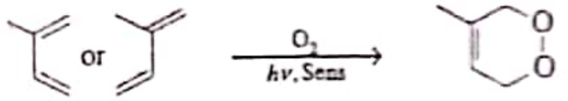
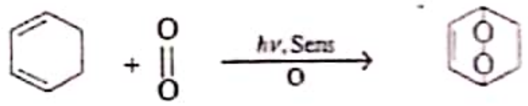
$$\text{Sens} \xrightarrow{h\nu} {}^3\text{Sens}^*$$
$$O_2 \text{ (triplet)} + \text{Sens}^* \text{ (triplet)} \longrightarrow O_2 \text{ (singlet)} + \text{Sens.}$$
$$A + O_2 \text{ (Singlet)} \longrightarrow AO_2$$

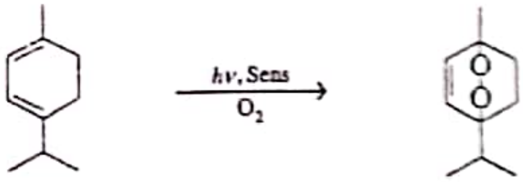
Photo oxidation of Alkenes and Polyenes

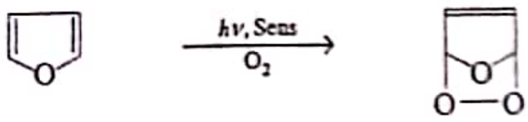
Alkenes, dienes and polyenes are attacked by singlet oxygen. The singlet oxygen may be generated by thermal methods (e.g. by the reaction of hydrogen peroxide with sodium hypochlorite) by excitation of grand state oxygen (triplet oxygen) in a microwave discharge or by the use of visible radiation and photochemical sensitiser such as methylene blue, Rose Bengal, chlorophyll, ribofavin, fluorescein or halo fluorescein.

✓ Acyclic or cyclic conjugated dienes gives 1, 4–cyclo addition reaction with singlet oxygen to form six membered cyclic adduct i.e. cyclic peroxide.



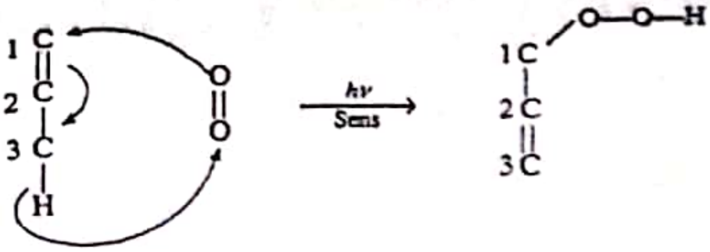


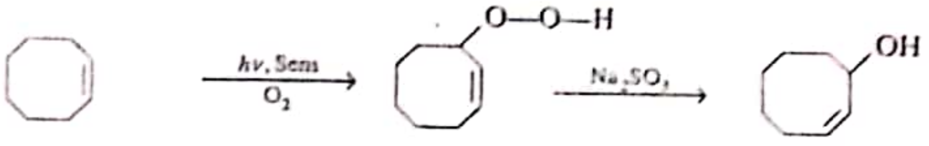


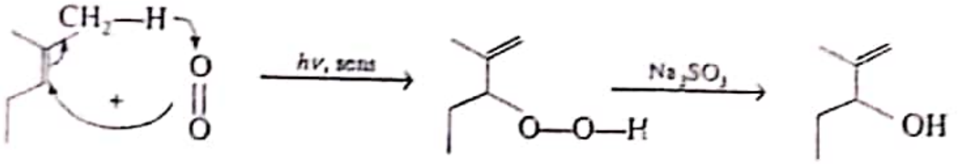


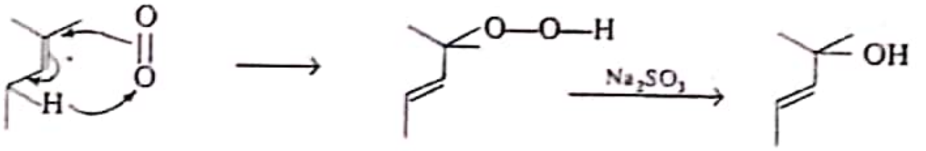
The formation of hydro peroxides in photosenitised oxygen-transfer reactions that follow the Schenck type of mechanism occurs only when hydrogen is present on allylic carbon. The reaction has, moreover, some definite steric and electronic requirements. Oxygen always becomes attached to one of the double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

✓

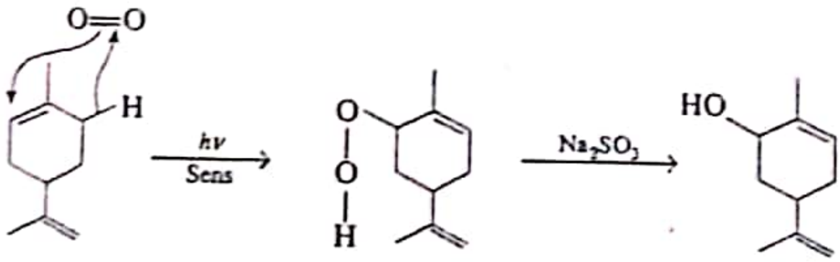




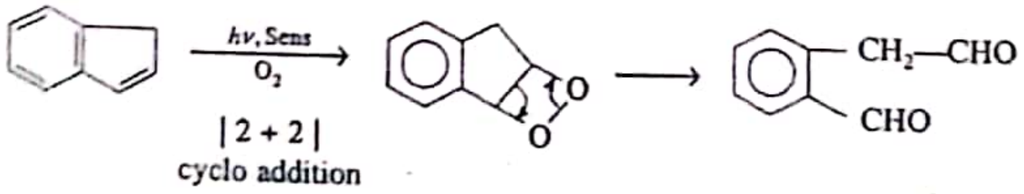


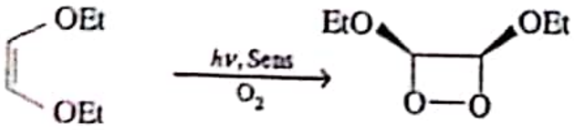


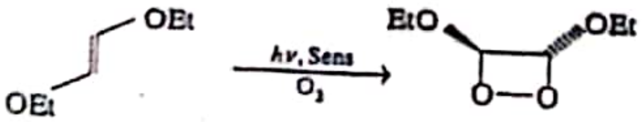
The above reactions do not proceed through free radicals. The oxidation with singlet oxygen occurs by concerted mechanism like the ene reaction.



Some substituted alkenes behaves differently with singlet oxygen and form a dioxetane in a cyclo addition reaction. Some dioxetanes are stable but others readily decompose to two carbonyl compounds. Electron rich alkenes undergo this reaction and reaction is stereospecific.

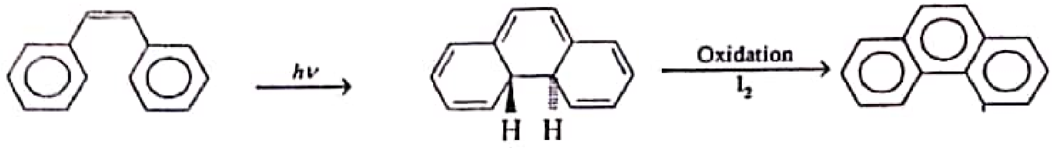






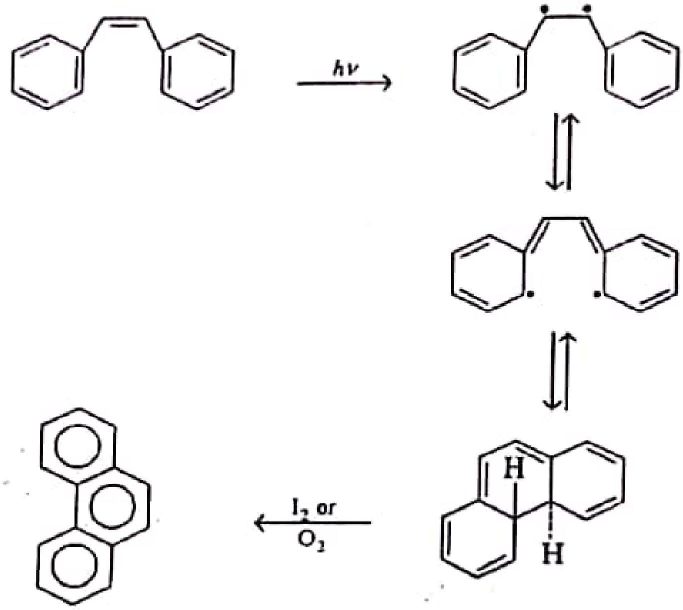
The oxidative cyclisation of conjugated trienes to form aromatic system is one of the more extensively studied photochemical oxidations. The conversion of *cis*-stilbene to phenanthnene is a main example of such a ring closure. The reaction takes place in the presence of hydrogen acceptors (O_2, I_2, $FeCl_3$)

✓



Mechanism of the reaction is as follows:

✓



CHAPTER 10

Photo Chemistry of Alkenes, Dienes Aromatic Compounds, Diazo and Azides

10.1 PHOTO CHEMISTRY OF ALKENES

10.1.1 Cis-Trans Isomerisation of Alkenes

The photochemical interconversion of *cis* and *trans* isomers of alkenes can be achieved by direct irradiation or by the use of triplet photosensitisers.

