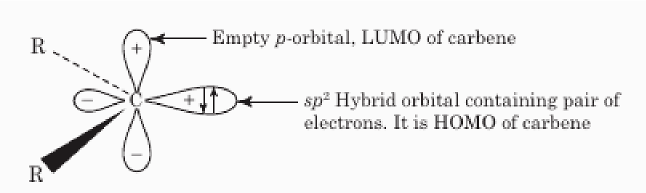
[2 + 2] Chelotropic Cycloadditions

Chelotropic Reactions of Alkenes with Singlet Carbenes

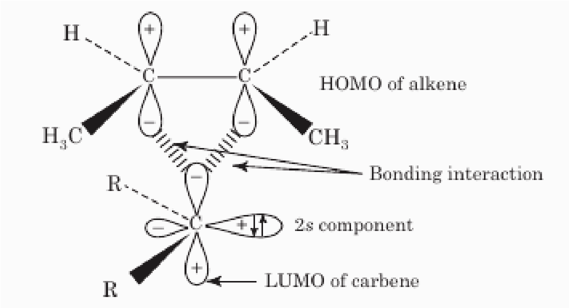
Alkene reacts with carbene to form cyclopropane or substituted cyclopropane. This addition reaction is stereospecific with singlet carbenes. Reaction is thermal allowed reaction.



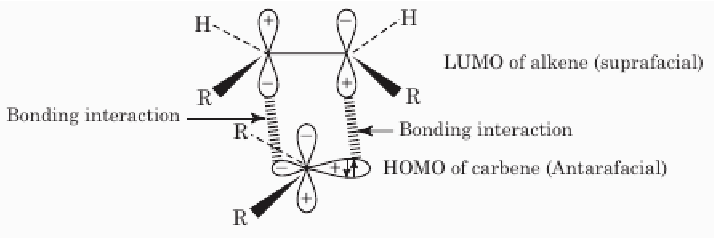
The reaction is concerted reaction. An examination of the orbitals of carbene shows that a bonding overlap between HOMO of a carbene and LUMO of an alkene or LUMO of carbene and HOMO of alkene is possible. In singlet carbene hybridisation of carbon is sp2. It has three sp2 hybrid orbitals and one empty p-orbital perpendicular to the plane defined by the carbon atom and the two substituents on it. Out of three sp2 hybrid orbitals two are bonding and one is non-bonding having two electrons in it.



Concerted cycloaddition reaction between alkene and carbene is [2 + 2] cycloaddition reaction. This reaction is possible only if the carbene approaches the alkene sideways so that the plane defined by the carbon atom and its two substituents parallels the plane of the alkene. In this orientation, the empty p-orbital of the carbene pointing towards the electrons of the π bond of alkene.



Interaction between HOMO of alkene and LUMO of carbene



Interaction between LUMO of alkene and HOMO of carbene

Chelotropic reaction of carbene is [2 + 2] cycloaddition reaction. Thus, chelotropic reaction of carbene with alkene is symmetry forbidden if both components interact suprafacially. Antarafacial reaction of a simple alkene is sterically very unlikely, so that the reaction is likely to involve the C ¨ H2 antarafacially.

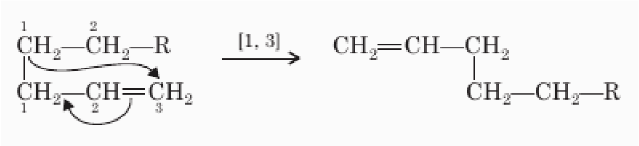
Sigmatropic Rearrangement

Sigmatropic rearrangements are another class of concerted pericyclic reactions governed by orbital symmetry. This rearrangement involves a concerted reorganisation of electrons during which a group attached by a σ (sigma) bond migrates to the terminus of an adjacent π (pi) electron system. The reactions are called sigmatropic rearrangement because a σ (sigma) bond appears to move from one place to another during the reaction. There is a simultaneous shift of the π (pi) electrons. The number of the π (pi) and σ (sigma) bonds remain separately unchanged.

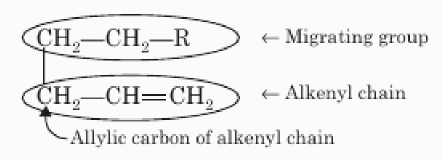
Classification

Sigmatropic rearrangements are classified by a double numbering system (i, j or m, n) that refers to the relative positions of the atom or group involved in the migration. This method of classification is different from those for cycloaddition or electrocyclic reactions which are classified by the number of π (pi) electrons involved in the cyclic transition state.

The method used in classifying sigmatropic rearrangement is best explained by the following examples:

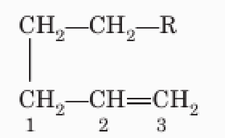


In sigmatropic rearrangement substrate can be divided in two parts: Alkenyl (or polyalkenyl) chain and migrating group. All substrates have at least one allylic carbon in alkenyl chain for sigmatropic rearrangement.



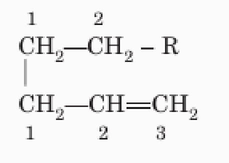
Numbering of Alkenyl Chain

Numbering of alkenyl chain is always started from the allylic carbon and this carbon is numbered-1



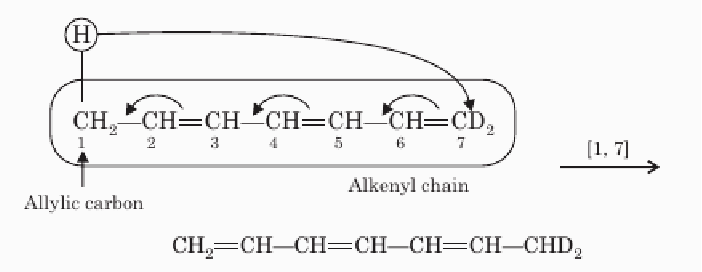
Numbering for Migrating Group

Atom (H, C or heteroatom) of migrating group bonded with allylic carbon by σ (sigma) bond is always given number-1



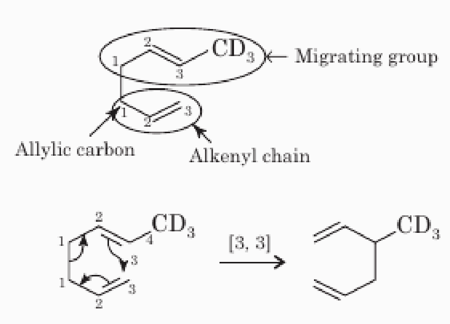
Name of the Rearrangement

In the example (1) atom-1 of the migrating group migrates on the atom-3 of the alkenyl chain. Therefore, this rearrangement would be classified as a [1, 3] sigmatropic rearrangement. In 1, 3 [(i.e., i, j) i = 1 and j = 3] i indicates position of atom in the migrating group and j indicates position of atom in the alkenyl chain.



The above reaction is example of [1, 7] sigmatropic rearrangement.

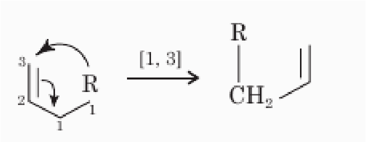
It is not always the first atom of the migrating group that becomes bonded to the alkenyl chain in the rearrangement. Consider the following example:



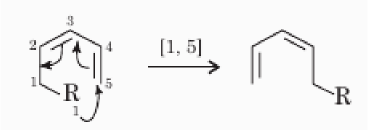
In this rearrangement atom-3 of the migrating group migrates on the atom-3 of the alkenyl chain. Therefore, this rearrangement is an example of [3, 3] sigmatropic rearrangement.

The sigmatropic rearrangements can be divided into two classes.

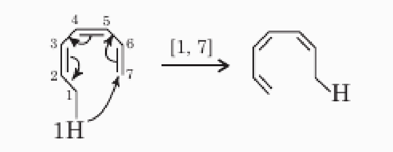
1. Those where the migrating atom or group is bonded through the same atom in both reactant and product.



