

Symmetry allowed reactions proceed smoothly on heating.  
 Symmetry forbidden reactions proceed usually on photolysis. Three main families of Pericyclic reactions are - Electrocyclic reaction, Cycloaddition reaction and Sigmatropic reactions. These reactions are very important because -

- ① They create new C-C  $\sigma$  bonds, and hence are used for Carbon skeleton construction.
- ② Reactions are independent of external influences such as - effect of solvent, change of concentration, catalysis and side reactions.
- ③ Stereospecificity of these reactions is very high.

II - Lect. Dr. P.K. Shams. - Pericyclic Reaction 4-2008 10-4-20

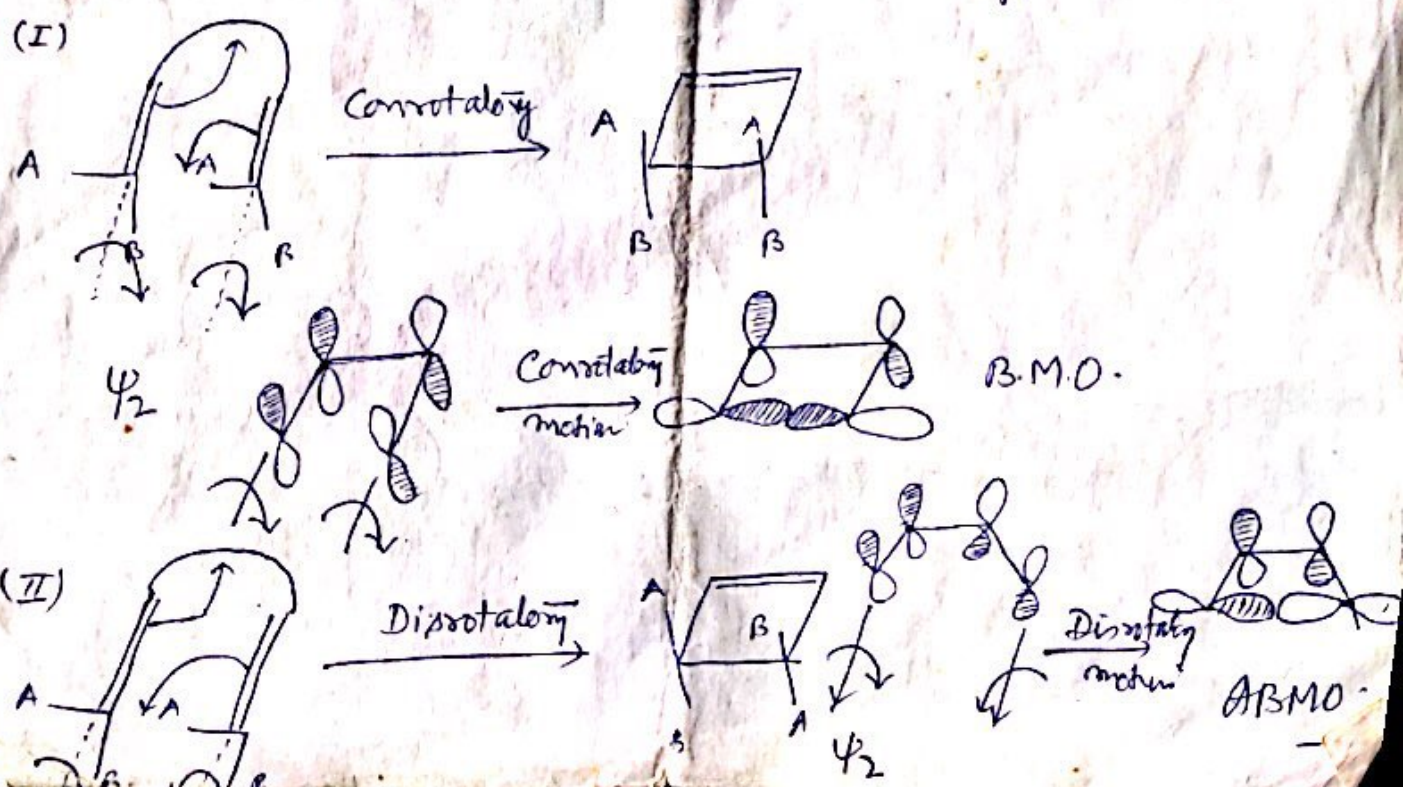
③ Orbital Symmetry or HOMO Theory or Frontier Orbital Approach.