Cis-Trans Isomerisation By Direct Irradiation

Alkenes display a characteristic photochemical inter conversion of *cis* and *trans* isomers.

Trans-stilbene
λmax = 295 nm
$\varepsilon_t$max = 27,000

cis-stilbene
λmax = 280 nm
$\varepsilon_c$max = 13,500

Usually the *trans* isomer is thermodynamically more stable and photolysis establishes a mixture that is richer in *cis* isomer. Therefore irradiation provides a method for converting a *trans* alkene to *cis* alkene. After certain extent of irradiation the *cis-trans* ratio no longer changes. This is called the *photostationary state*. The composition of photostationary state depends on the absorption maximum and molar excitation coefficient of the isomers. Because of its longer wave length maximum and higher excitation coefficient the *trans* isomer will be absorbing substantially more light than the *cis* isomer. The relative amount of light absorbed by the *cis* and *trans* isomers at any wave length will be proportional to their excitation coefficient ε_c and ε_t at that wave length. Assuming that the quantum yield for conversion of *cis* → *trans* is approximately equal to that for *trans* → *cis*, the conversion of *trans* alkene to *cis* will occur faster than the conversion process when the two isomers are in equal concentration. On continued photolysis, a photostationary state will be achieved at which the rate of *trans* → *cis* conversion is equal to that of *cis* → *trans*, conversion. At that point the concentration of the *cis* isomer will be grater than of the *trans* isomer

Direct irradiation gives initially the vertical excited singlet states, *cis-S* from *cis-*S_0 and *trans-*S_1 from *trans* S_0. Decay of these spectroscopic states t ground state isomers may occur directly (Fig. 10.1) or through a common lower energy state (Fig. 10.2). The evidence favours the latter, with the non planar singlet state (referred to as the perpendicular or orthogonal state) as the common intermediate.

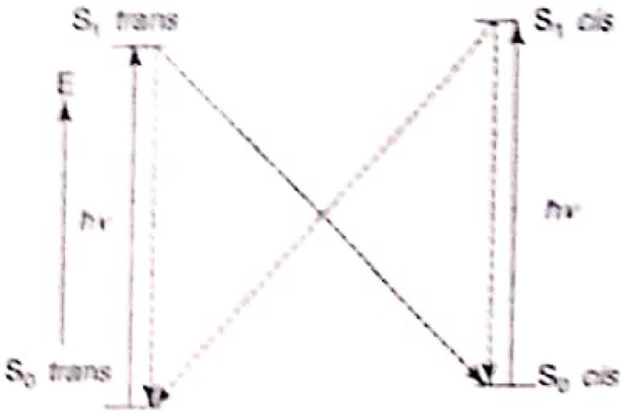


Fig. 10.1

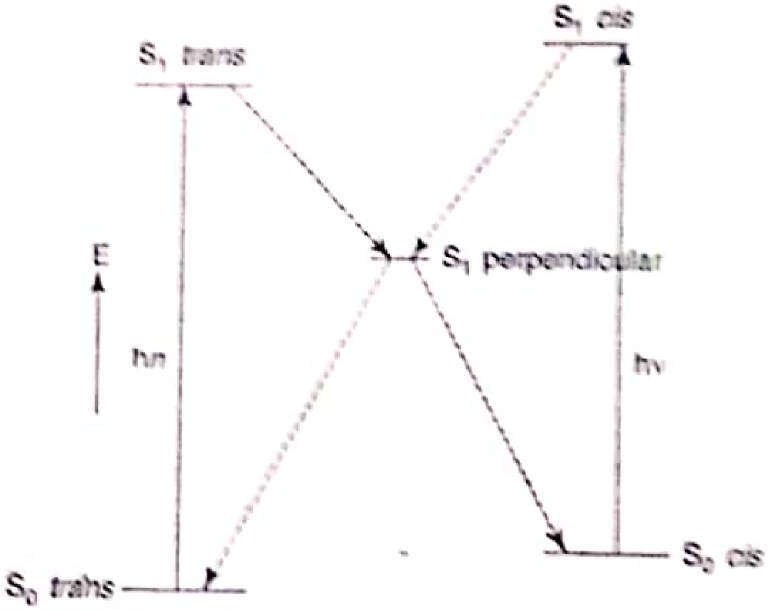


Fig. 10.2

Formation of Perpendicular State as the Common Intermediate

The isomerisation of alkenes is believed to take place via an excited state (Fig. 10.2) in which the two sp^2 hybrid carbons are twisted 90° with respect to one another. This state is referred to as the perpendicular sate. This geometry is believed to be the minimum energy geometry for both the singlet and triplet excited states.

The isomerisation occurs because the π bond which normally prevents it, is lost in the passage to the excited state, in which the two sets of substituents now occupy mutually perpendicular planes (Fig. 10.3). Thus *cis-trans* isomersation disappears on excitation. When the excited molecule drops back to the So state either isomer can be formed.

$$C_6H_5{-}CH{=}CH{-}C_6H_5 \xrightarrow{h\nu} \underset{93\%}{\textit{cis}\text{-stilbene}} + \underset{7\%}{\textit{trans}\text{-stilbene}}$$

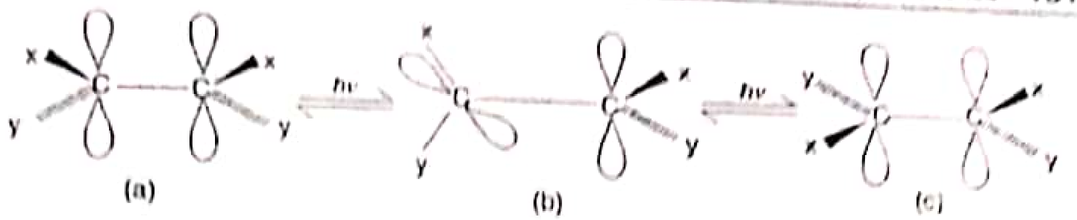


Fig. 10.3

Sensitised *cis-trans* Isomerisation

The photo-isomeriation can also be carried out by photosensitisation. Under these conditions, the composition of photostationary state depends on the triplet energy of the senistiser. With sinsitiser having triplet energies above 60 kcal/mole, *cis-trans* ratio is slightly more than one but a range of sensitiser having triplet energies of 52 to 58 kcal/mole offered much higher *cis-trans* ratio in the photostationary state. The higher *cis-trans* ratio in this region result from the fact that the energy required for excitation of *trans* isomer is less than for excitation of *cis*-isomer.

Thus, sensitiser having triplet energies in the range of 52 to 58 kcal/mole, selectively excits the *trans* isomer. Since the rate of *trans-cis* conversion is increased, the composition of the photostationary state is then enriched in *cis* isomer.

$$(C_6H_5)_2CO \xrightarrow{h\nu} {}^1[(C_6H_5)_2CO] \xrightarrow{ISC} {}^3[(C_6H_5)_2CO]$$

$$cis\text{-}trans\ \text{stilbene} + {}^3[(C_6H_5)_2CO] \longrightarrow {}^3[C_6H_5CH\overset{\text{IIIII}}{=}CH{-}C_6H_5] + (C_6H_5)_2CO$$

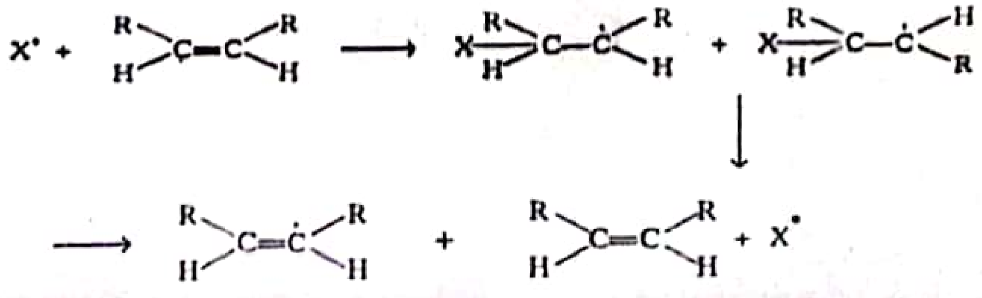
$$\downarrow$$

$$\underset{93\%}{cis\text{-stilbene}} + \underset{7\%}{trans\text{-stilbene}}$$

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

(i) $X_2 \xrightarrow{h\nu} X^\bullet + X^\bullet$

(ii)