R is bonded to carbon in reactant as well as in product

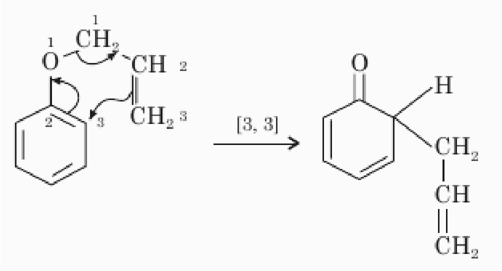


1, 5-shift of alkyl group, R is bonded to carbon in reactant as well as in product

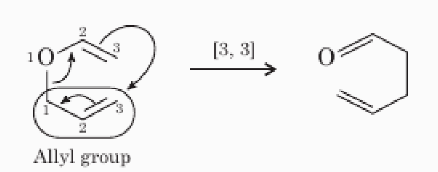


1, 7-shift of hydrogen. H is bonded to carbon in reactant as well as in product

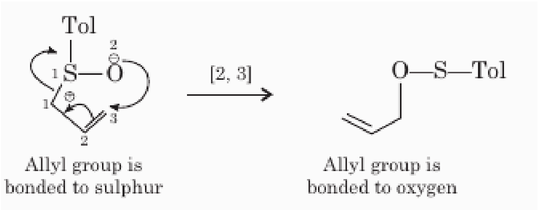
2. Those where the migrating atom or group is bonded through different atoms in reactant and in product.



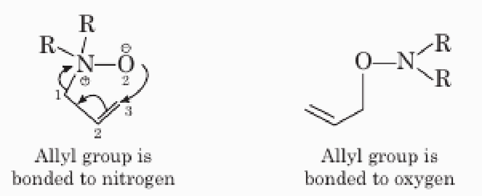
This is [3, 3] sigmatropic rearrangement in which carbon of allyl group is bonded to oxygen in the reactant and carbon in the product.



This is [3, 3] sigmatropic rearrangement of an allyl vinyl ether. Migrating group is bonded to the oxygen in the reactant which is bonded to the carbon in the product.



[2, 3] Sigmatropic rearrangement of an allyl sulphoxide

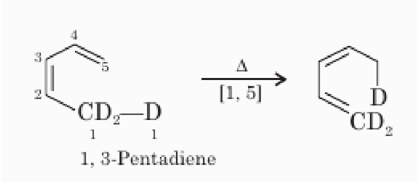


[2, 3] Sigmatropic rearrangement of an amine oxide

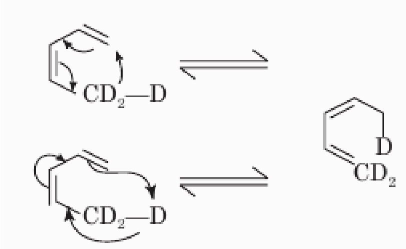
Mechanism of Sigmatropic Rearrangement

FMO Method

Consider the following reaction

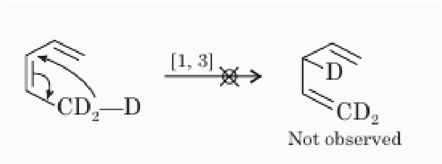


When 1, 3-pentadiene is heated, it gives [1, 5] sigmatropic rearrangement. It is simple to construct an arrow formalism picture of the reaction. The arrow could run in either direction, clockwise or anticlockwise. That is not true for a polar reaction in which the convention is to run the arrow from pair of electrons towards the electron deficient.



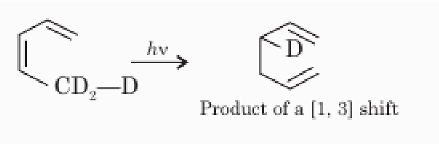
An arrow formalism description of the [1, 5] shift of deuterium in 1, 3-pentadiene

In the given example deuterium of sp3 hybrid carbon migrates on to the sp2 hybrid carbon (carbon-5). The given compound has also carbon-3 as sp2 hybrid carbon. Thus this compound can also give [1, 3] sigmatropic rearrangement on heating, but [1, 3] shift is not observed.



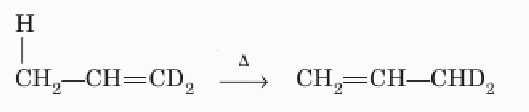
An arrow formalism can easily be written and it might be reasonably argued that the [1, 3] shift requiring a shorter path than the [1, 5] shift, should be easier than why [1, 3] shifts not observed on heating?

A second strange aspect of this reaction comes from photochemical experiments. When 1, 3-pentadienes are irradiated the product of the reaction include the molecules formed through [1, 3] shift but not those of [1, 5] shifts.



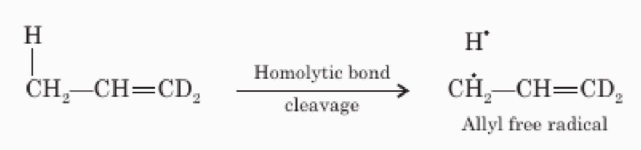
Product of a [1, 3] shift

So any mechanism proposed must include an explanation of why thermal shifts are [1, 5] whereas photochemically induced shifts are [1, 3]. We can use the frontier orbital approach to analyse these reactions and see why this is so. Let us first consider the following thermally induced sigmatropic rearrangement which is a [1, 3] shift.



$$\overset{\text{H}}{\overset{|}{\text{CH}_2}}\text{—CH=CD}_2 \xrightarrow{\Delta} \text{CH}_2\text{=CH—CHD}_2$$

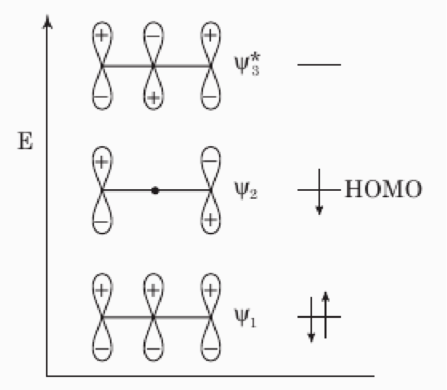
For the purpose of analysing the orbitals, it is assumed that the σ (sigma) bond connecting the migrating group to its original position undergoes homolytic cleavage to yield two free radicals. This is not how the reaction takes place because reaction is concerted. But this assumption does allow analysis of the molecular orbitals.



$$\overset{\text{H}}{\overset{|}{\text{CH}_2}}\text{—CH=CD}_2 \xrightarrow[\text{cleavage}]{\text{Homolytic bond}} \overset{\text{H}^{\bullet}}{\dot{\text{C}}\text{H}_2}\text{—CH=CD}_2$$

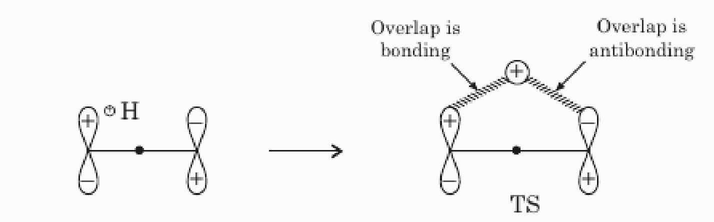
Allyl free radical

The products of the hypothetical cleavage are a hydrogen atom and an allyl free radical, which contains three p-orbitals. The π (pi) molecular orbitals of allyl free radical are shown in Figure



The actual shift of hydrogen could take place in one of the two directions.

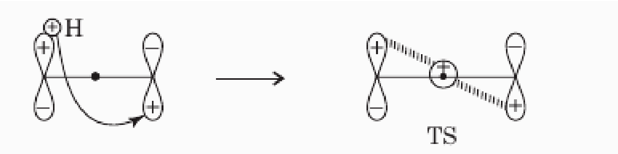
In the first case, the migrating group could remain on the same side of the π (pi) orbital system. Such a migration is known as a suprafacial process. In the thermal 1, 3 sigmatropic rearrangement a suprafacial migration is geometrically feasible but symmetry forbidden.



In the C—H bond the overlapping lobes are of the same sign

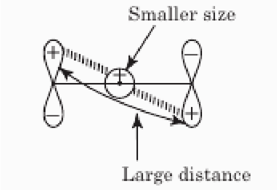
Symmetry forbidden (phase incorrect for overlapping)

Let us consider the second mode of migration for a symmetry allowed [1, 3] sigmatropic shift to occur, the migrating group must shift by an antarafacial process—that is, it must migrate to the opposite face of the orbital system.