Let us examine - Thermal Cyclization of 1,3 Butadiene.



The above electrocyclic reaction involving conversion of 2  $\pi$  bonds into 1  $\sigma$  and 1  $\pi$  bond. The reaction is completely stereospecific. Substituents on bond which breaks in cyclobutane must rotate to come into developing plane of butadiene molecule. There are two rotational ways in which this change can occur -

- ① Conrotatory motion - when bonds rotate in the same direction
- ② Disrotatory motion - when bonds rotate in opposite direction.

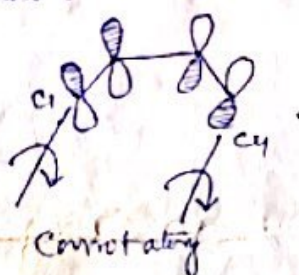


## Relationship between Stereochemistry and Orbital Symmetry

In cyclisation  $2\pi$  electrons of polyene form the new  $\sigma$  bond of cycloalkene. We have to emphasize on Highest Occupied Molecular Orbital (HOMO) of the polyene. Electrons in this orbital are the valency electrons of the molecule, which are least tightly held and easily pushed about during a reaction.

Let us start with thermal cyclisation of a di-substituted butadiene  $R-C_1=C_2-C_3=C_4-R$ . The HOMO of conjugated diene is  $\psi_2$ , it is the electron in this orbital, which will form the  $\sigma$  bond, that closes the ring.

Bond formation requires overlap. In this case  $C_1$  and  $C_4$  of the conjugated diene, should overlap, which are the front carbons.

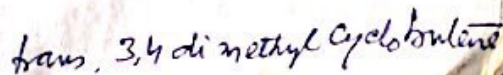
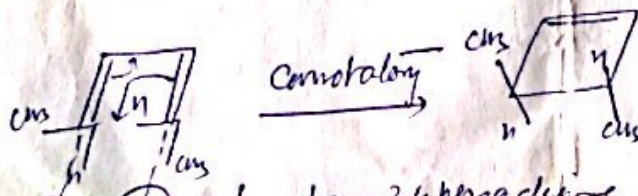
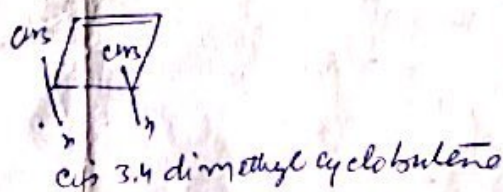
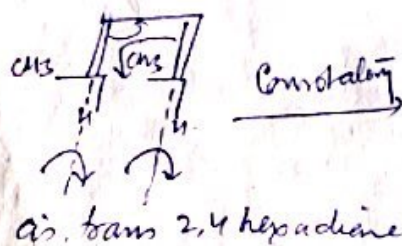


To bring these lobes into position for overlap, there must be rotation about two bonds, which can participate in either of the two ways -

- ① Conrotatory motion
- ② Disrotatory motion

In this case Conrotatory motion brings about the lobes of same phase together and a bond is formed. Disrotatory motion, on the other hand, brings together the lobes of opposite phase, leading to the anti bonding and repulsive situation.

It is due to Conrotatory motion that desired stereochemistry is met.



