

# PHOTOCHEMISTRY 02

## Photochemistry of Olefines

Alkenes by absorption of light activated to higher energy singlet and triplet state and undergoes chemical reaction.

These reactions are mainly :-

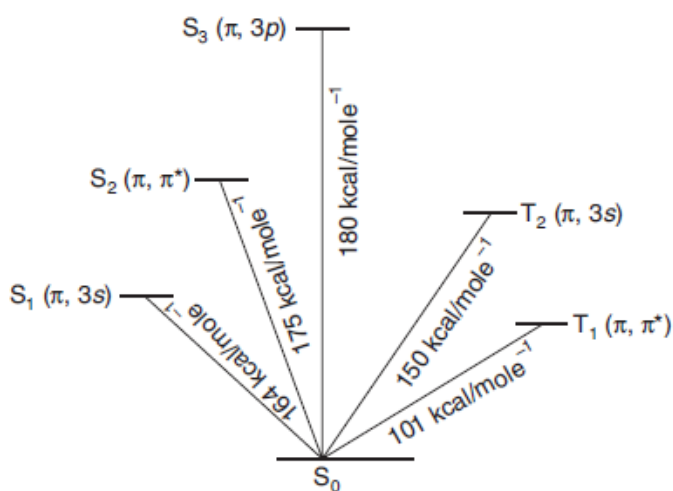
1. Cis-trans isomerization
2. Dimerisation and
3. Cycloaddition reactions

### Cis-trans isomerization:-

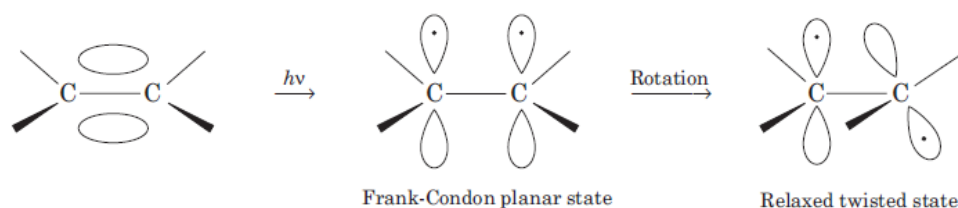
The most commonly observed photochemical reaction of alkenes is cis-trans isomerization which can occur by both direct and sensitized irradiation.

This isomerization reaction is usually associated with  $\pi - \pi^*$  excited states.

### Different electronic states of ethylene



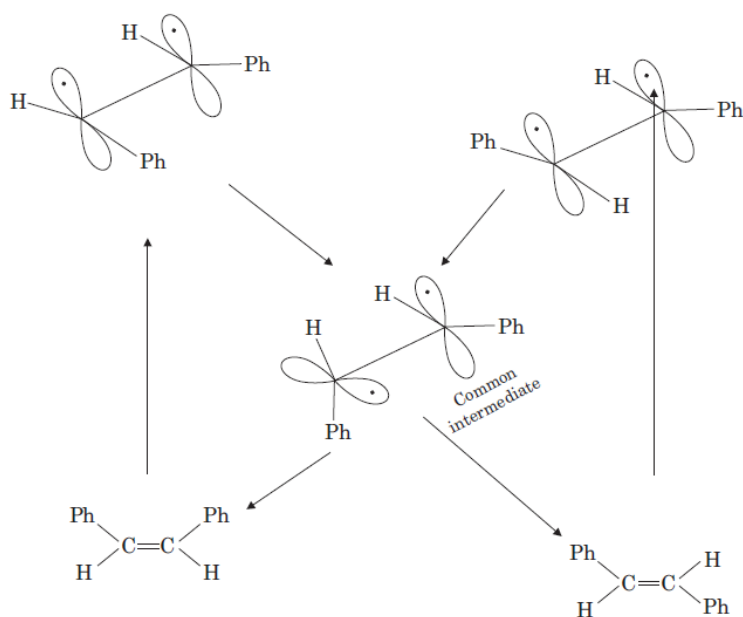
Excitation of a planar alkene like ethylene results initially in the formation of planar excited state molecule according to the Franck-Condon principle. The initially formed planar group—methylene in the case of ethylene—through  $90^\circ$  around the central bond to give the lowest energy conformation 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.