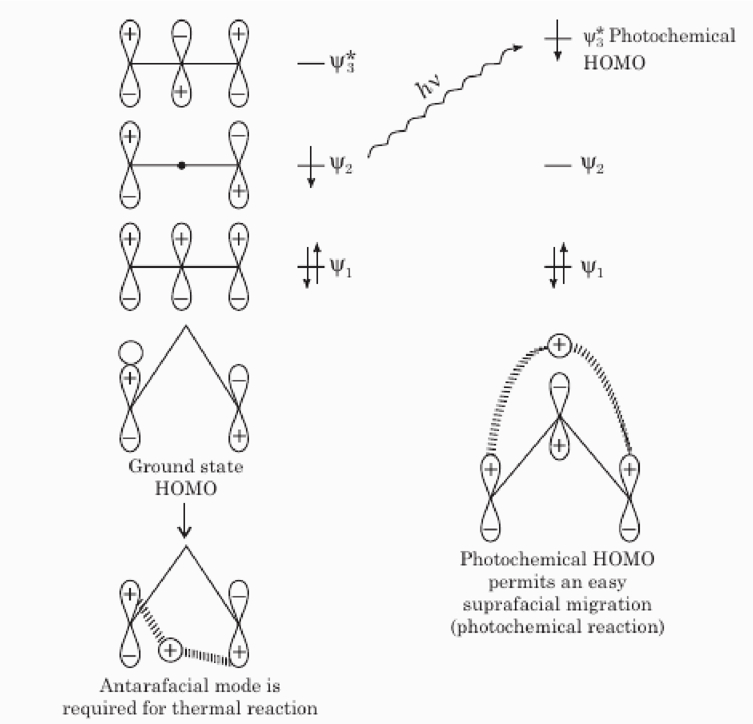
Overlap is bonding, symmetry allowed but geometry difficult

While symmetry-allowed a [1, 3] antarafacial sigmatropic rearrangement of hydrogen is not geometrically favorable. Why? The problem is that the 1s orbital is smallest and cannot effectively span the distance required for an antarafacial migration. In other words, size of 1s orbital of hydrogen is smallest and distance between two lobes of interacting p-orbitals of carbon is maximum hence orbital of 1s cannot interact effectively with p-orbitals at same time in the formation of transition state.



Symmetry allowed but geometrically difficult

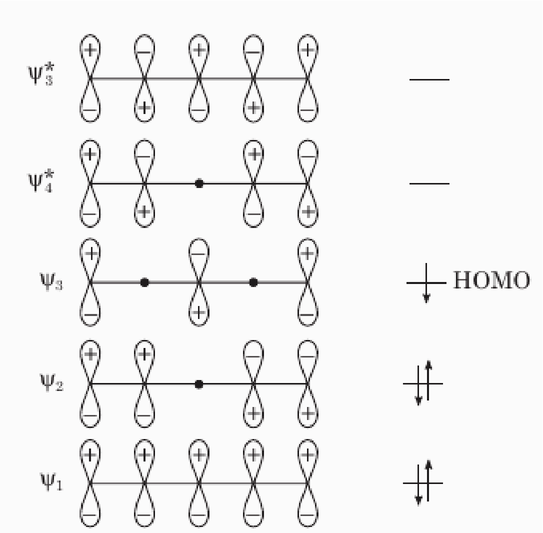
[1, 3] sigmatropic shifts take place in the presence of UV light but examples are rare. Consider again what happens when a molecule absorbs a photon. LUMO of ground state will become HOMO of excited state known as photochemical HOMO.



Suprafacial migration is possible in ψ_3^* photochemical HOMO of the reaction

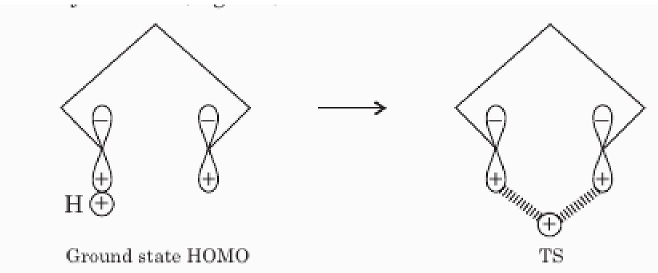
[1, 5] Sigmatropic Rearrangement:

The products of hypothetical cleavage in this case are hydrogen free radical and pentadienyl radical. π MOs of pentadienyl radical is given below :



π Molecular orbitals of the pentadienyl radical

[1, 5] Sigmatropic shift is thermally allowed and photochemically forbidden. If we again assume a homolytic bond cleavage for purpose of analysis, we must consider the molecular orbitals of pentadienyl radical



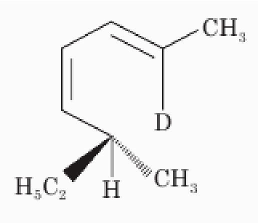
Suprafacial migration:

The [1, 5] suprafacial shift is symmetry allowed and geometrically feasible.

Consider photochemical [1, 5] sigmatropic rearrangement. In this case ψ4* will be photochemical HOMO.

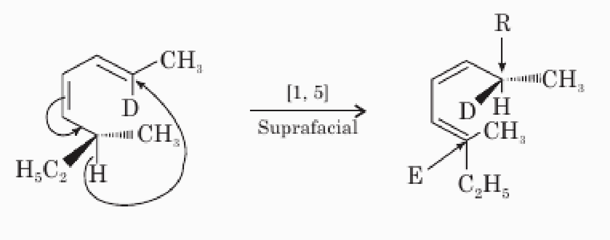
Stereochemistry of [1, 5] sigmatropic Rearrangement

Consider the following compound:



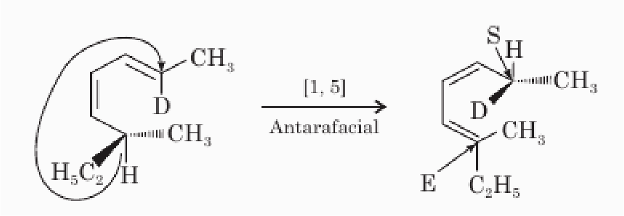
Compound has S-configuration at C-6 and E configuration at C-2.

Case I: Suppose migration is suprafacial



If migration is suprafacial then product has R-configuration at C-5 and E-configuration at C-1.

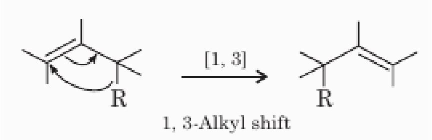
Case II: Suppose migration is antarafacial



If migration is antarafacial then product has S-configuration at C-7 and E-configuration at C-2. Experimentally it has been found that the product of the reaction is due to suprafacial migration. Thus, the theory is confirmed by this experimental result.

Sigmatropic shift of alkyl groups

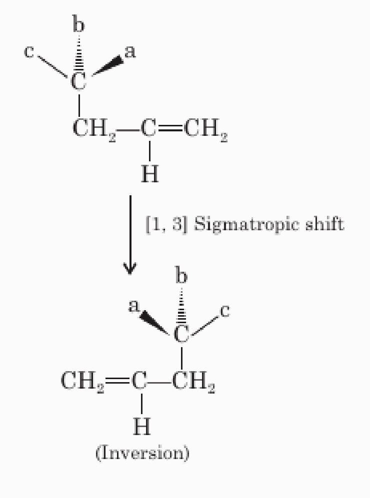
Sigmatropic migration involving alkyl group shifts can also occur.