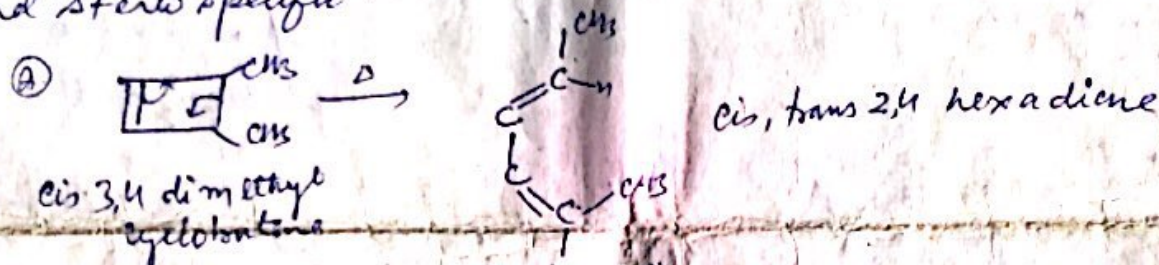


1,3,5 hexatriene      1,3 Cyclohexadiene



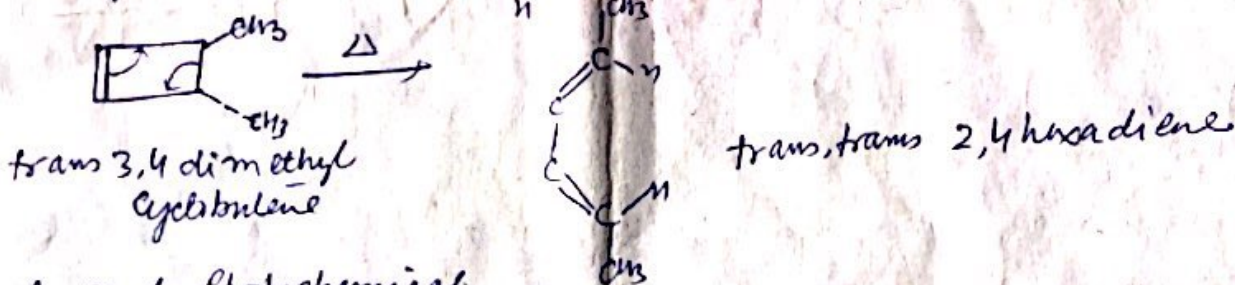
Let us consider the interconversion of 3,4 dimethyl cyclobutene and 2,4 hexadiene. The cyclobutene molecule exists in two forms cis and trans while hexadiene, exists in three forms cis, cis, trans and trans, trans. cis-cyclobutene yields only one of the three isomeric dienes. The trans cyclobutene gives a different isomer.

Thus the reaction is completely stereospecific and stereoselective. Similarly, the interconversion of the corresponding dimethyl cyclohexadienes and 2,4,6 octadienes are also stereoselective and stereospecific.



