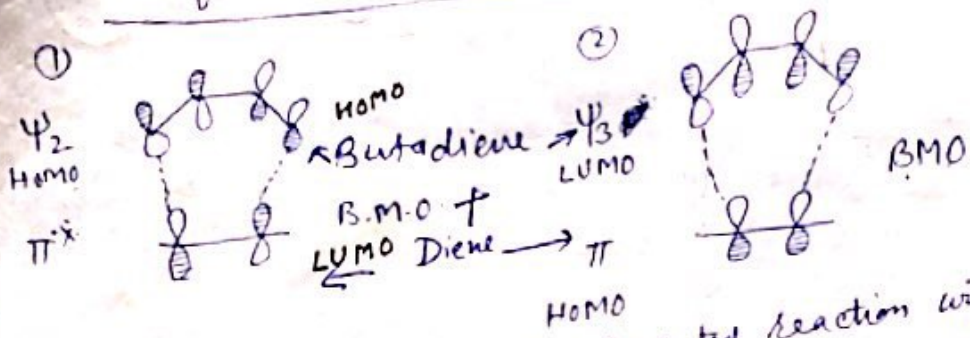
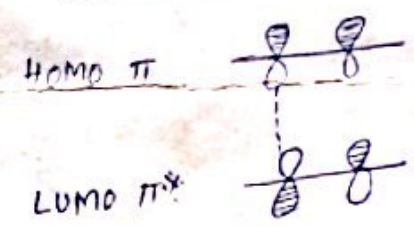


Cycloaddition Reaction

M.Sc. II Ind Sem. H-2008  
 In cycloaddition, two components are commonly involved and the feasibility of a particular process will be determined, whether overlap can take place between HOMO of one component and LUMO of other component.  
 Then for a diene and monoene component. (CYCLO-ADDITION Reactions.)



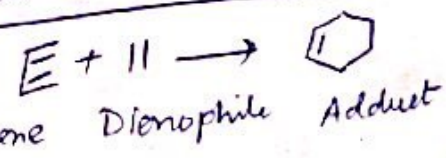
The situation is bonding and a concerted reaction will take place. It hardly matters which component will have HOMO or LUMO. The cycloaddition is said to be symmetry allowed reaction.  
 For two monoene components:



No bonding takes place. The situation is nonbonding and concerted reaction will not take place. This cycloaddition is said to be symmetry forbidden.

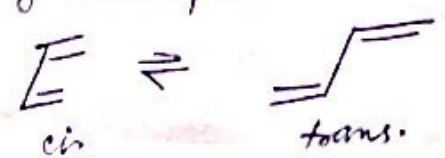
This is a general situation for thermal concerted reaction that those involving  $(4\pi + 2\pi)$  systems proceed smoothly e.g. Diels-Alder reaction of alkenes do not occur.

Diels-Alder Reaction



The reaction occurs very easily, spontaneously and requires moderate application of heat. There are several aspects of stereochemistry of Diels-Alder reaction.

① The diene must be in cis conformation, which permits the ends of the conjugated system, to reach the doubly bonded carbons of dienophile.

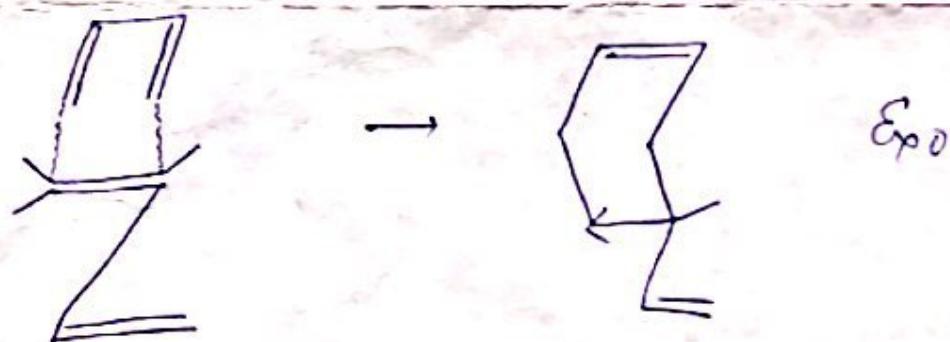
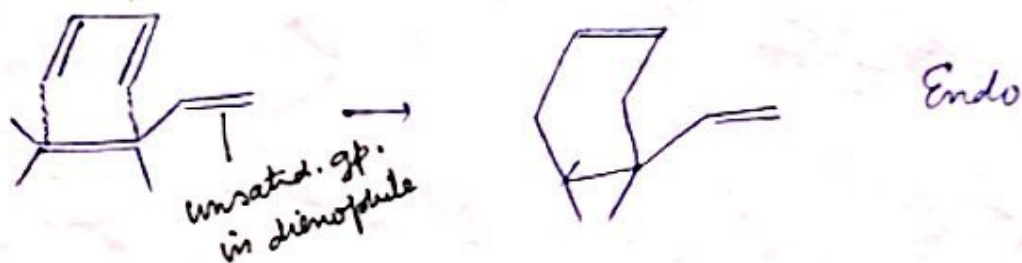


(2) The addition of alkene should be *Sym*.