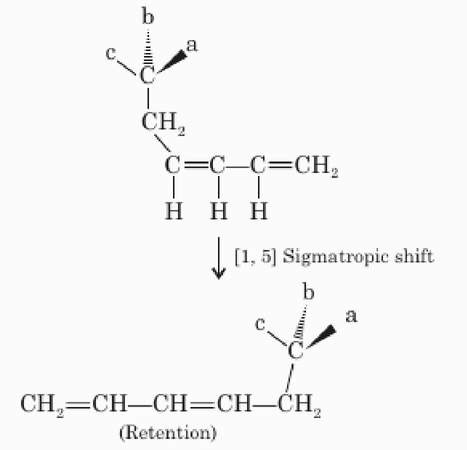


When an alkyl group migrates, there is additional stereochemical feature to consider. The shift can occur with retention or inversion at the migrating centre. The allowed process includes the suprafacial 1, 3-shift with inversion and the suprafacial 1, 5-shift with retention. Thus, if the group that migrates is bonded to the backbone by a chiral carbon, then:

1. [1, 3] Suprafacial migration of the group proceeds with inversion of configuration at the chiral centre.

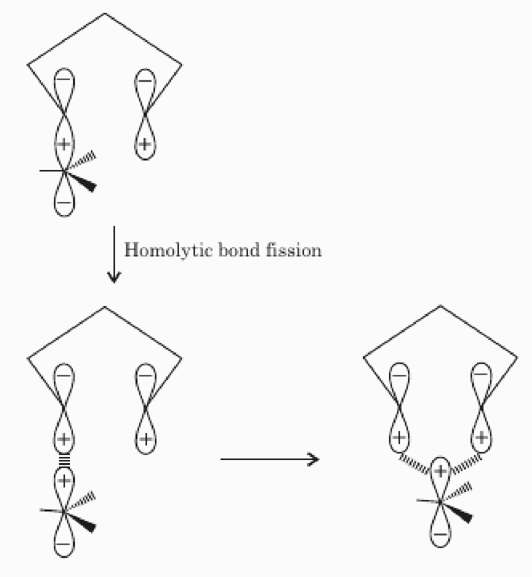
2. [1, 5] Suprafacial migration of the group proceeds with retention of configuration at the chiral centre.



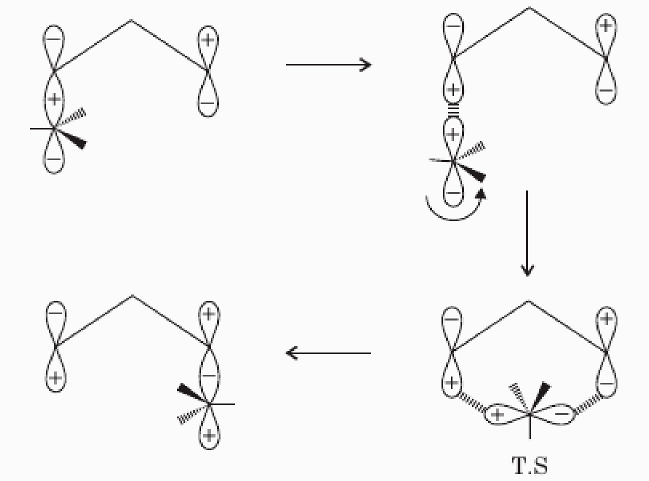


As compared to a hydrogen atom which has its electron in a 1s orbital that has only one lobe, a carbon free radical (for imaginary TS) has its odd electron in a p-orbital which has two lobes of opposite sign. A consideration of the imaginary

TS, shows that if in place of hydrogen one has carbon, then during a thermal suprafacial [1, 5] process, symmetry can be conserved only provided the migration carbon moves in a manner that the lobe which was originally attached to the π (pi) system remains attached to it.

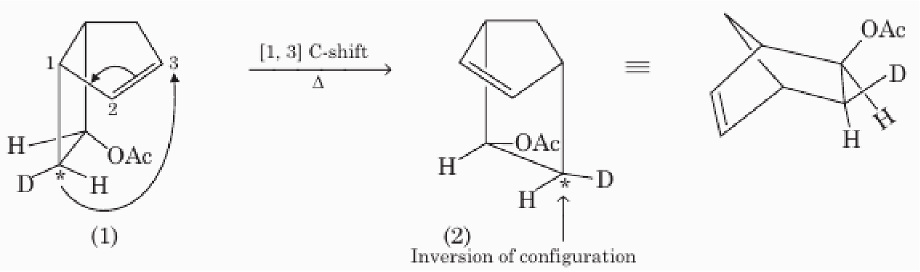


The only way for this to happen is the retention of configuration within the migrating group. However, a related [1, 3] thermal suprafacial would involve opposite lobes. Thus, if the migrating carbon was originally bonded via its positive lobe, it must now use its negative lobe to form the new C—C bond. The stereochemical outcome of such a process is the inversion of configuration in the migrating group is shown below:

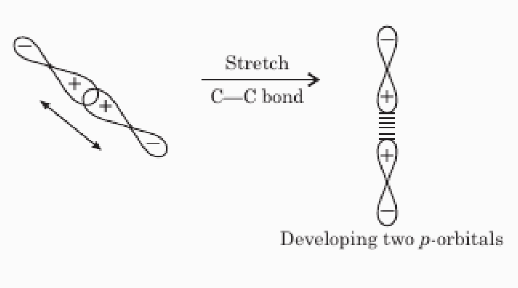


A thermal suprafical [1, 3] migration. Configuration in the migrating group will be inverted. Compound (1) when heated at 300°C it gives compound (2).

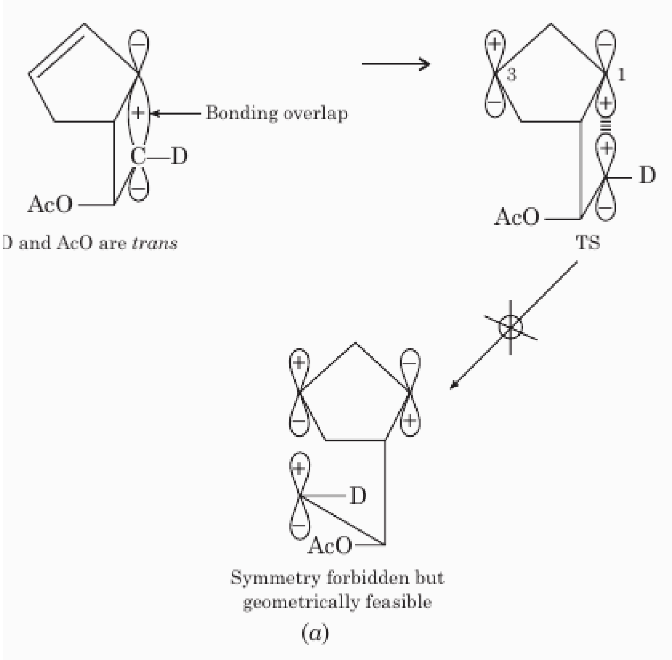
This is 1, 3 sigmatropic shift with inversion at the migrating centre.

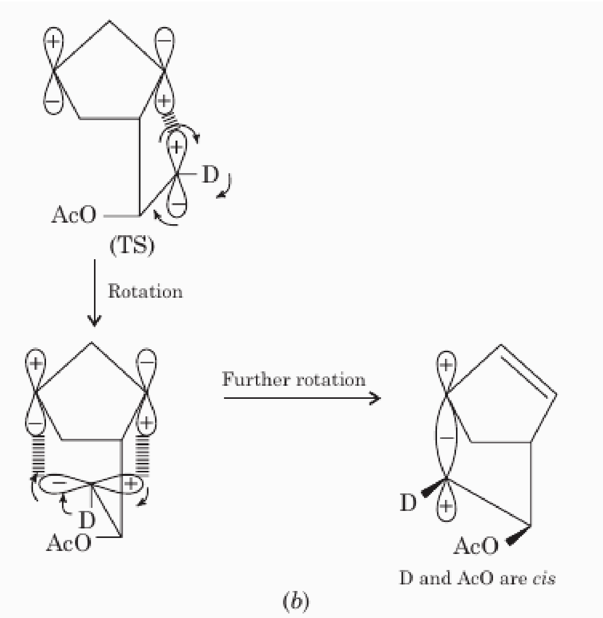


As the crucial bond between the alkyl system and the migrating carbon stretches, during the course of formation of transition state, the phase relationship between two bonded lobes must be mentioned.