cis 3,4 dimethyl cyclobutene

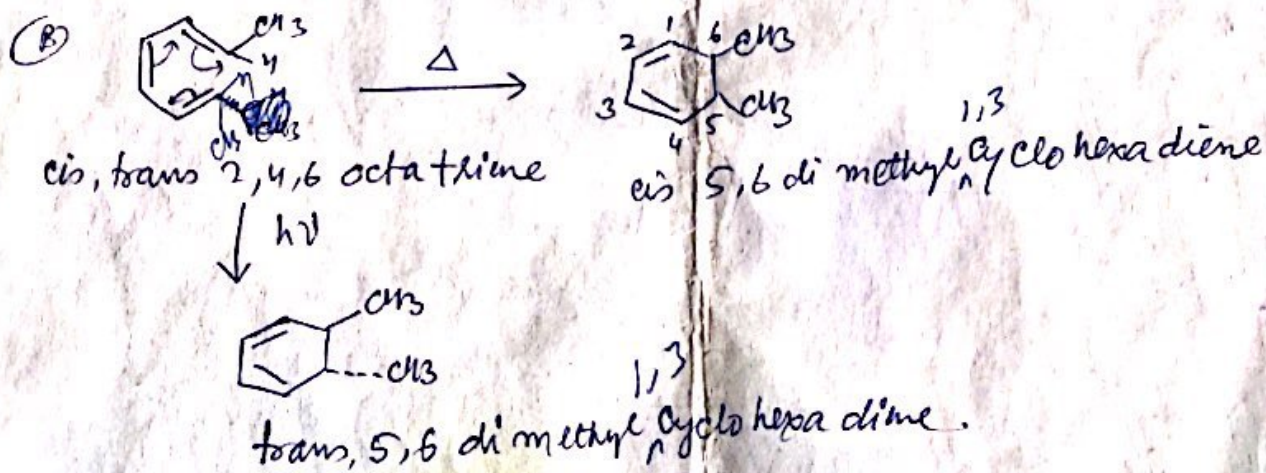
cis, trans 2,4 hexadiene



trans 3,4 dimethyl cyclobutene

trans, trans 2,4 hexadiene

3) Thermal and photochemical reactions differ in stereochemistry.



cis, trans 2,4,6 octatriene

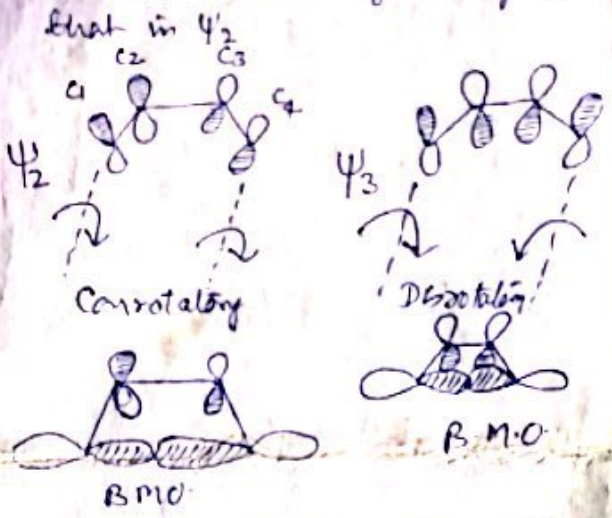
cis 5,6 dimethyl cyclohexadiene

trans 5,6 dimethyl cyclohexadiene

Stereochemical Aspects in Photochemical reactions.

It can account for the opposite stereochemistry in photochemical reactions. On absorption of light, butadiene molecule gets excited and during the process one electron from  $\psi_2$  gets elevated to  $\psi_3$ . Now HOMO would be  $\psi_3$  instead of  $\psi_2$  and it is the electron present in  $\psi_3$  which has to be considered.

In  $\psi_3$  relative symmetry of terminal carbons is opposite to that in  $\psi_2$ .



Now it is disrotatory motion that brings together the lobes of same phase to form BMO.

Thus stereochemistry gets reversed in photochemical reactions.