10.1.2 Dimerisation Reactions of Alkenes

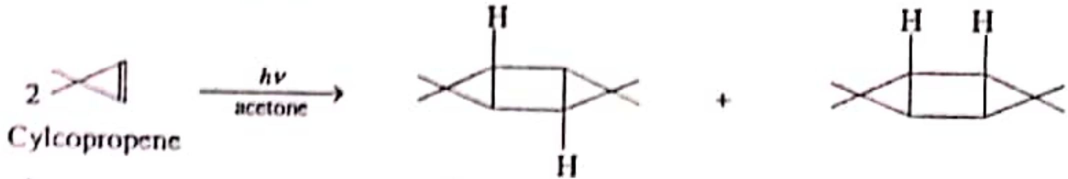
Alkenes give two types of dimerisation reactions

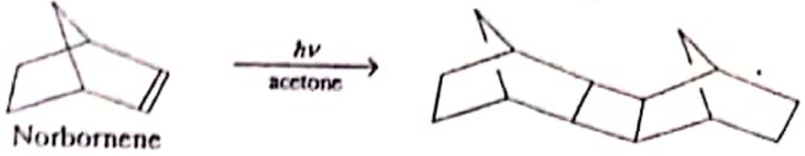
(1) **Concerted [2 + 2] cyclo addition reaction (pericyclic reactions) and**

(2) **Non concerted cycloaddition reactions.**

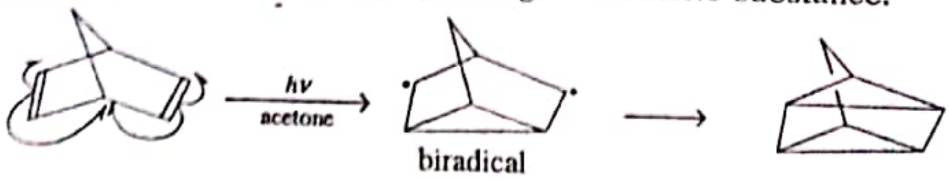
Non concerted cycloaddition reactions are two step reactions involving a biradical intermediate and with non stereospecific or only partially stereospecific formation of products.

Inter and intramolecular cycloaddition reactions of alkenes can be brought by triplet sensitiser and are therefore often accompanied by *cis-trans* isomerisation. Most simple alkenes have high triplet energy to be sensitised efficiently by organic sensitiser, and mercury sensitisation in many cases cause intramolecular fragmentation or rearrangement rather than intermolecular cyclo addition. The dimerisation of cyclic alkenes with three, four or five membered ring can be sensitised with high energy organic sensitiser such as acetone (but not benzophenone, which gives oxetane). Dimersation process involves the generation of an excited state triplet molecule which subsequently reacts with a ground state olifin molecule.

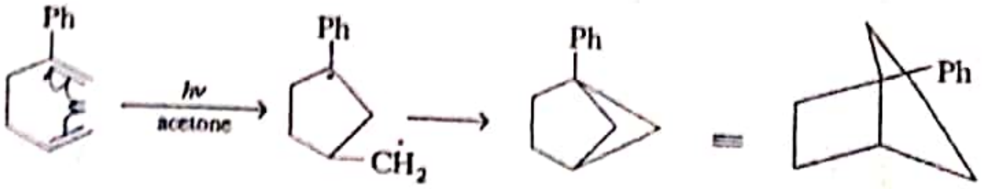




Interestingly, there may be an intramolecular reaction between two properly situated double bonds in a molecule yielding an isomeric substance.

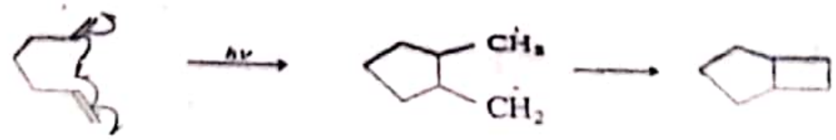


1, 5 Dienes give bicyclo [2, 1, 1] hexanes in preference to bicyclo [2, 2, 0] hexanes.

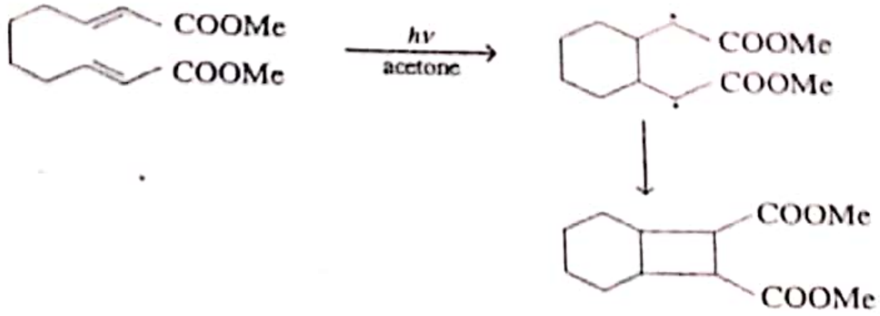


1, 6 and 1, 7 dienes undergo the expected straight cycloaddition in the triplet state to give bicyclo [3, 2, 0] heptanes and bicyclo [4, 2, 0] octanes.

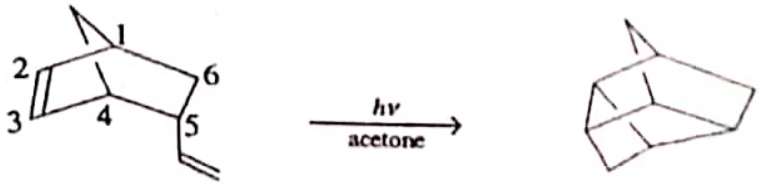
(i)



(ii)

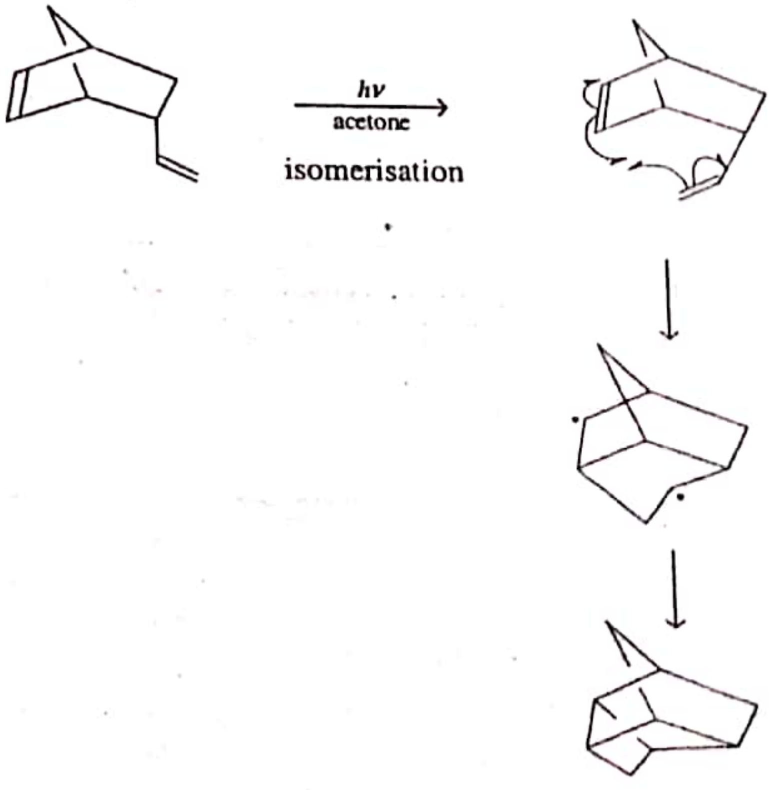


In exceptional cases geometry of the system prevents formation of a five membered ring in the cycloaddition of 1, 5-dienes and the alternative mode of ring formation predominates.