We also know the symmetry of HOMO of the developing allyl systems and can fill in the lobes





(*b*)

In this case migration occurs using the back lobe of migrating carbon, and now a bonding interaction is created. The migrating carbon suffers inversion as reattachment takes place to the position-3 of the allyl framework. In order to preserve bonding overlap with C-1 and C-3 rotation must occur, and the trans starting material is thus converted into cis product.

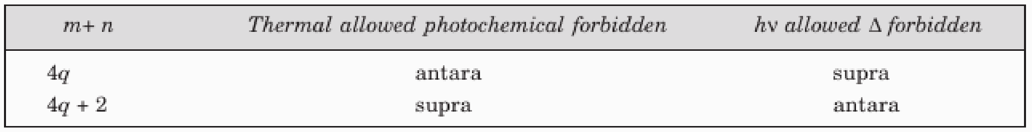
Selection Rules for sigmatropic Rearrangement

The stereochemistry (i.e., migration of group is suprafacial or antarafacial) of sigmatropic rearrangement is a simply function of number of electrons involved (as with other pericyclic reactions, the number of electrons involved is easily determined from the curved-arrow formalism: Simply count the curved arrow and multiply by two). All suprafacial sigmatropic reactions occurs when there are (4q + 2) electrons involved in the reaction—that is an odd number of electron pairs or curved arrows.

Selection rule of [1, n] sigmatropic rearrangement when migrating group is hydrogen atom.

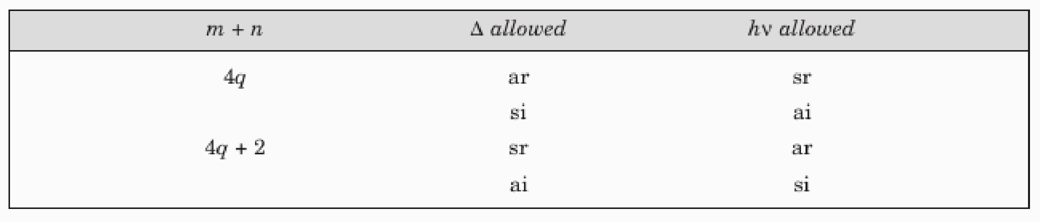
If sigmatropic reaction of the order (m + n) (for hydrogen m = 1) has m + n = 4q + 2 then thermal reaction is suprafacial and photochemical reaction will be antarafacial. However, for those cases in which m + n = 4q then thermal reaction is antarafacial and photochemical reaction will be suprafacial.

Selection rule for [1 + n] in which migrating group is hydrogen



m+ n	*Thermal allowed photochemical forbidden*	*hν allowed Δ forbidden*
$4q$	antara	supra
$4q + 2$	supra	antara

Selection rule for [1 + n] in which migrating atom is carbon



$m + n$	Δ allowed	$h\nu$ allowed
$4q$	ar	sr
	si	ai
$4q + 2$	sr	ar
	ai	si

s and a refer to supra and antara and r and i refer to retention and inversion in the configuration of the migrating centre.

The Woodward-Hoffmann Rule for Sigmatropic Rearrangement

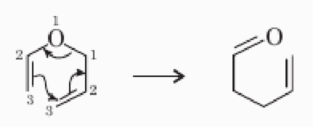
According to Woodward-Hoffmann rule a thermal (ground state) sigmatropic rearrangement is symmetry allowed when total number of (4q + 2)s component and (4r)a component is odd.

Similarly a sigmatropic change in the first excited state is symmetry allowed when total number of (4q + 2)s and (4r)a component is even.

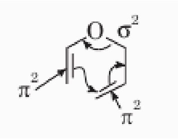
Woodward-Hoffmann rule for sigmatropic rearrangement where migrating group is not hydrogen

Here we will discuss [3, 3] sigmatropic rearrangement and in this case we will consider the Claisen rearrangement.

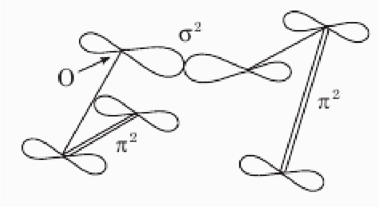
1. Draw the mechanism for the reaction.



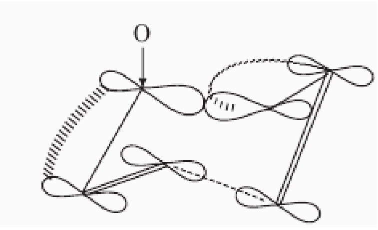
2. Choose the components. Only the bonds taking part in the reaction mechanism must be included.



3. Make a three-dimensional drawing of the way the components come together for the reaction, putting orbitals at the ends of the components.



4. Join up the components where new bonds are to be formed. Make sure you join orbitals that are going to form new bonds.

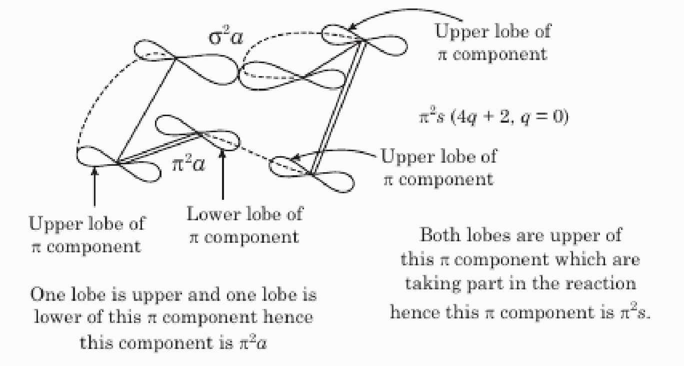


5. Label each component s or a. See below for the π and σ bond symmetries.

(a) Whether π component is s or a

If both upper lobes or both lower lobes of the π (pi) component are involved in the reaction then the component will be s and it is label as π2s.

If one upper lobe and other lower lobe of the π (pi) component are involved in the reaction then the component will be a and it is label as π2a.



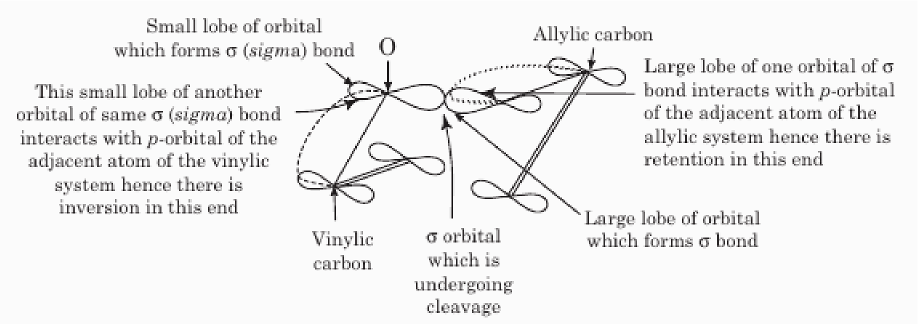
(b) Whether σ component is s or a (when migrating atom is not hydrogen)

(i) If sp3-hybrid orbital uses its large lobe for reaction then there will be retention or the small lobe then there will be inversion.

Or

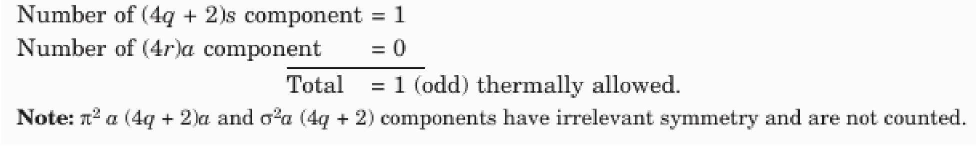
If large lobe of one orbital of the σ bond (which is undergoing cleavage) interacts with p-orbital of the adjacent atom (say atom-2 of allyl system) then at this end there will be retention. If small lobe of the other orbital of the σ bond (which is undergoing cleavage) interacts with p-orbital of the adjacent atom (say atom-2 of vinyl system) then at this end there will be inversion.

(ii) If there is retention at both ends or inversion at both ends then σ component is σ2s. If there is retention at one end and inversion at other end then σ component is σ2a.



Thus, σ component has retention at one end and inversion at another end hence σ component is σ2a.