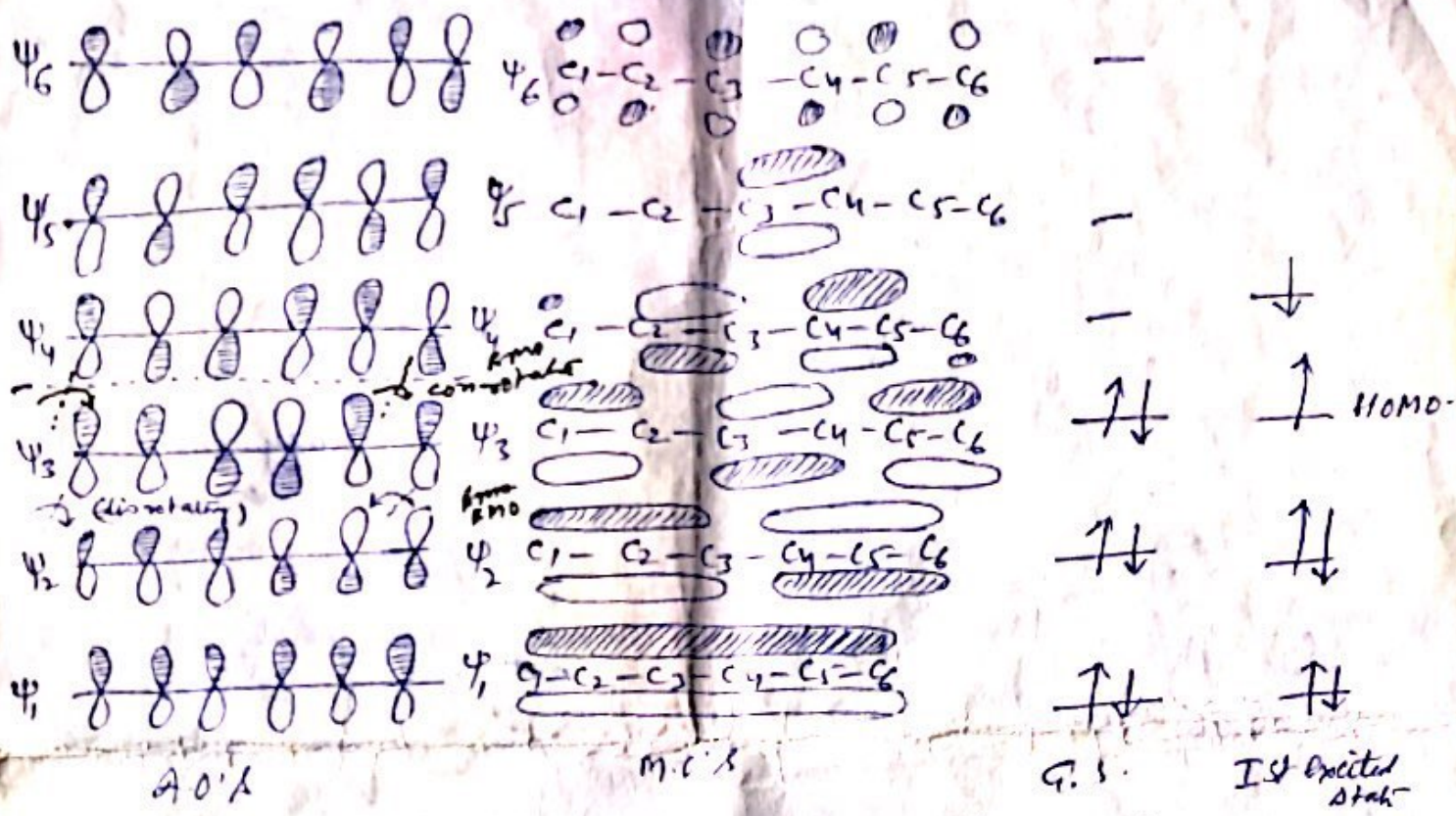
The exact stereochemistry depends on two things -

- ① No. of double bonds present in a polyene.
- ② Whether the reaction is thermal or photochemically induced one

It is due to orbital symmetry approach that these facts were accounted for much earlier even before their discovery by Woodward and Hoffmann.

Let us now consider, the stereochemistry of photochemical reactions of hexatriene.

P.T.O.