5-Vinylnorborene

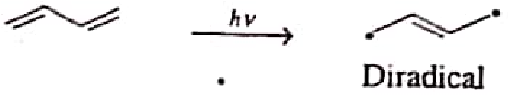
Product formation takes place as follows:

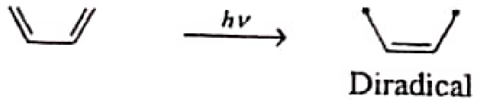


10.2 PHOTOCHEMISTRY OF CONJUGATED DIENES

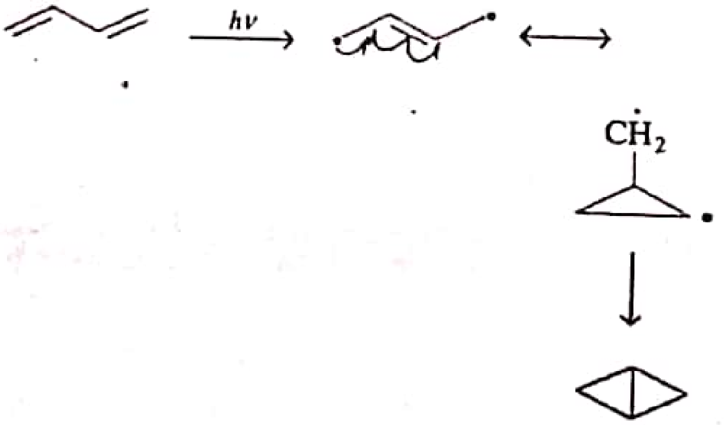
1, 3–Butadiene exists in solution as a mixture of S-*trans* (95%) and S-*cis* (5%) conformers.

Irradiation of butadiene promotes an electron from ψ_2 to ψ_3 ($\pi_1 \rightarrow \pi^*$) which results in the increased bonding between C_2 and C_3 at the expene of C_1 and C_2 and C_3 and C_4. In other words the lowest excited states of *S-trans* and *S-cis* butadiene should exhibit still larger energy barriers to rotation about the C_2—C_3 bond because of its double bond character. Thus conformational character of butadienes are retained in the excited states.





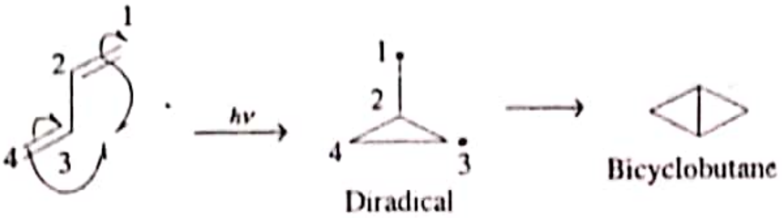
Direct irradiation of butadiene yields cyclobutene and bicycolo [1, 1, 0] butane. The formation of these products occurs directly from the S_1 state of the butadiene and assuming that the conformational characters of butadiene are retained in the S_1 state, it appears quite reasonable to speculate that *S-cis* butadiene is the precursor of cyclobutene while the excited state resembling *S-trans* butadiene gives rise to bicyclobutane.



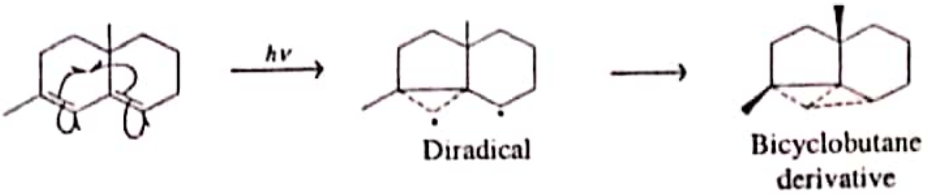
The formation of cyclobutane and bicyclobutane on irradiation of 1, 3-butadiene is a fairly general photochemical reaction.

Bicyclobutane Formation

The electrocyclic ring closure of conjugated dienes on direct irradiation is accompanied by formation of a bicyclo butane. Since this product is also formed in the mercury triplet sensitised reaction, it is proposed that the reaction proceeds in non-concerted process by formation of biradical as reaction intermediate.

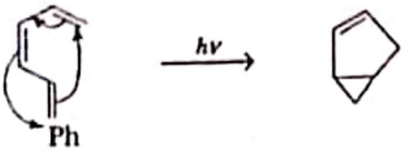


This reaction is given by S-*trans* conformation. Rigid diene system with S-*trans* geometry as in the hexalins give bicyclobutane on irradiation

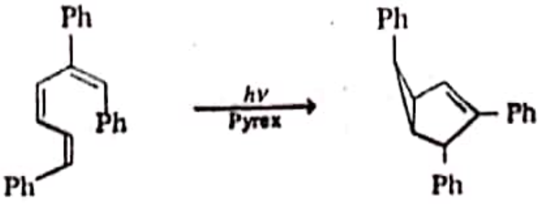


A related reaction is the ring-closure of conjugated triene on direct irradiation to give bicyclo [3, 1, 0] hexenes. The reaction is vinylogous to bicyclobutane formation from dienes.

(i)

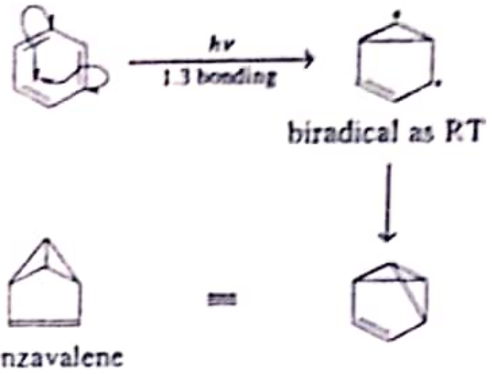


(ii)

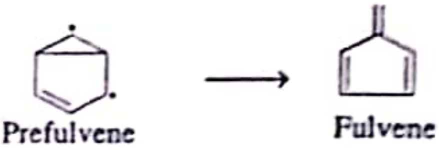


10.3 PHOTOISOMERISATION OF AROMATIC COMPOUNDS

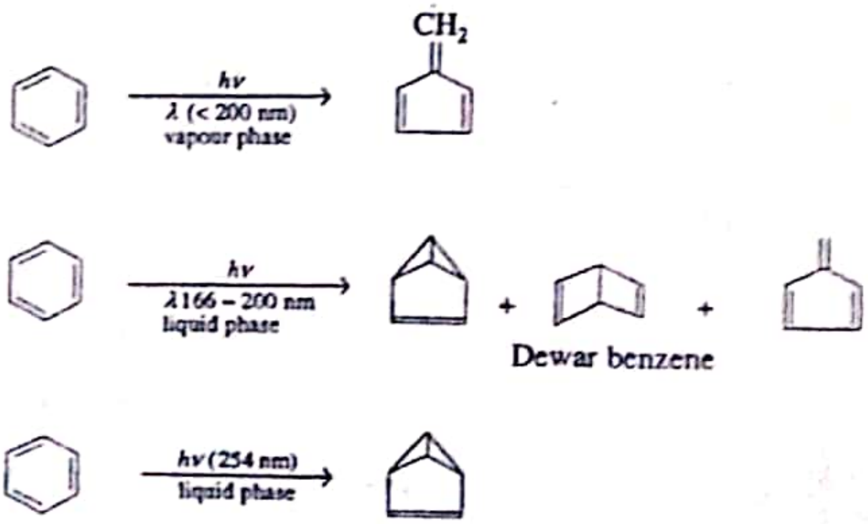
Irradiation of benzene and certain of its derivatives results in bond reorganisation and formation of non aromatic products. **Irradiation of liquid benzene with light of 254 nm wave length results in the formation of fulvene and a very small amount of benzvalene** i.e. tricyclo [3, 1, 0, 0] hex-3-ene. The key intermediate is believed to be a biradical formed by 1, 3-bonding. Formation of biradical is analongous to the formation of bicyclobutane from photoexcited butadiene



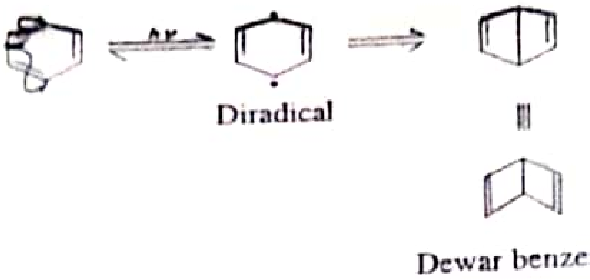
Fulvene is derived from prefulvene by carbon-carbon bond cleavage and 1, 2-hydrogen shift.



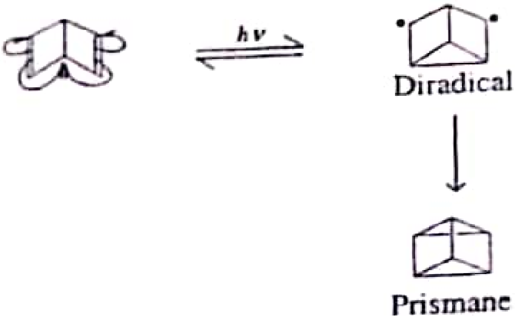
Several strained systems like that in Dewar benzene and prismane have been formed by the irradiation of substituted benzenes. These are the reaction intermediates of photo isomerisation of substituted benzene. Nature of intermediates depend on the state of the aromatic compound and wavelength of the light used for irradiation.