6. Count the number of (4q + 2)s and (4r) a components.



Number of $(4q + 2)s$ component $= 1$

Number of $(4r)a$ component $= 0$

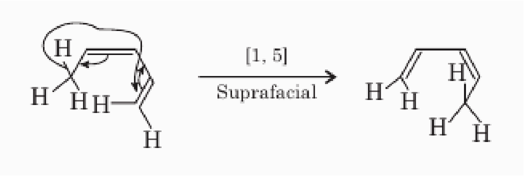
Total $= 1$ (odd) thermally allowed.

Note: $\pi^2 a$ $(4q + 2)a$ and $\sigma^2 a$ $(4q + 2)$ components have irrelevant symmetry and are not counted.

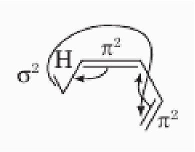
Woodward-Hoffmann rule for sigmatropic rearrangement where migrating group is hydrogen

Consider [1, 5] Sigmatropic hydrogen shifts

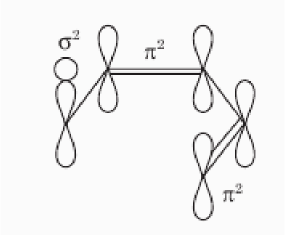
1. Draw mechanism for the reaction.



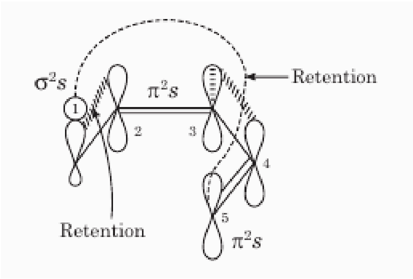
2. Choose the components. All bonds taking part in the reaction mechanism must be included and no others.



3. Make a three-dimensional drawing of the way the components come together for the reaction, putting in orbitals at the ends of the components.



4. Join up the components where new bonds are to be formed. Make sure you join orbitals that are going to form new bonds.

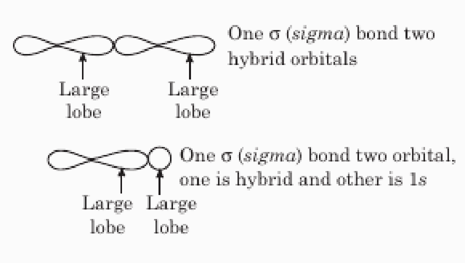


5. Label each components s or a. See below the σ (C—H) bond symmetry.

(i) The 1s orbital is spherically symmetrical and has no node, so whenever you draw the dotted line from 1s orbital it always means retention.

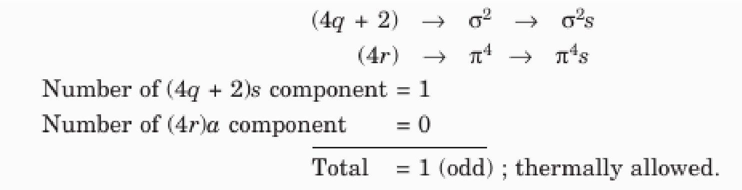
Or

Orbital of hydrogen which forms σ (sigma) bond is always treated as large lobe



(ii) If large lobe of one orbital of σ(C—H) bond (which is undergoing cleavage) interacts with p-orbital of the adjacent atom (atom-2) then at this end there will be retention. If small lobe of the one orbital of σ(C—H) bond (which is undergoing cleavage) interacts with p-orbital of the adjacent atom (atom-2) then at this end there will be inversion.

6. Count the number of (4q + 2)s and (4r)a components.



$(4q + 2) \rightarrow \sigma^2 \rightarrow \sigma^2 s$

$(4r) \rightarrow \pi^4 \rightarrow \pi^4 s$

Number of (4q + 2)s component = 1

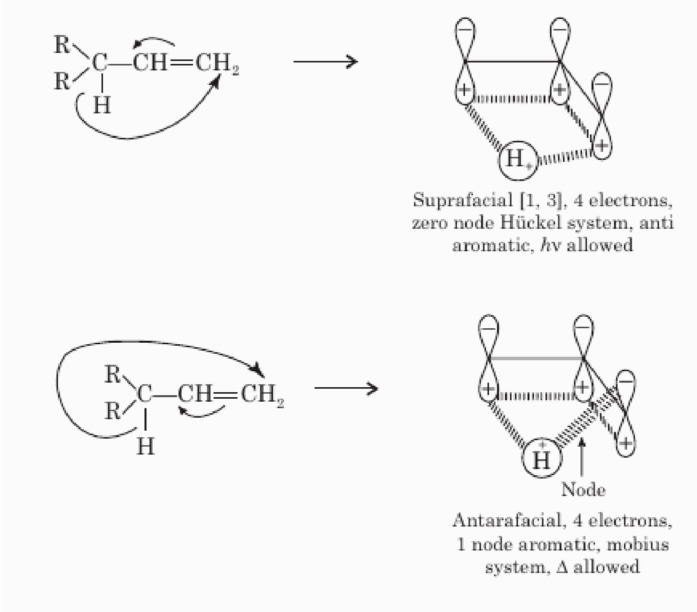
Number of (4r)a component = 0

Total = 1 (odd) ; thermally allowed.

Huckel-Mobius Method for Sigmatropic Rearrangement

According to Hückel-Mobius rule thermal sigmatropic rearrangements take place via aromatic transition state whereas photochemical sigmatropic rearrangements proceed via antiaromatic transition state. Consider the following two rearrangements:

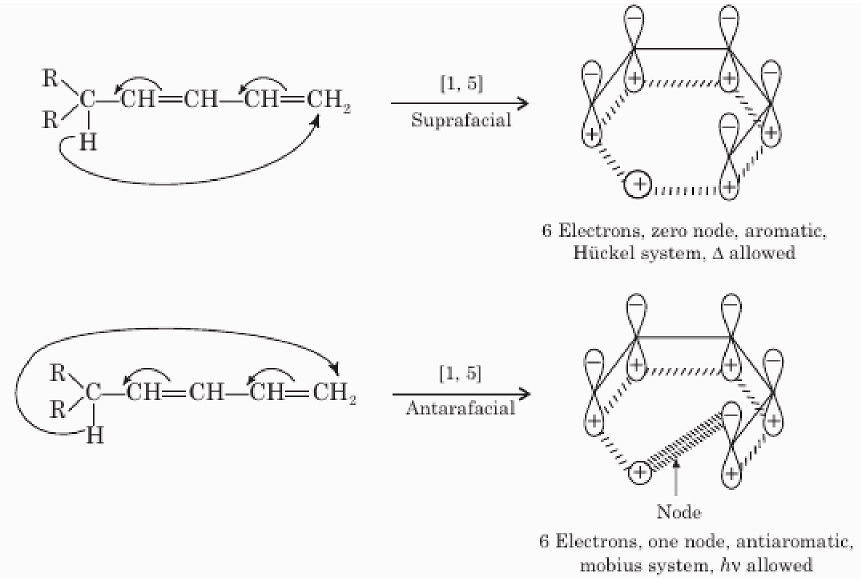
[1, 3] Sigmatropic Rearrangement



Suprafacial [1, 3], 4 electrons, zero node Hückel system, anti aromatic, $h\nu$ allowed

Antarafacial, 4 electrons, 1 node aromatic, mobius system, Δ allowed

[1, 5] Sigmatropic Rearrangement



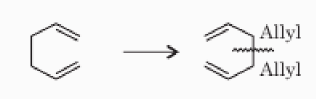
6 Electrons, zero node, aromatic, Hückel system, Δ allowed