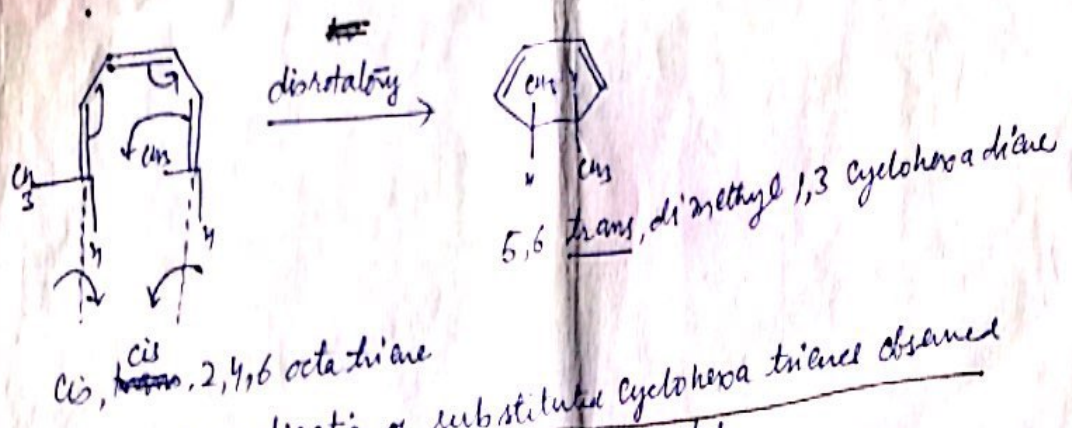
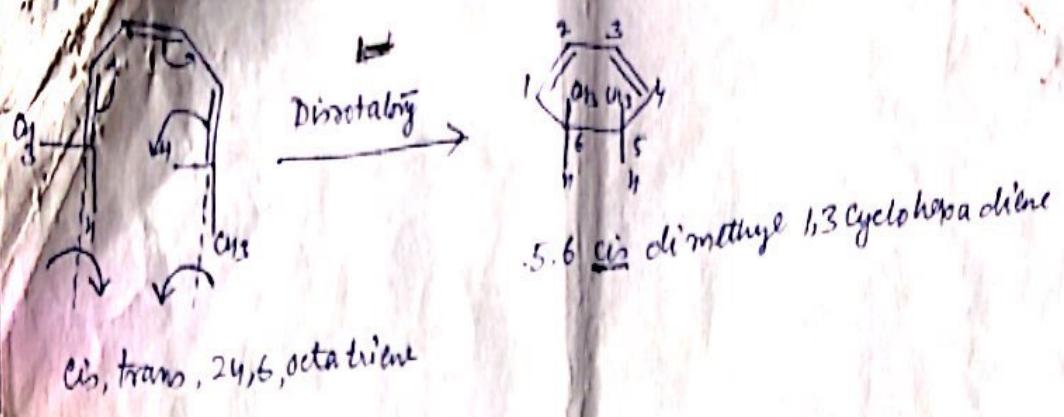


1,3,5 hexatriene - Configuration of  $\pi$  electrons in ground and first excited state

HOMO for ground state of hexatriene is  $\psi_3$ , if we compare it with HOMO for butadiene, which is  $\psi_2$ , we find that relative symmetry of both the terminal carbons is opposite in the two cases.

for Hexatriene it is disrotatory motion that brings about the bonding situation and gives rise to observed stereochemistry.

In the excited state (Photochemical reactions) the HOMO would be  $\psi_4$  in hexatriene, having the configuration of terminal carbons just reverse to that of  $\psi_3$ . Thus it would be the conrotatory motion that will bring about bonding situation and would give observed stereochemistry.



Thermal cyclization of substituted cyclohexa trienes observed  
Stereochemistry indicates disrotatory motion.

In photochemical excitations, irradiation results in promotion of an electron from  $\psi_3 \xrightarrow{h\nu} \psi_4$  i.e. orbital of next higher energy level. and the ground state LUMO ( $\psi_4$ ) now becomes HOMO. Under such conditions, conrotatory motion brings about the bonding situation.

Woodward Rules for Electrocyclic Reactions

	No. of electrons	Reaction	Motion	Result
(1)	$4\pi$	Thermal	Conrotatory	BMO
(2)	$4\pi$	Photochemical	disrotatory	BMO
(3)	$(4n+2)\pi$	Thermal	disrotatory	BMO
(4)	$(4n+2)\pi$	Photochemical	Conrotatory	BMO