Formation of relaxed twisted state (orthogonal state)

## Cis-Trans Isomerisation of Alkenes by Direct Irradiation

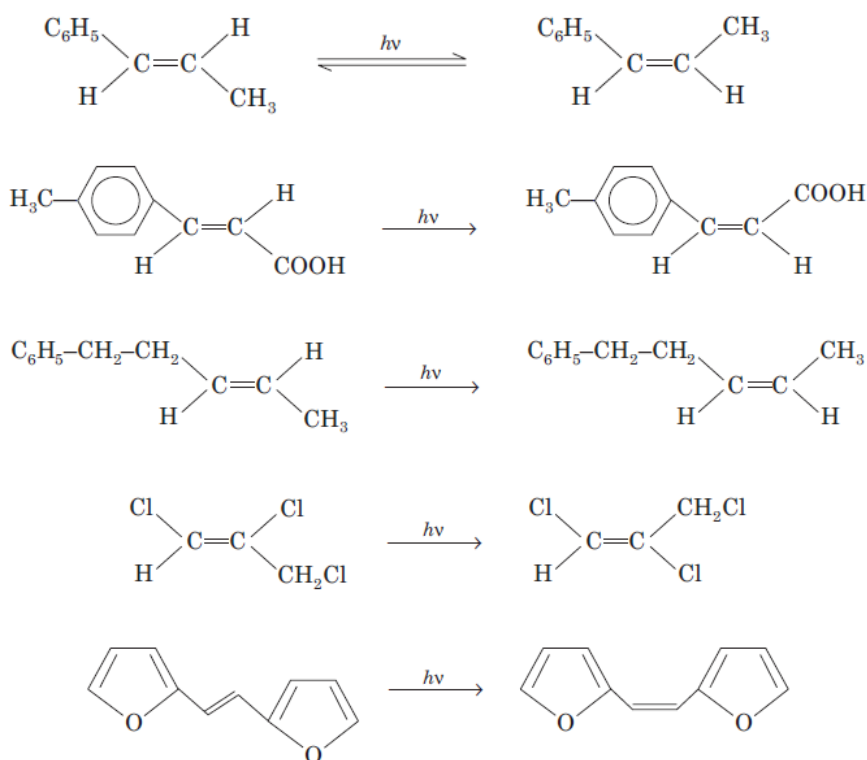
The most common substrate for isomerisation is the **stilbenes**.



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 10.3. 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 ( $\epsilon_{\text{max trans}} = 16300$ ) than does the *cis* form ( $\epsilon_{\text{max cis}} = 2880$ ) and consequently the *trans* isomer is converted almost completely into the *cis*.

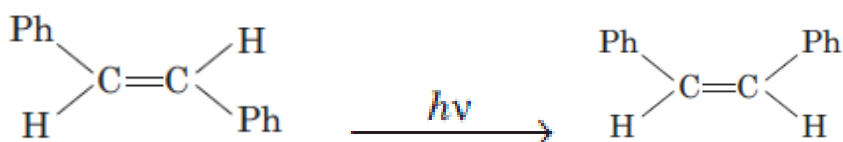
The synthetic utility value of *trans-cis* isomerisation lies in the fact that the more stable alkene can be readily converted into the less stable alkene.