Formation of Prismane and Dewar benzene as reaction intermediates. Formation of Dewar benzene is analogous to the butadiene-cyclobutene inter, conversion.

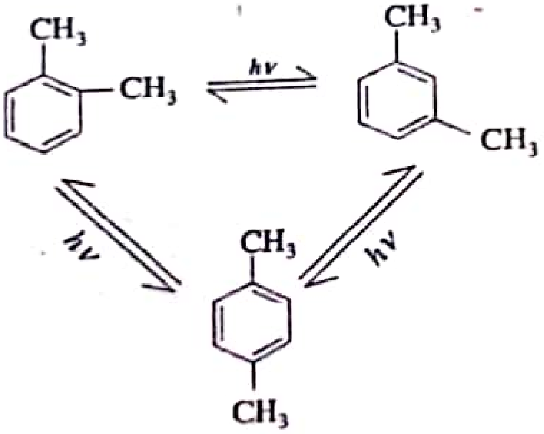


Dewar benzene on further [2 + 2] cycloaddition gives prismane.



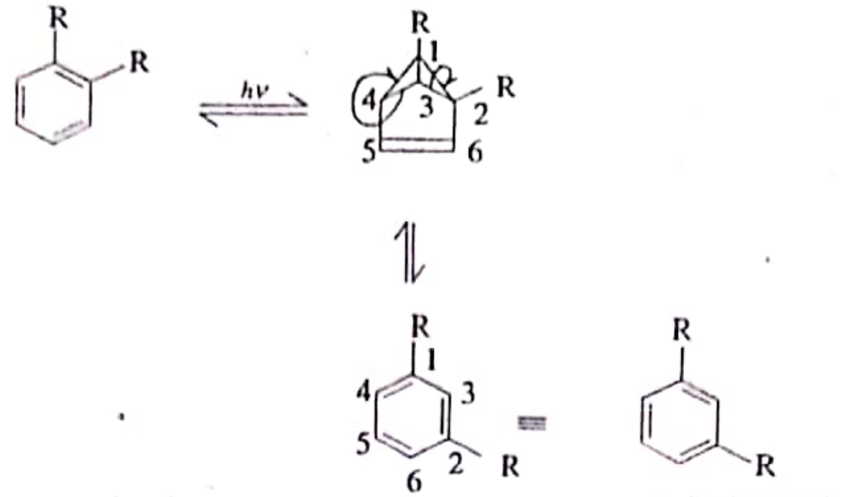
All these strained intermediates i.e. benzvalene, prismane and Dewar benzene are thermally labile and ultimately isomerise into benzonoid compounds.

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

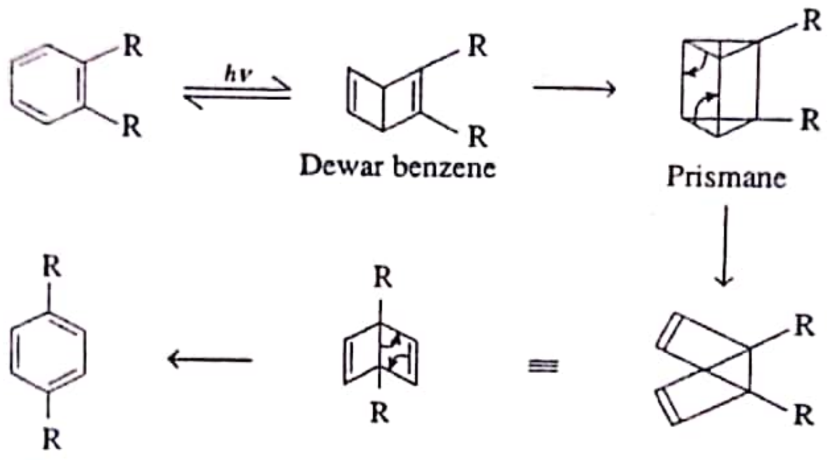


Conversion of *o*-xylene into *m*-xylene and *m*-xylene into *p*-xylene is due to 1, 2-alkyl group shift. Similarly conversion of o-xylene into *p*-xylene and visa-versa is due to the 1, 3-alkyl group shift.

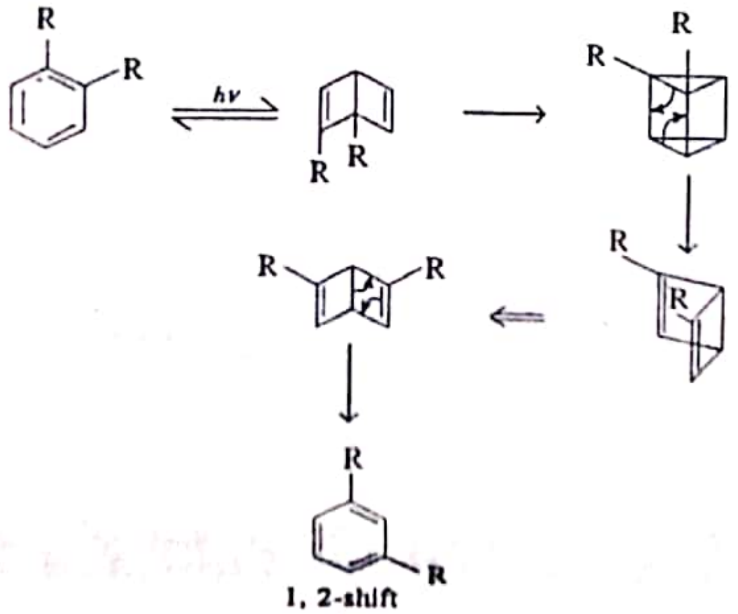
1, 2-Alkyl group shift takes place by benzvalene as well as prismane intermediates whereas 1, 3-alkyl group shift takes place only by prismane intermediate.



1, 2-shift of R



1, 3-shift of alkyl group.



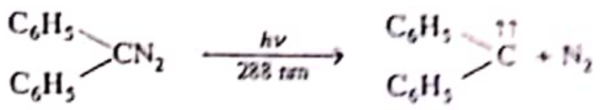
1, 2-shift

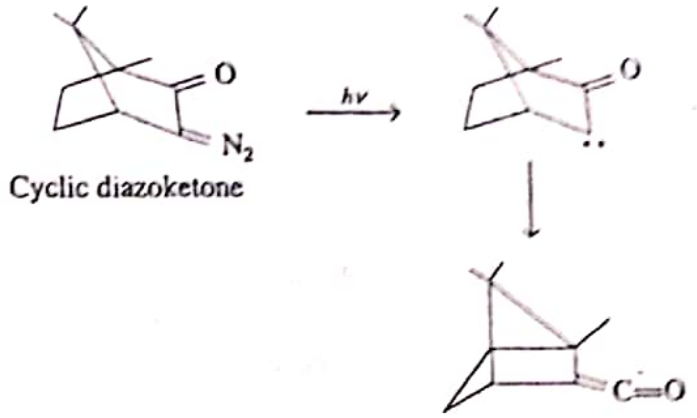
10.4 PHOTO CHEMISTRY OF DIAZO COMPOUNDS

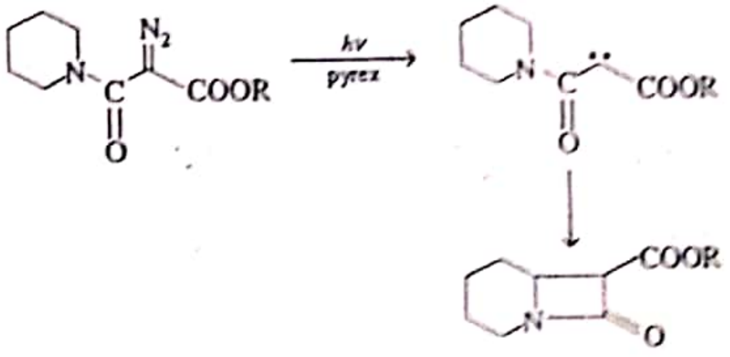
Diazoalkanes exibits a weak absorption band in the visible region (400 – 500 nm) which is attributed to a $n \rightarrow \pi^*$ transition.

$$R_2C{=}\overset{\oplus}{N}{=}\overset{\ominus}{N} \longleftrightarrow R_2\overset{\ominus}{C}-\overset{\oplus}{N}\equiv\ddot{N} \longleftrightarrow R_2-\overset{\ominus}{C}-\ddot{N}=\overset{\oplus}{N}$$

The corresponding excited states fragment readily to give molecular nitrogen and a carbene and this is a widely used method for the generation of these divalent carbon species. Direct irradiation leads initially to a singlet state of the diazo compound and thence to a *singlet carbene*, although collisional deactivation to give *triplet carbene* before further reaction occurs may be important for those carbenes whose triplet state is lower in energy than the singlet state, especially at higher pressure in the vapour phase or in solution. Triplet sensitised decomposition of diazoalkanes gives rise directly to triplet carbene by way of the triplet excited state. These processes provide a valuable route to carbene and are employed for intramolecular reaction as in the ring contraction of cyclic diazoketones and in β-lactum formation from α-diazoamides.