6 Electrons, one node, antiaromatic, mobius system, $h\nu$ allowed

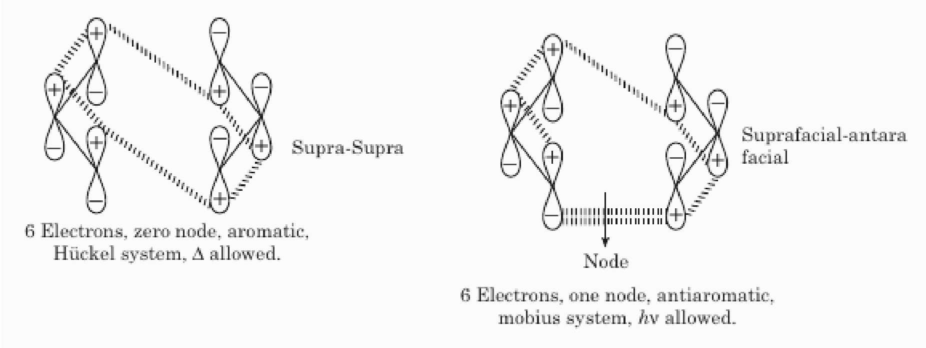
The selection rules for sigmatropic rearrangement of order (1, j) by this method are summarised in table

Number of electrons involved (1 + j)	*Number of nodes*	*Aromaticity*	*Shift mode*
$4n$	0	antiaromatic	supra, $h\nu$
$4n$	1	aromatic	antara, Δ
$4n + 2$	0	aromatic	supra, Δ
$4n + 2$	1	antiaromatic	antara, $h\nu$

[3, 3] Sigmatropic rearrangements

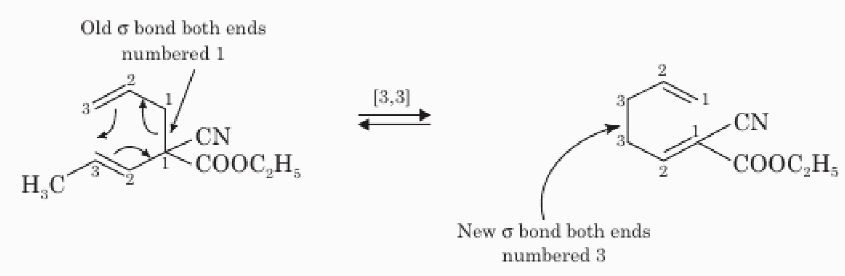


The transition state for such processes is represented as two interacting allyl fragments as mentioned earlier. In this there can be two stereochemical variations-suprafacial-suprafacial (or antarafacial-antarafacial) and suprafacial-antarafacial as shown in the following transition states:

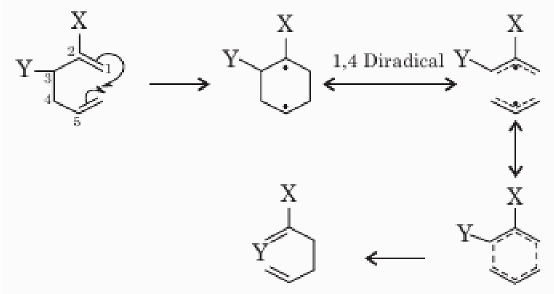


Cope Rearrangement

The most important sigmatropic rearrangement are the [3, 3] process involving carbon-carbon bond. The thermal rearrangement of 1, 5-dienes by [3, 3] sigmatropy is called Cope rearrangement. The reaction proceeds in the thermodynamically favoured direction.

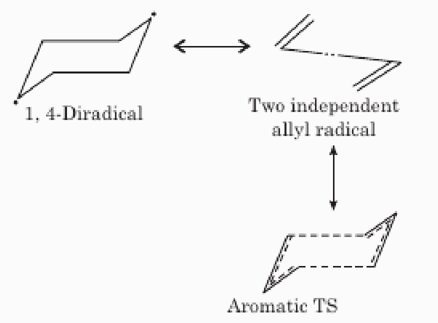


This particular reaction is called a [3, 3] sigmatropic rearrangement because the new s bond has a 3, 3 relationship to the old σ (sigma) bond.

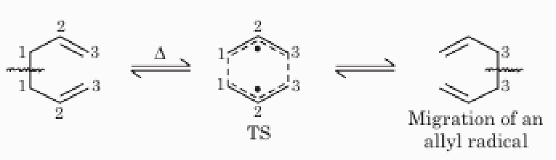


Conjugated substituents at C-2, C-3, C-4 or C-5 accelerate the rearrangement. Donor substituents at C-2 and C-3 have an accelerating effect. The effect of substituents can be rationalised in terms of the stabilisation of the transition state by depicting their different effect on two interacting system.

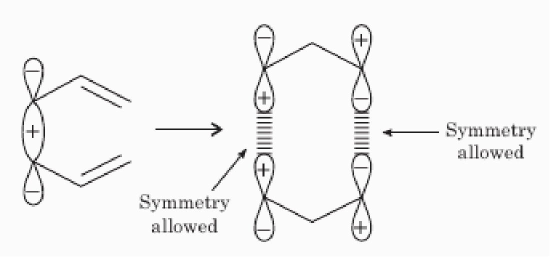
The transition state involves six partially delocalised electrons being transformed from one 1, 5-diene system to another. The transition state could range in character from a 1, 4-diradical to two nearly independent allyl radical, depending on whether bond making or bond breaking is more advanced. The general framework for understanding the substituent effects is that the reaction are concerted with relatively late transition state with well developed C-1-C-6 bonds



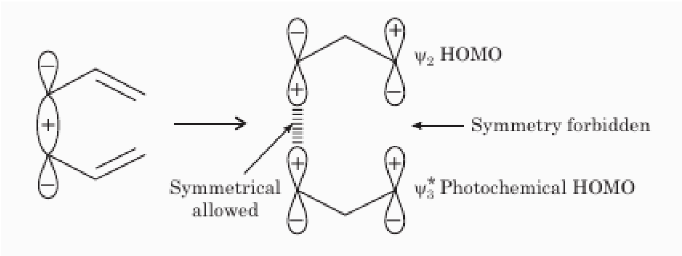
In Cope rearrangement the migrating group is allyl radical. An analysis of the symmetry of the orbitals involved shows why this reaction is a relatively facile thermal process but is not commonly observed on photochemical activation. As we break the C(1)–C(1) bond the phases of the overlaping lobes must be the same. The HOMO of the allyl radical is y2 and that information allows us to fill the symmetries of the two allyl radicals making up of transition state



Reattachment at the two C(3) positions is allowed because the interaction of the two lobes on the two C(3) carbons is bonding.

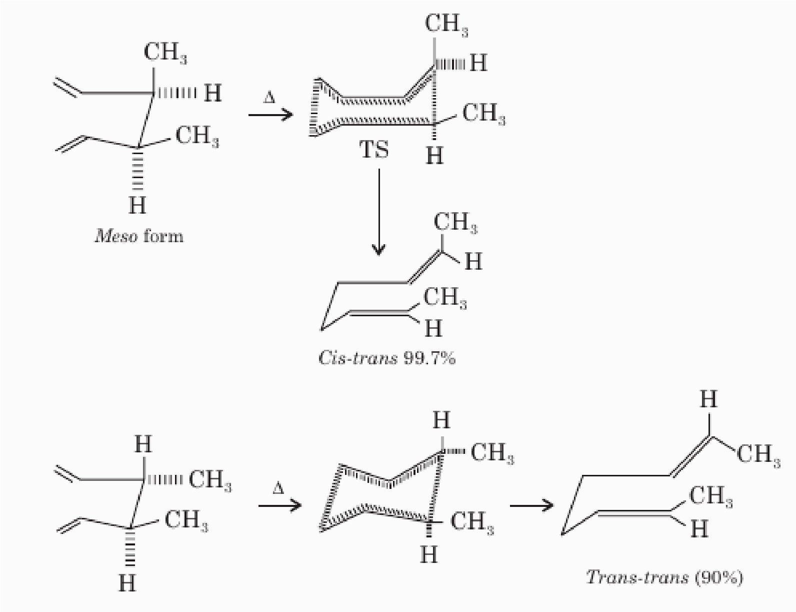


If interaction is carried out in the presence of UV light then one electron is promoted from the HOMO to the LUMO and LUMO will become photochemically HOMO.