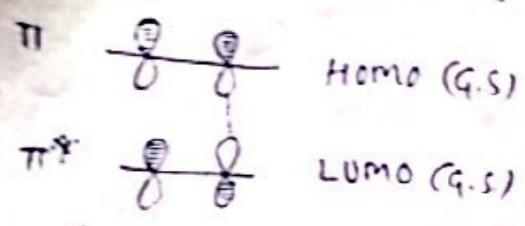
This stereoselectivity evidences that Diels-Alder reaction is a concerted one. i.e. both the new bonds are formed in the same transition state.

(3) Finally - Diels-Alder reaction takes place in Endo, rather than Exo sense. i.e. any other unsaturated group in the dienophile tends to lie near the developing double bond in the diene species.



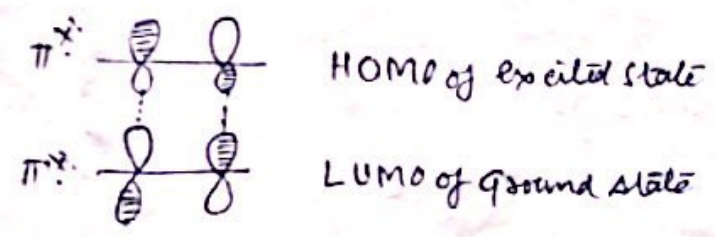
In cyclisations, two new  $\sigma$  bonds are formed by use of  $\pi$  electrons of the reactants. Of thermal cycloadditions,  $(4+2)$  is easy and  $(2+2)$  is difficult. Of  $(2+2)$  cycloadditions, the thermal reaction is difficult, and the photochemical reaction is easy.

to consider a thermal cyclisation of  $(2+2)$  in dimerisation of ethylene <sup>(12)</sup>  
 involving overlap between HOMO  $\pi$  of one molecule with the  
 LUMO  $\pi^*$  of the other. Both  $\pi$  and  $\pi^*$  are of opposite symmetry.  
 Interaction is antibonding and repulsive, and concerted reaction does not occur.



Symmetry forbidden  
 (2+2) Thermal Cyclisation

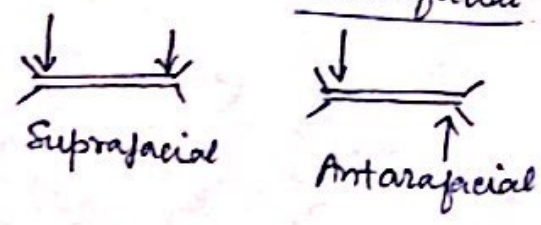
Photochemical (2+2) cycloadditions are  
 symmetry allowed. It involves overlap of  
 HOMO  $\pi^*$  of an excited molecule with  
 the LUMO  $\pi^*$  of a ground state molecule.



Symmetry allowed (2+2) Photochemical  
 cycloadditions.

In a concerted reaction, both the bonds  
 to a component are being formed or broken  
 on the same face, the process is said to be

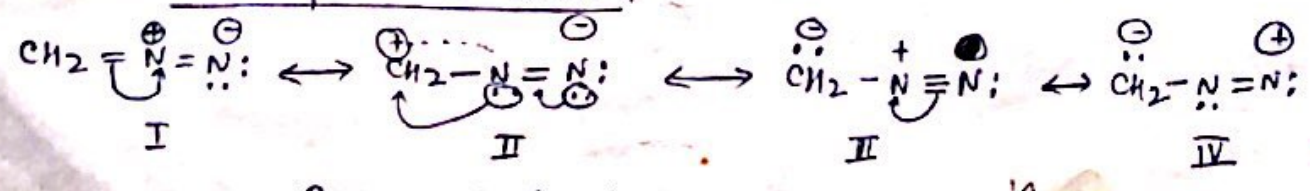
suprafacial, if the bonds are being formed on opposite faces, the  
 process is called antarafacial



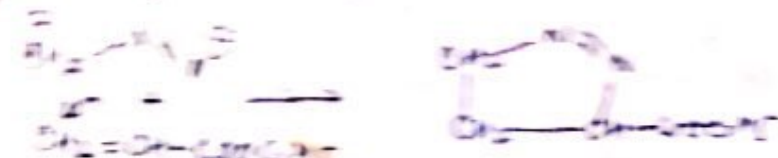
Thus Diels-Alder reaction is  
 suprafacial with respect to both the  
 components. Cycloadditions are reversible  
 The cycloreversions follow same symmetry  
 rules as cycloaddition.

② 1,3 di Polar addition

The  $4\pi$  component in a  $(4+2)\pi$  electron system need not to be  
 either four atom system or it should involve carbon atoms only  
 so long as symmetry requirements can be fulfilled. The most  
 common of these non-dienic  $4\pi$  electron system, involve three  
 atoms and have one or more dipolar canonical structures. Hence  
 the term 1,3 di polar addition.