10.5 PHOTO CHEMISTRY OF AZIDES

Azides are similar to diazoalkanes. It also gives molecular nitrogen and nitrene in excited state.

Aliphatic azides gives aliphatic nitrene. Aliphatic nitrenes normally give imine by a hydrogen shift.

$$CH_3-CH_2-CH_2-N_3 \xrightarrow{h\nu} CH_3-CH_2-CH_2-\ddot{N}$$

CHAPTER 11

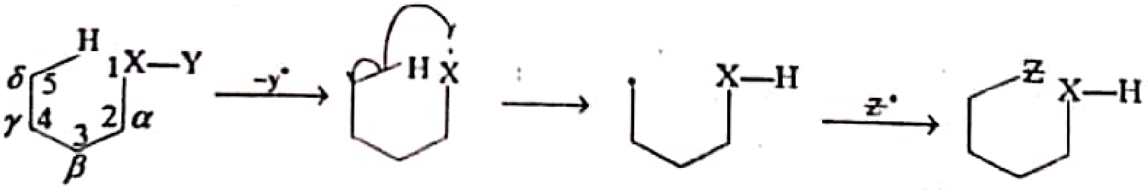
Photo Substitution Reactions at sp^3 Hybrid Carbon Having at Least One Hydrogen

11.1 INTRODUCTION

Substitution reaction at sp^3-hybrid carbon takes place when carbon has either leaving group or has at least one hydrogen. Replacement of hydrogen is possible when neighbouring group activates the carbon. Ionic attack at unactivated C—H bonds is uncommon. Free radical on the other hand, can often be obtained with enough energy to break unactivated C—H bonds. Intermolecular reactions of this type (free radical hologenation, sulphonation, nitration etc.) are of limited value because the reagents are unselective and mixture of products generally result. However it has been found that in many molecules intramolecular free radical attack sp^3 hybrid carbon having hydrogen can become quite specific when molecule meet certain structural and geometrical requirements. The reaction leads to the introduction of functional group at this carbon and number of reactions of this type have become of synthetic importance.

The key step in these reactions is an intramolecular abstraction of hydrogen from δ-carbon (carbon-5) resulting in the transfer of a hydrogen atom from δ-carbon to the attacking free radical in the same molecule. Transfer of hydrogen atom from δ-carbon leads to the formation of six membered transition state which is very common in photochemistry.

The reaction can be represented as follows (in equations-1)



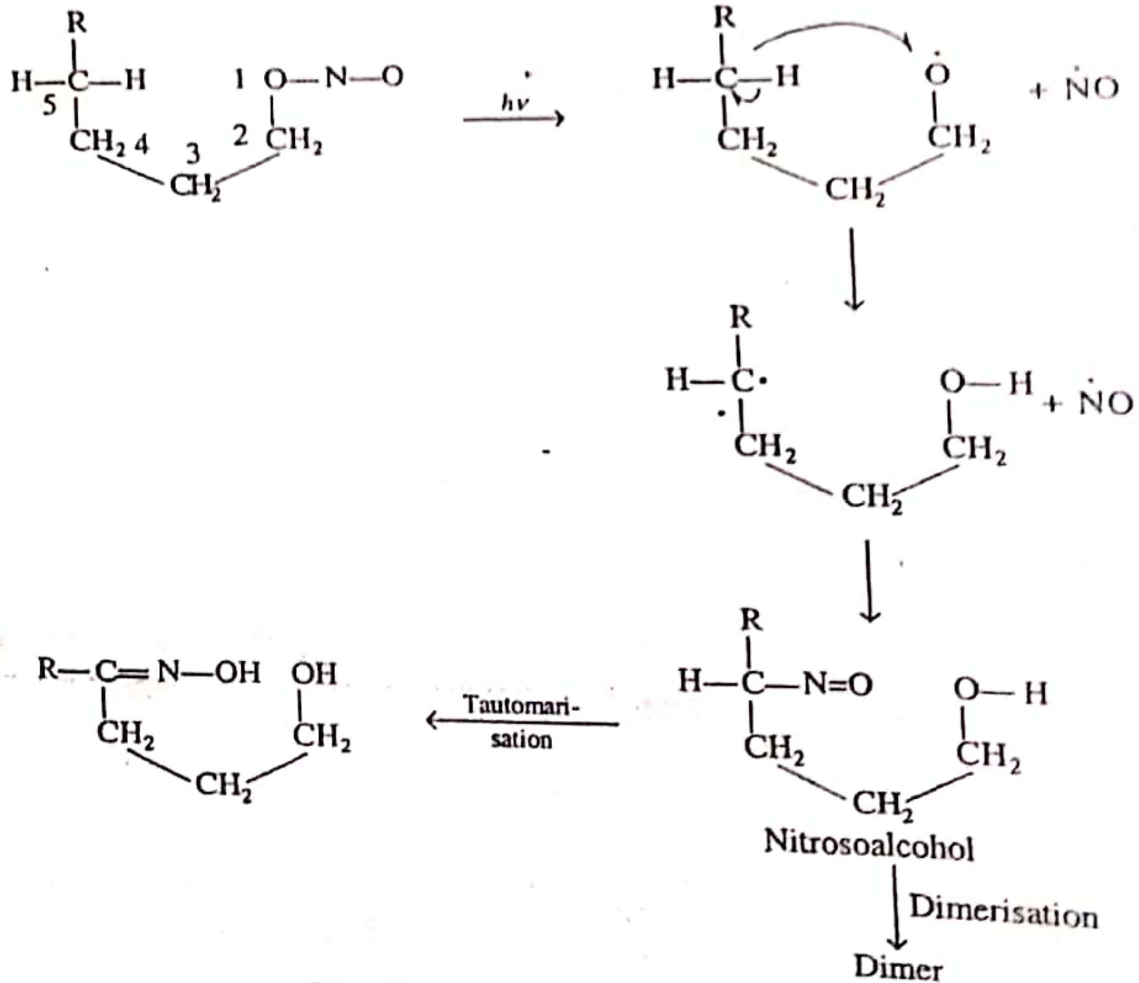
(i)

Z = y or some different group

In the above reaction X in most of the cases is either oxygen or nitrogen. The most common reaction of this class is *Barton* reaction (when X is oxygen) and *Hofmann-Loeffler-Freytag* reaction (when X is nitrogen).

11.2 BARTON REACTION

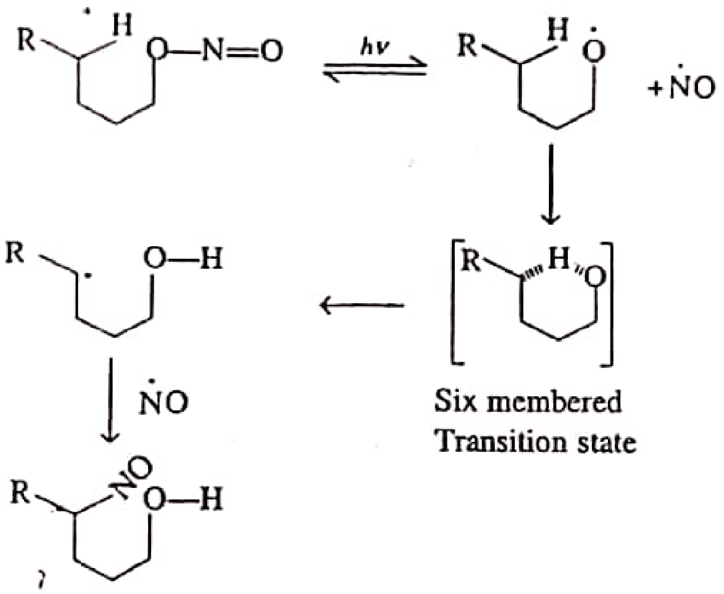
It has been known for many years that vapour phase photolysis or pyrolysis of organic nitrites (X = O, Y = NO) **gives alkoxy radicals and nitrogen** monoxide. **It has been found that when the structure of the molecule is such as to bring the** $-\overset{|}{\underset{|}{C}}-O-N{=}O$ group and a $-\overset{|}{\underset{|}{C}}-H$ 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 (I) to give carbon radical. This carbon radical capture nitrogen monoxide to give nitrosoalcohol. This nitrosoalcohol may be isolated as dimer or may rearranged 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*. The complete reaction is as follows (scheme-I)