Examples:



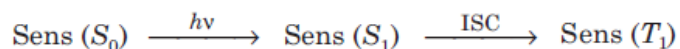
### Summary of Direct irradiation of alkenes ----

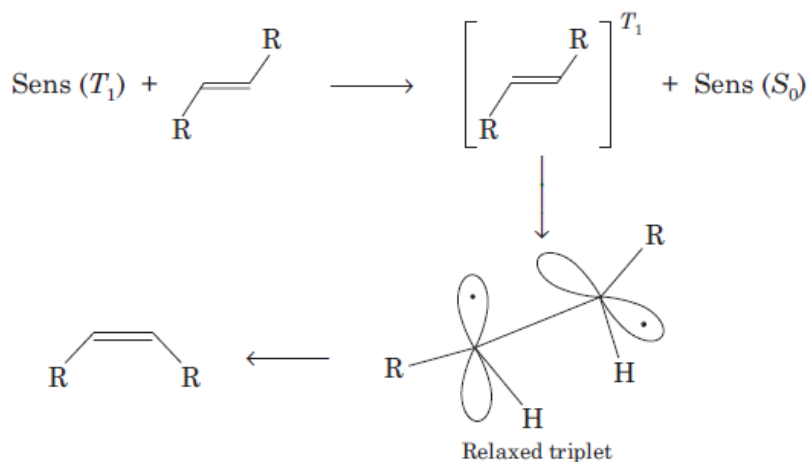
- Direct irradiation of simple alkenes is difficult.
- Most common substrate is stilbene
- Irradiation of either cis or trans stilbene at 313 nm results in the formation of 93% cis and 7% trans stilbene



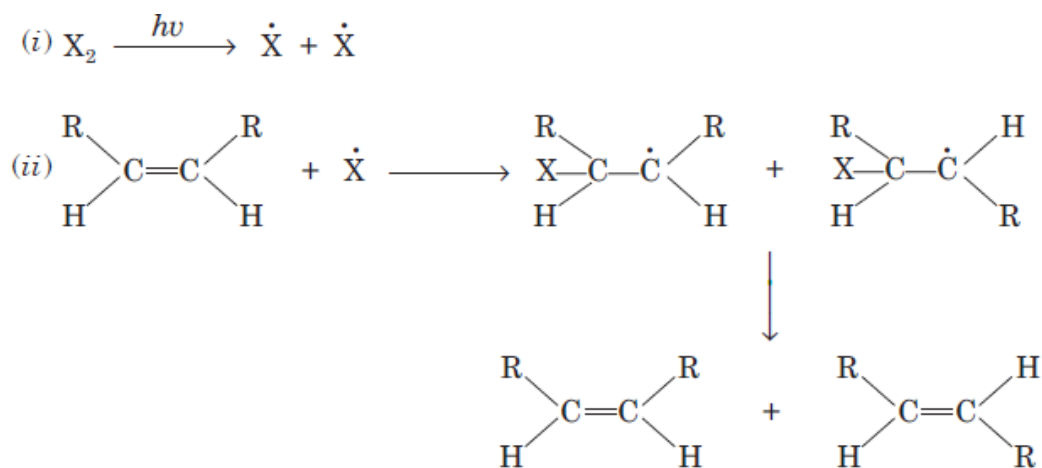
### Sensitised cis-trans isomerisation

Sensitised *cis-trans* isomerisation of an alkene can be brought about by the use of a triplet sensitizer such as ketone. The sensitised isomerisation of stilbene is a typical example.