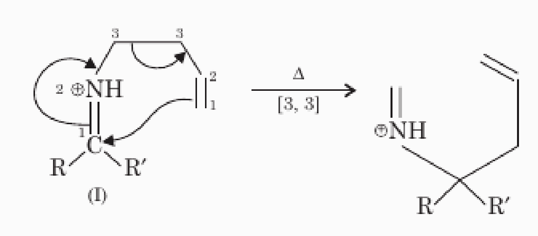
Stereochemistry of Cope Rearrangement

The Cope rearrangement usually proceeds through the chair like transition state. The stereochemical features of the reaction can usually be predicted and analysed on the basis of a chair transition state that minimises steric interactions between substituents. Rearrangement of the meso diene through such transition state then would give the cis-trans isomer while in the case of the rearrangement of the racemic mixture the trans-trans isomer is the major product and this is actually the result.



Aza Cope Rearrangement

Iminium compound of type (I) also gives Cope rearrangement. Which is known as Aza Cope rearrangement.



Compound (I) can be prepared from 4-aminoalkenes.

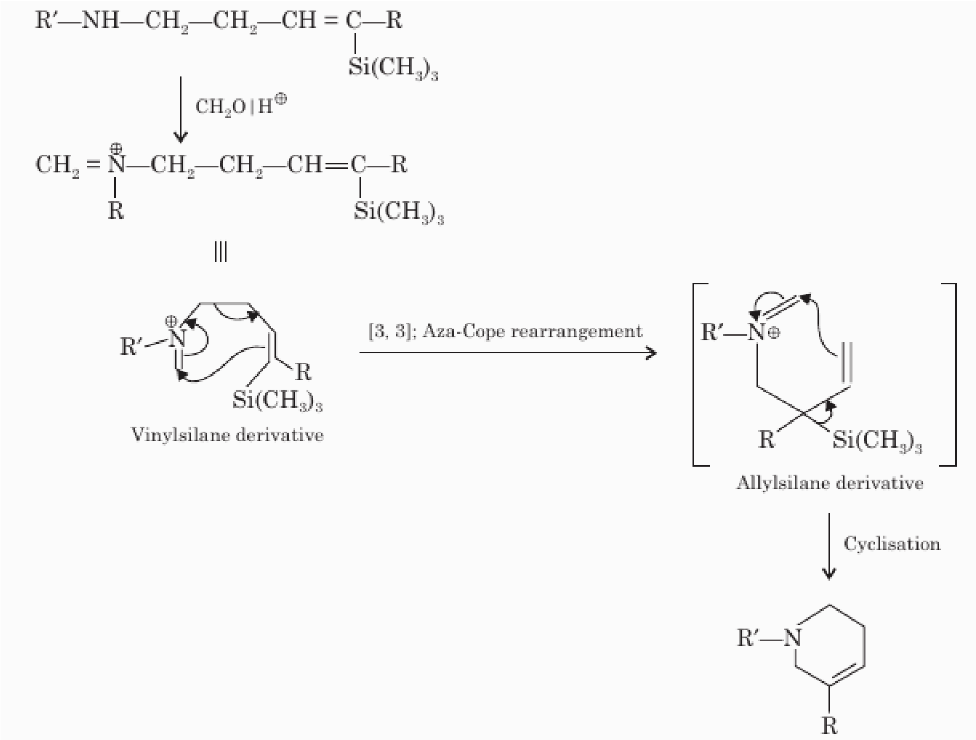
$$H_2N—CH_2—CH_2—CH=CH_2$$

4-Aminoalkene

4-Aminoalkenes react with carbonyl compounds to give iminium compound of type (I).

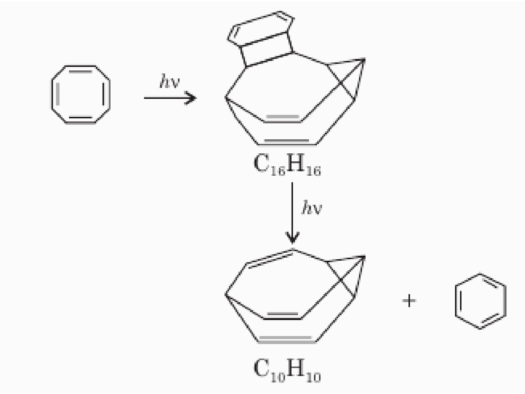
$$\begin{array}{c} H_2N—CH_2—CH_2—CH=CH_2 \\ \Big\downarrow \; CH_2O \mid \overset{\oplus}{H} \\ CH_2=\overset{\oplus}{N}H—CH_2—CH_2—CH=CH_2 \end{array}$$

Iminium compound of type (I) is very useful when it is prepared from 4-(trimethylsilyl)3-alkenylamines because in this case rearranged product undergoes cyclisation to give six membered nitrogen heterocyclic compound. Thus, the overall reaction is as follows:

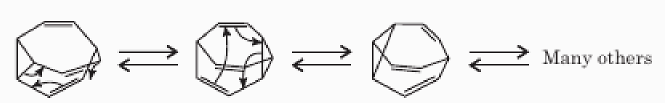


Fluxional Tautomerism

A number of compounds continually undergo rapid degenerate Cope rearrangement at room temperature. One such compound is bullvalene which was first prepared in 1963 by G. Schroder from cyclo-octatetraene as follows:



The [3, 3] sigmatropic rearrangements in bullvalene rapidly interconvert identical forms of the molecule.

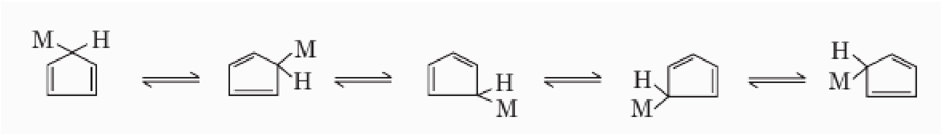


Bullvalene: Tricyclo [3, 3, 2, 0] deca 2, 7, tricyclo.

If the carbons could be individually labelled, there would be 1,209,600 different structures of bullvalene in equilibrium. Each one of these forms is interconverted into another at a rate of about 2000 times per second at room temperature.

Molecules such as bullvalene that undergo rapid bond shifts are called fluxional molecules. In fluxional molecules their atoms are in a continual state of motion associated with rapid changes in bonding. The rearrangement may involve either bond reorganisation or atom (or group) migration.

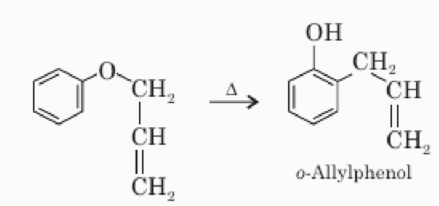
Other neutral completely fluxional organic molecules have not appeared, although the phenomenon of fluxionality appears to be rather more common in organic cations and organometallic compounds. The fluxionality of the σ (sigma) bonded metal cyclopentadienide involves atom migration.



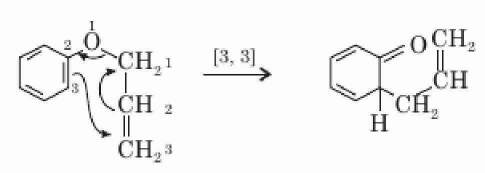
Fluxionality is most readily ascertained by means of nuclear magnetic resonance spectroscopy. Conversion of one structure into other in fluxional molecule is known as valence tautomerism and isomers are known as valence tautomers.

Claisen Rearrangement

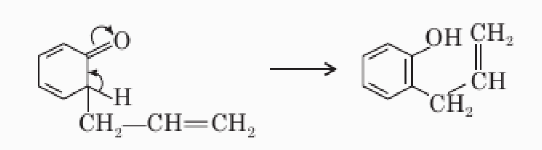
Claisen rearrangement is the first sigmatropic rearrangement which was discovered. The original sigmatropic rearrangement occurs when allyl phenyl ether is heated without solvent. The product of the rearrangement is o-allylphenol.



The above Claisen rearrangement is two step reaction. The first step in this reaction is [3, 3] sigmatropic rearrangement



This is one step mechanism without ionic intermediates. In this case numbering start from the heteroatom oxygen having σ (sigma) bond and allylic carbon of the allyl group. The second step in the reaction is a simple ionic proton transfer to regenerate aromaticity.



In this reaction allyl group turns inside out which is confirmed by unsymmetrical allyl ether.