The reaction is type 2 which is from electrophile to the double bond of the diene. The reaction proceeds via formation of a transition state for the displacement.



Diene reaction

The only difference between the 1,4-addition and Diels Alder reaction is that the former involves less symmetrical and more polar transition state.

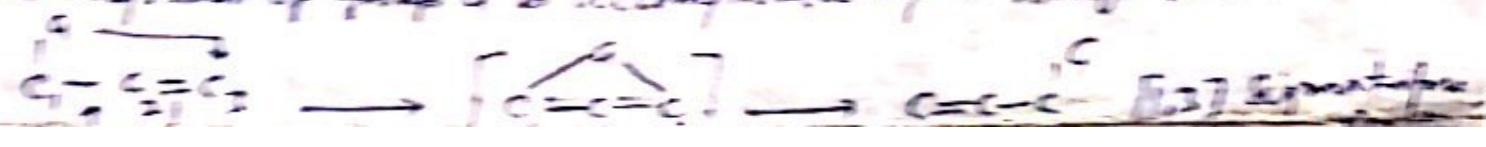
(3) Sigmatropic Rearrangement

A concerted reaction of the type in which

a group migrates with its sigma bond, within a pi framework of a polyene is termed Sigmatropic Rearrangement.



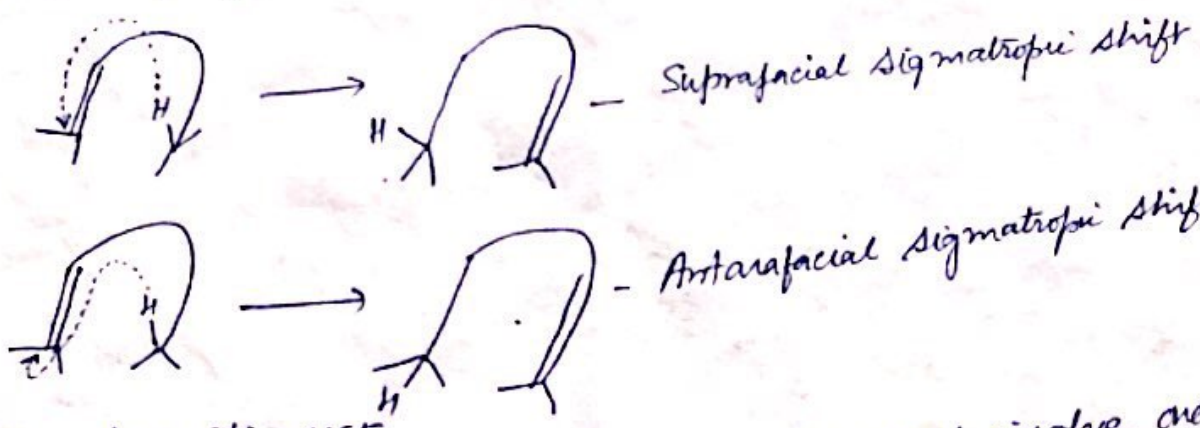
The migration of group C is accompanied by a shift in double bond



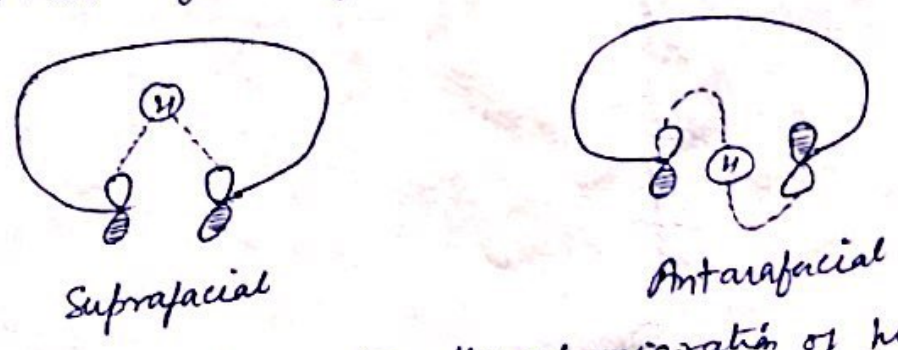
In the transition state of a sigmatropic reaction, the migrating group is bonded to both migration origin and migration terminus. The nature of this transition state is very important.

Let us now consider the simplest case in sigmatropic reactions -

① migration of hydrogen. Stereochemically this shift can be of two types, suprafacial or antarafacial



In the transition state a three center bond is required and this must involve overlap between '1s' orbital of hydrogen and lobes of 'p' orbital of carbon atom. Whether a suprafacial or antarafacial shift is allowed, depends upon the symmetry of these terminal orbitals.



Symmetry allowed migration of hydrogen

A sigmatropic rearrangement depends on geometry of the system as well as symmetry requirements also.

In [1,3] and [1,5] antarafacial shifts will be extremely difficult since, they would require pi framework to be twisted far from planarity, which is required for delocalisation. Practically [1,3] and [1,5] sigmatropic reactions are limited