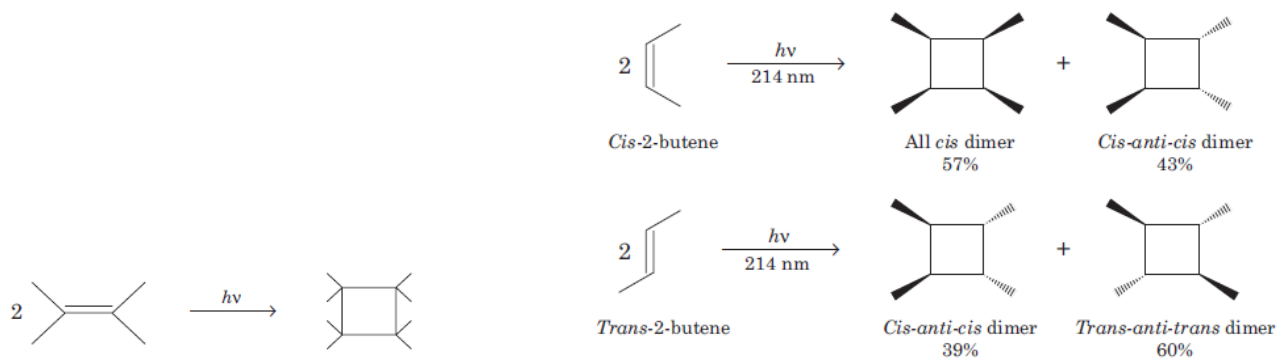


Sometimes photochemical *cis-trans* isomerisation may also take place in the presence of halogens. It appears that under these conditions there is a photochemical product of halogen atoms which adds to the alkene yielding a radical. Elimination of halogen from this radical yields a constant ratio of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

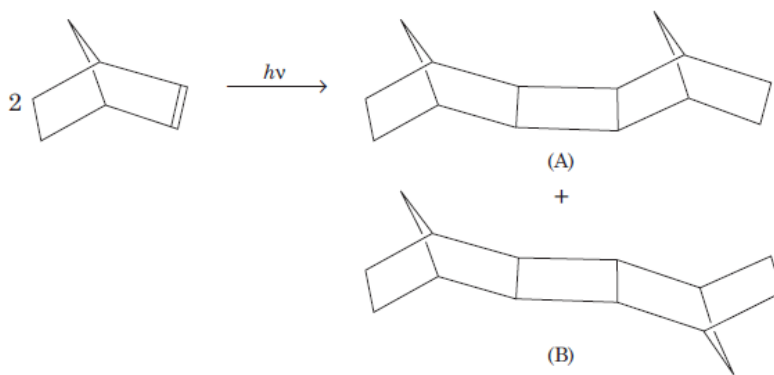


## DIMERISATION OF ALKENES

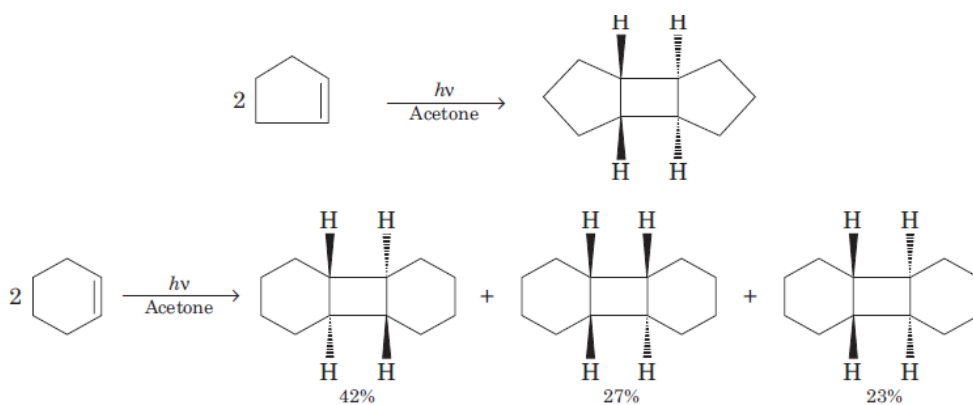
An alkene in its  $S_1$  or  $T_1$  state reacts with either the same (photodimerisation) or a different photocycloaddition) alkene in the ground state to produce a cyclobutane derivative.



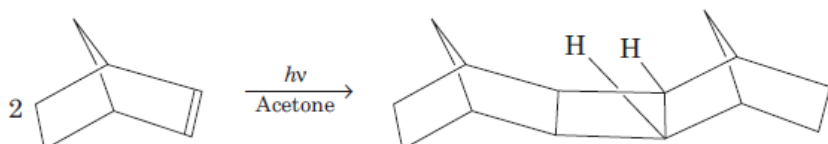
Cyclohexene also dimerises, yielding a mixture of dimeric products while norbornene affords two dimers (A) and (B) in a ratio of 1 : > 10.