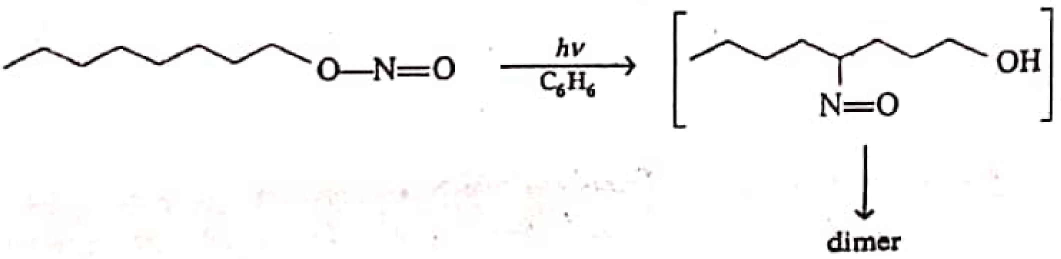
Scheme-I Formation of nitrosoalcohol.

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.

Quantum yield of the reaction is 0.76. This confirmed that the reaction is photo chemical reaction and not the free radical chain reaction. In free radical chain reactions quantum yield is always more than one. Photolysis of nitrite ester is reversible process which has been confirmed by the use of N^{15} nitrite ester. Photolysis of nitrite ester gives an alkoxyl radical and nitrogen monoxide in reversible step which are completely dissociated from each other. The alkoxyl radical rearranges rapidly, by abstraction of hydrogen, to a carbon radical. This carbon radical can be captured by radical trapping reagents to give transfer products. The normal fate of the carbon radical in the absence of trapping reagents is to react relatively slowly with nitrogen monoxide to give nitrosoalcohol.

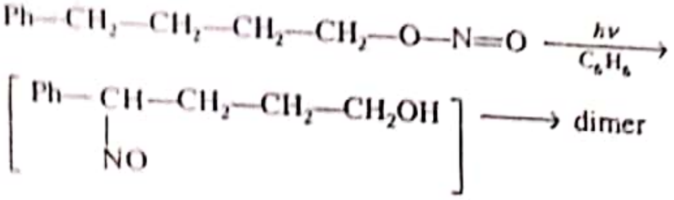


There is ample evidence to support the view that hydrogen transfer step takes place through a six membered transition state. In practice reaction occurs at most exclusively by abstraction of a hydrogen atom from the δ-carbon. Photolysis of 1-octyl nitrite in benzene gave only dimer of 4-nitroso-1-octanol.

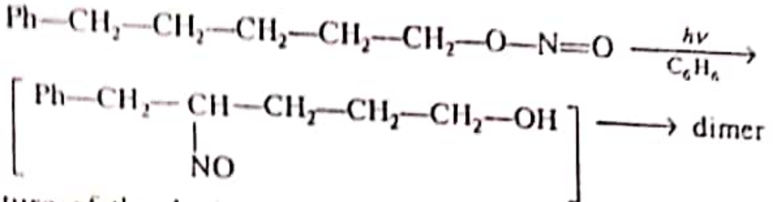


(2)

Similarly 4-phenyl-1-butylnitrite and 5-phenyl-1-pentyl nitrite are readily converted into dimer of 4-nitroso 4-phenyl butanol and 4-nitroso 5-phenyl pentanol respectively.



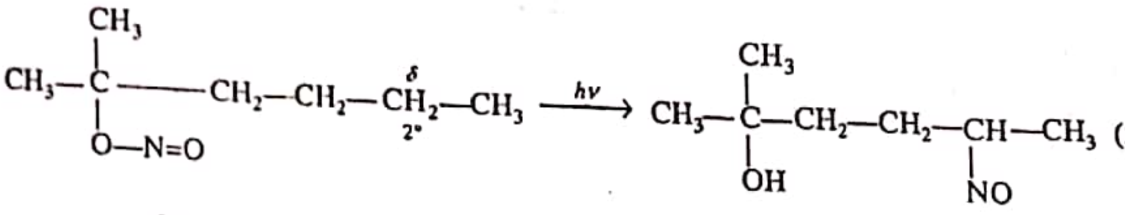
$$Ph-CH_2-CH_2-CH_2-CH_2-O-N=O \xrightarrow[C_6H_6]{h\nu} \left[Ph-\underset{\substack{|\\ NO}}{CH}-CH_2-CH_2-CH_2OH \right] \longrightarrow \text{dimer} \tag{3}$$



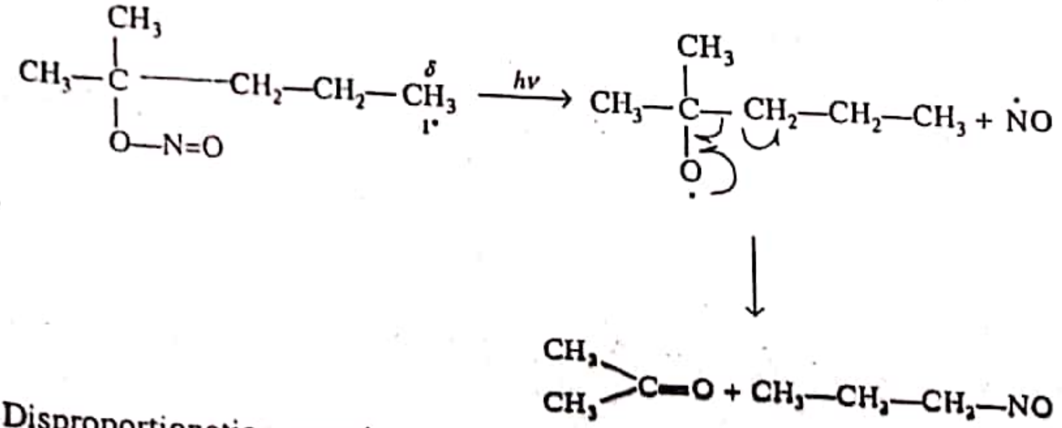
$$Ph-CH_2-CH_2-CH_2-CH_2-CH_2-O-N=O \xrightarrow[C_6H_6]{h\nu} \left[Ph-CH_2-\underset{\substack{|\\ NO}}{CH}-CH_2-CH_2-CH_2-OH \right] \longrightarrow \text{dimer} \tag{4}$$

Structure of the 4-nitroso-4-phenyl butanol and 4-nitroso-5-phenyl-pentanol can be rationalised by assuming a six membered cyclic transition state in the hydrogen transfer step. In case of 5-phenyl-1-pentylnitrite, none of the product is formed by a abstraction of hydrogen from benzylic carbon which would required a seven membered transitions state. In the same way, photolysis of 3-phenyl propyl nitrite ($C_6H_5-CH_2-CH_2-CH_2-O-NO$) did not yield any product corresponding to abstraction of benzylic hydrogen atom through five membered cyclic transitions state, even through abstraction of benzylic hydrogen should be highly favorable thermodynamically.

Intramolecular hydrogen abstraction by alkoxyl radicals is always acompanied 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.



$$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ O-N=O}}{C}}-CH_2-CH_2-\overset{\delta}{\underset{2^\circ}{CH_2}}-CH_3 \xrightarrow{h\nu} CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ OH}}{C}}-CH_2-CH_2-\underset{\substack{|\\ NO}}{CH}-CH_3 \tag{5}$$

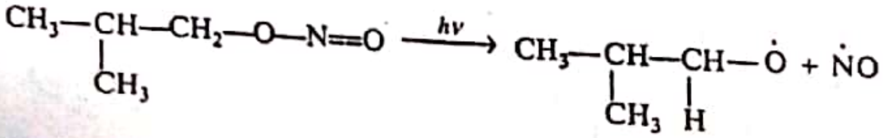


$$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ O-N=O}}{C}}-CH_2-CH_2-\overset{\delta}{\underset{1^\circ}{CH_3}} \xrightarrow{h\nu} CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ \dot{O}}}{C}}-CH_2-CH_2-CH_3 + \dot{N}O$$

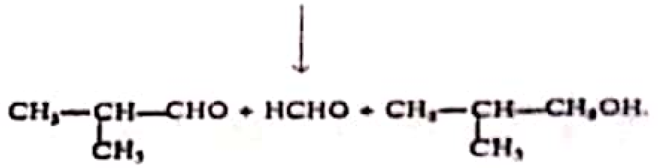
$$\downarrow$$

$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>C=O + CH_3-CH_2-CH_2-NO$$

Disproportionation reactions also occur in primary and secondary nitrites having no hydrogen on δ-carbon.