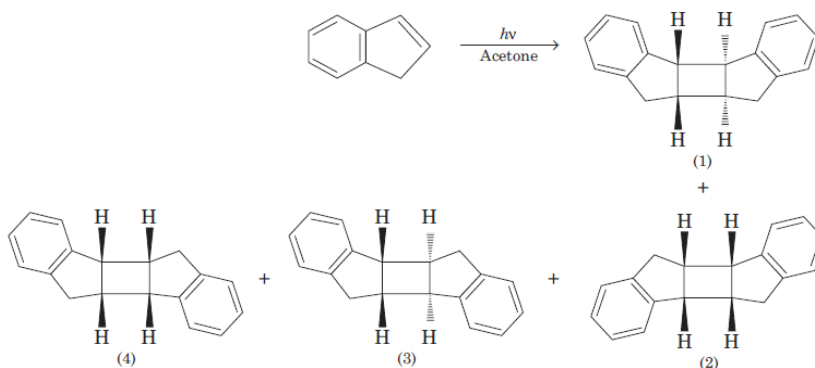
The dimerisation of alkenes and cycloalkenes is best sensitised by aliphatic ketones. Oxitane are formed from aromatic ketones.



Norbornene can also be made to dimerise on sensitisation and that is preferred for the formation of the *exo-trans-endo* dimer.

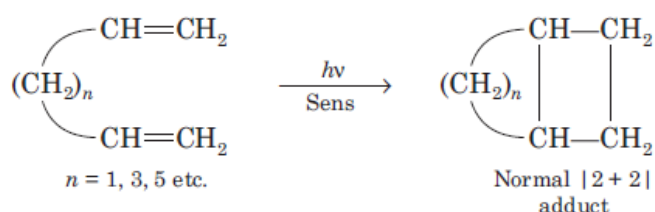


Four dimers that differ in regio and stereochemistry are formed by photodimerisation of indene.

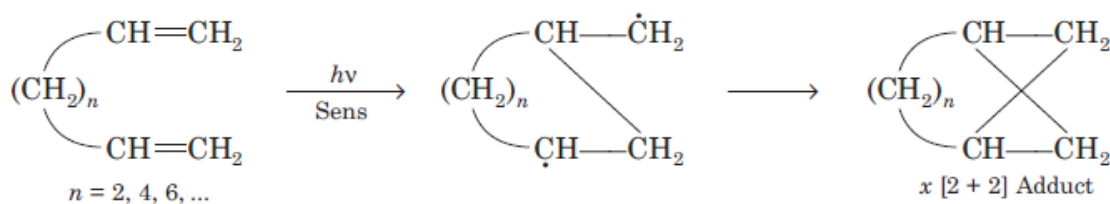


## Intramolecular Dimerisation

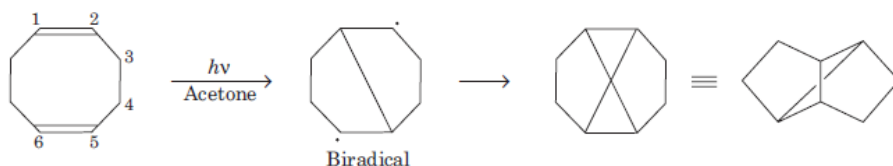
The photochemistry of nonconjugated dienes with isolated double bonds resembles with simple alkenes. Such type of alkenes give intramolecular | 2 + 2 | cycloaddition reactions to give bicyclic products. The products of sensitised intramolecular cycloadditions depend on the number of —CH<sub>2</sub>— groups between the two double bonds. If the number of intervening groups is odd, *e.g.*, 1, 4-pentadiene or 1, 6-pentadiene, the major product results from a normal | 2 + 2 | cycloaddition.



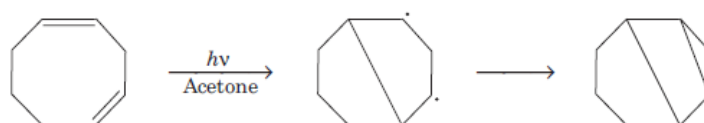
If the number  $n$  is even *e.g.*, 1, 5-hexadiene, the major product is formed *via* a “cross”, *i.e.*,  $x [2 + 2]$  cycloaddition to form two crossed  $\sigma$  (*sigma*) bonds.



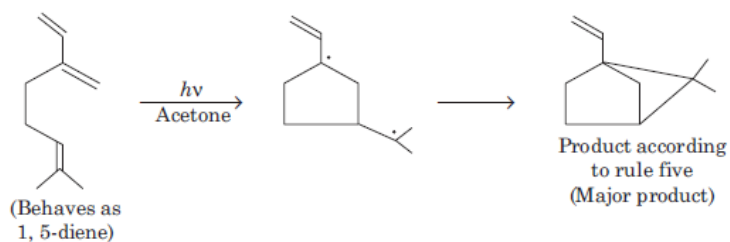
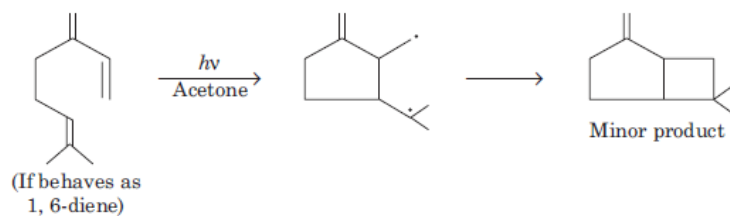
This feature is even more prominent in cyclic dienes, *e.g.*,  $n = m = 2$  (1, 5-cyclooctadiene) in which  $x [2 + 2]$  cycloadduct is the only product.



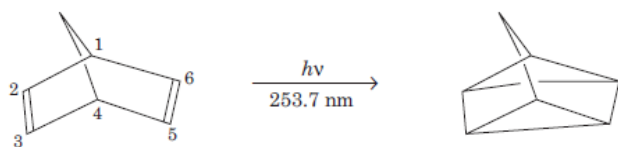
If  $n = 1$  and  $m = 3$  or *vice-versa* (*i.e.*, 1, 4-cyclooctadiene), the normal | 2 + 2 | cycloadduct is formed.



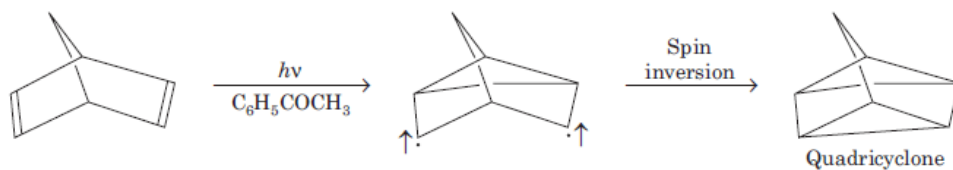
The photoreaction of 1, 5-hexadiene from the  $T_1$  state follows the rule of **five** which states that if triplet cyclisation can lead to rings of different sizes, the one formed by 1, 5 addition is preferred kinetically. If there is several possibilities for 1, 5 addition leading to different biradicals, the most stable one is formed.



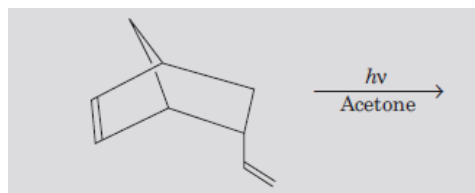
## | 2 + 2 | cycloaddition by direct irradiation



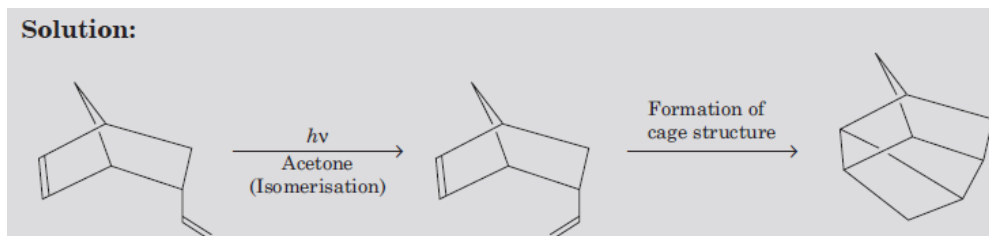
In the presence of sensitizer product formation takes place by triplet state.