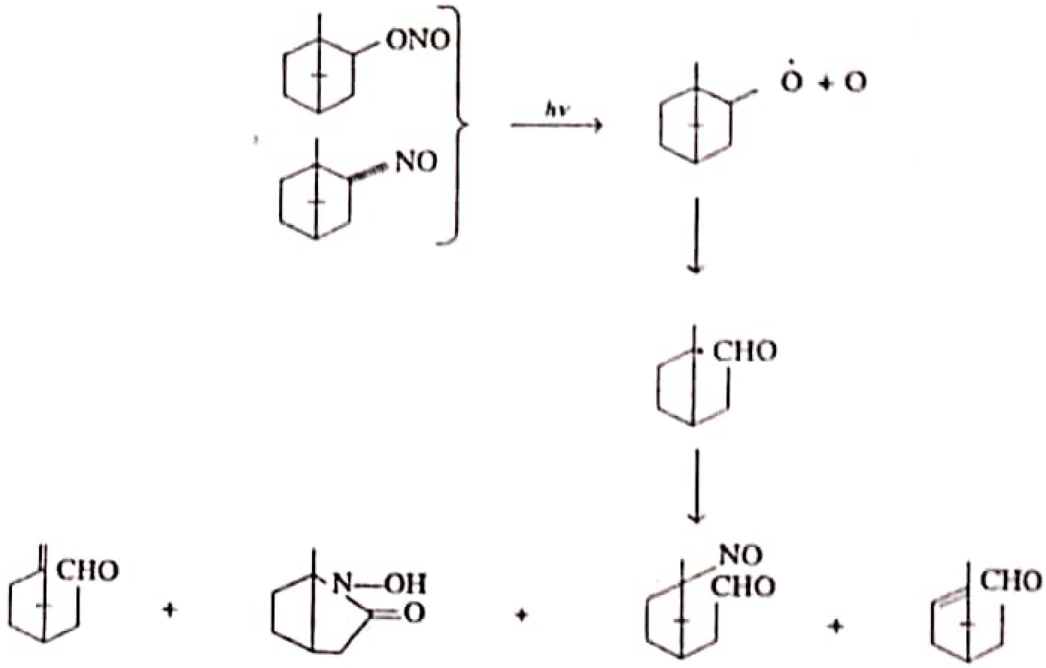


$$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-O-N=O \xrightarrow{h\nu} CH_3-\underset{\substack{|\\ CH_3}}{CH}-\underset{\substack{|\\ H}}{CH}-\dot{O} + \dot{N}O$$

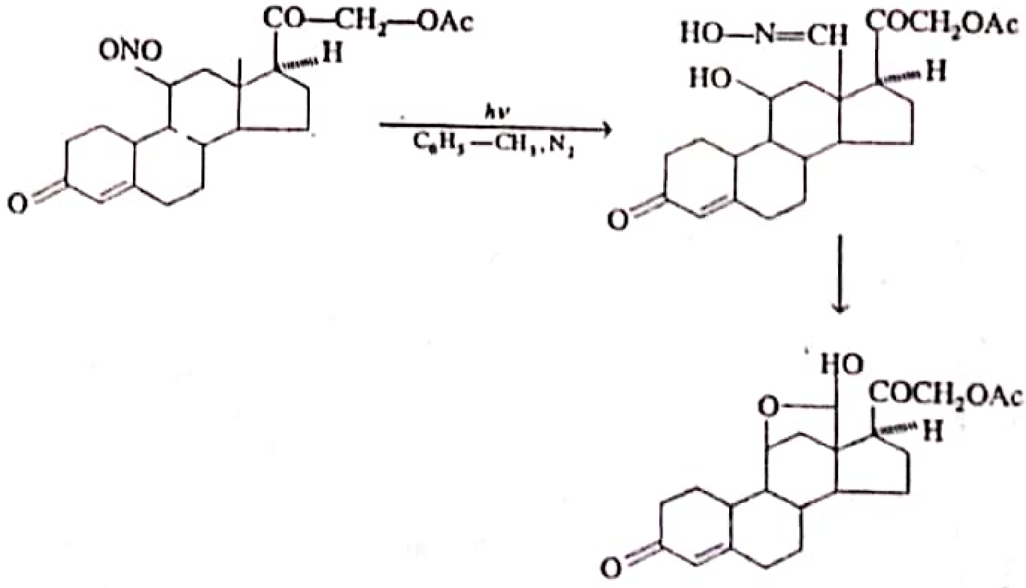


$$\xrightarrow{}\ \mathrm{CH_3{-}\underset{CH_3}{CH}{-}CHO + HCHO + CH_3{-}\underset{CH_3}{CH}{-}CH_2OH.}$$

dl-Bornyl and *dl*-isobornyl also undergo disproportionation rather than Barton reaction.

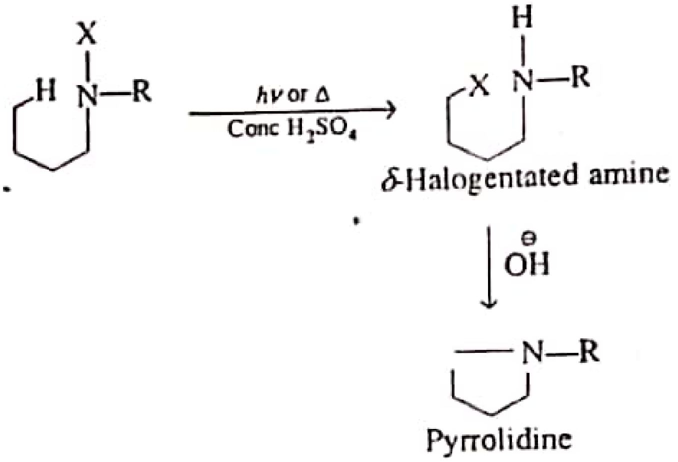


The reaction has found application predominantly in the chemistry of steroids mainly because of its great selectivity in the hydrogen-abstraction step. One of the first examples reported by Barton was the partial synthesis of aldosterone acetate.



11.3 THE HOFMANN-LOEFFLER-FREYTAG REACTION

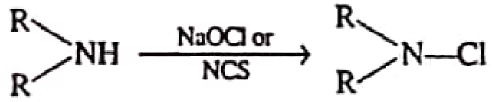
This reaction is given by N-haloamines having hydrogen on δ-carbon. The reaction is effected by warming a solution of the halogenated amine in strong acid (concentrated sulphuric acid or concentrated CF_3COOH) or by irradiation of the acid solution with ultraviolet light. The product of the reaction is the δ-halogenated amine. This product is not generally isolated in this reaction. This product on basification gives pyrrolidine and its derivatives.



(i)

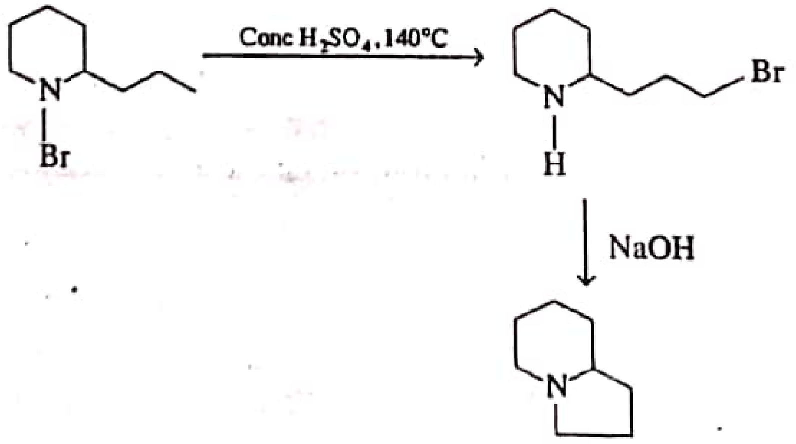
Both N-chloro and N-bromo amines are used as starting material but the N-chloroamines give better result. N-choloamines are obtained from primary and secondary amines by the action of sodium hypochlorites or N-chlorosuccinamide (NCS).

$$R\text{—}NH_2 \xrightarrow[NCS]{NaOCl\ or} R\text{—}NHCl \qquad (2)$$



$$R_2NH \xrightarrow[NCS]{NaOCl\ or} R_2N\text{—}Cl \qquad (3)$$

The first example of this reaction was reported by A.W. Hofmann (equation-4).



δ-conecceine

(4)

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