Complete the following cycloaddition reaction:



**Solution:**



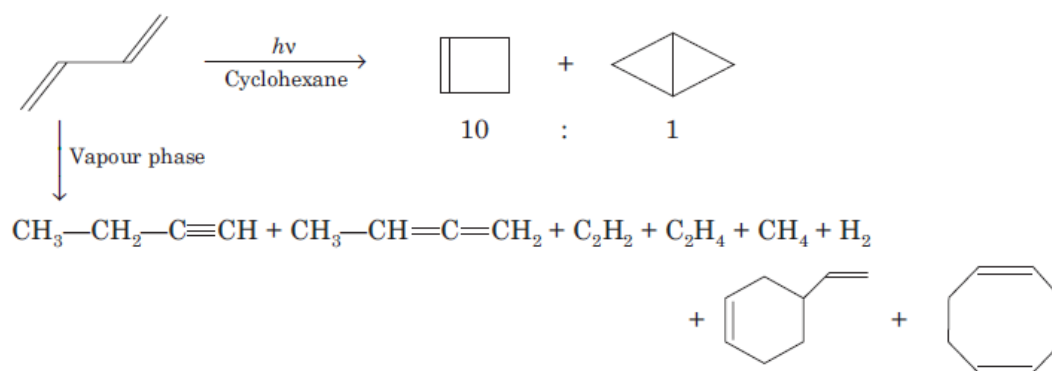
## PHOTOCHEMISTRY OF CONJUGATED DIENES

Conjugated dienes can give the following type of photochemical reactions:

- (i) *Cis-trans* isomerisation
- (ii) Sigmatropic shift
- (iii) Disrotatory electrocyclic ring closure
- (iv) Intramolecular  $x [2 + 2]$  cycloaddition

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.

### BUTADIEN



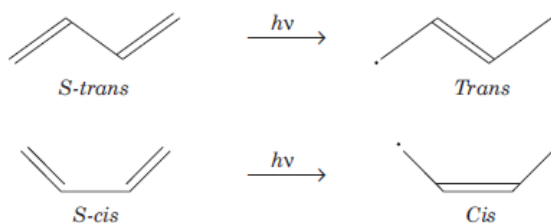
### Photochemistry of Conjugated Dienes in Solution

#### Intramolecular $x[2 + 2]$ Cycloaddition Reaction

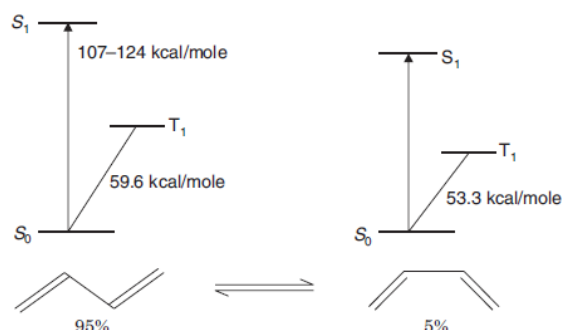
1, 3-Butadiene exists in solution as a rapidly equilibrating mixture of *S-transoid* (95%) and *S-cisoid* (5%) conformers.

Irradiation of butadiene promotes an electron from HOMO to LUMO ( $\psi_2 \rightarrow \psi_3^*$ ) which results in the increased bonding

between C-2 and C-3.

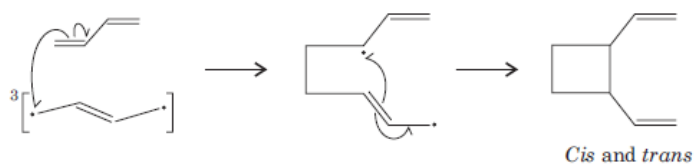


#### The energy of the excited states of butadienes:





when acetophenone is the sensitiser,



In benzil sensitised reaction,

