

Pericyclic Reactions

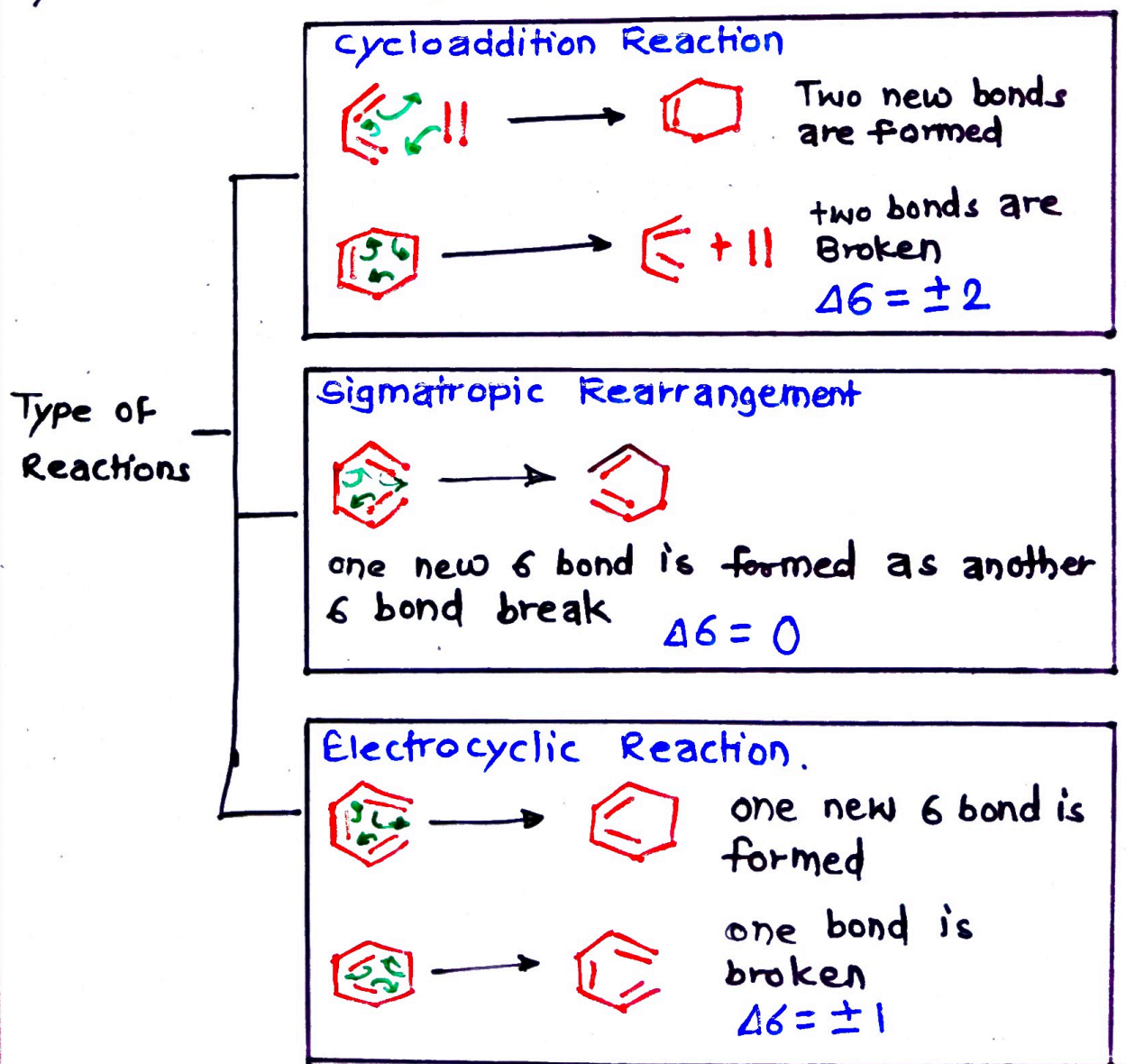


Introduction:-

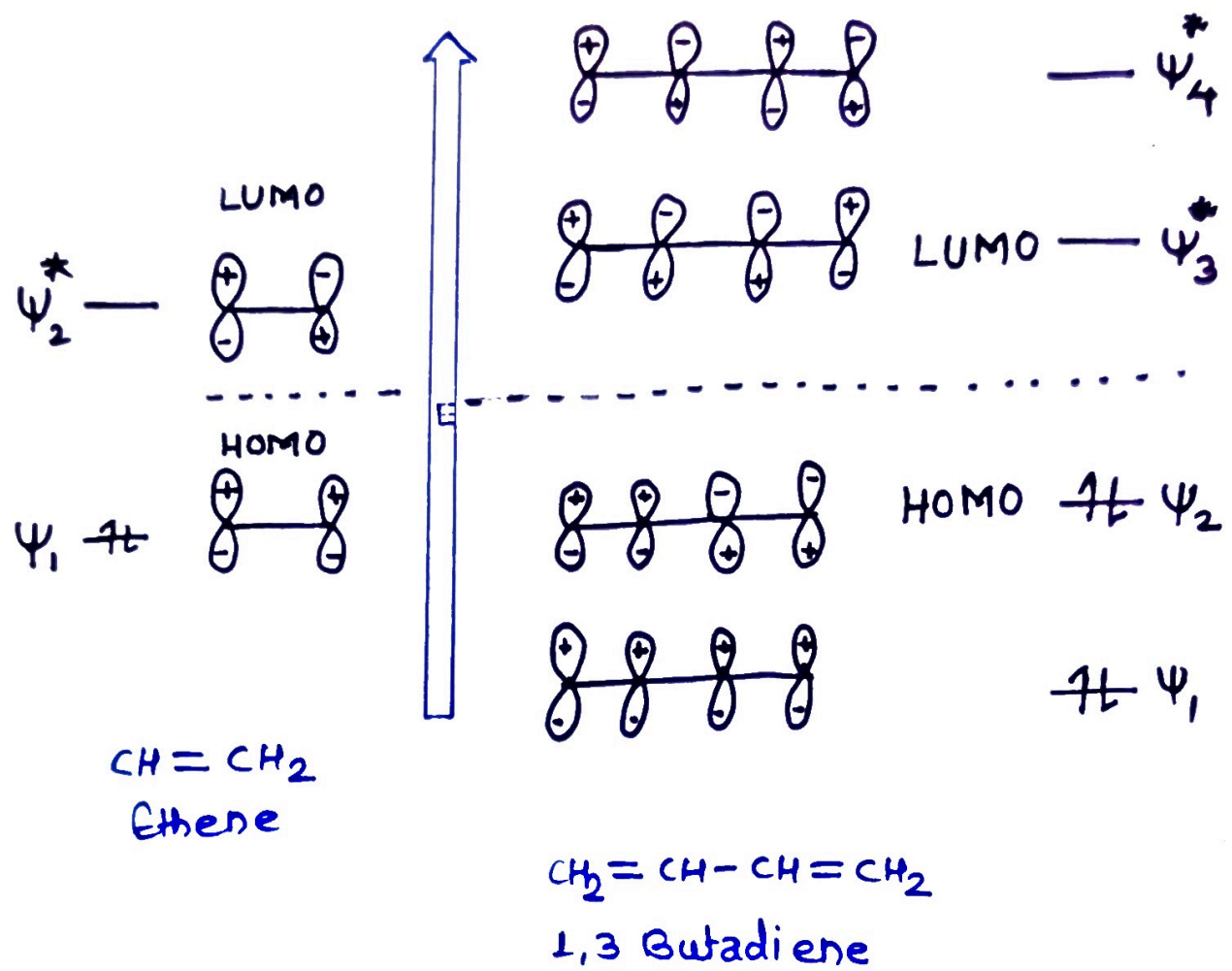
- * These reactions do not involve the intermediate formation of either ions or radicals.
- * These reactions are not affected by polar reagents, solvent changes, radical initiators etc.
- * They are initiated by heat (thermolysis) or light (photolysis) and are highly stereospecific.
- * The most remarkable observation about this reaction is thermal and photochemical processes yield product with different stereochemistry.

Classification:-

The types of pericyclic reactions are distinguished by the number of σ bond made or broken.



* The phase of orbitals of ethene, 1,3-butadiene in the ground state are presented below, since only orbitals of the same phase will overlap to result in bonding. The orbitals of the different phase lead to repulsive anti-bonding situation.



HOMO - Highest occupied molecular orbital
 LUMO - Lowest unoccupied molecular orbitals.

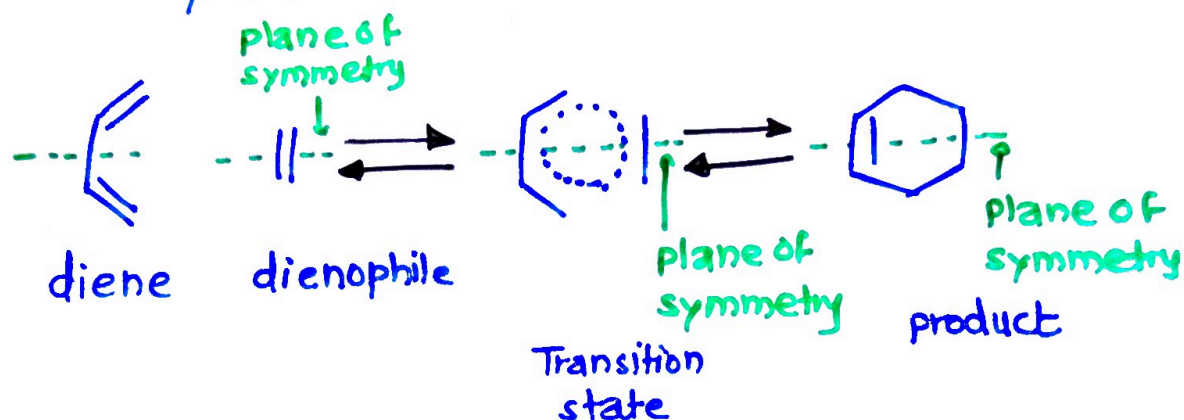
conservation of molecular orbital symmetry :-

* Woodward and Hoffmann in 1965 pointed out that symmetry of the molecular orbitals which participate in the chemical reaction determines the course of reaction and they proposed principle of the conservation of symmetry in concerted reaction.

* A pericyclic reaction can take place only provided symmetry of all reactant molecular orbitals is the same as the symmetry of the product molecular orbitals (symmetry allowed Reaction)

- * In concerted reaction, the symmetry present in the reactant is maintained during the course of reaction and is present in the product as well (principle of conservation of orbital symmetry).

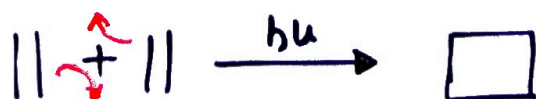
Example:- In Diels-Alder reaction, the reactants, the diene and the dienophile each has plane of symmetry which is maintained in the transition state as well as in the product cyclohexene.



CYCLOADDITION REACTIONS:-

- * The reaction of alkene with alkene and other polyenes in which two molecules react to form a cyclic product with π electrons being used to form two new σ bonds are called cycloaddition reaction.
- * These reactions are classified on the basis of π electrons involved, in each component (4+2) cycloaddition reaction is known Diels-Alder reaction.

2+2 cycloaddition Reaction: (4n)

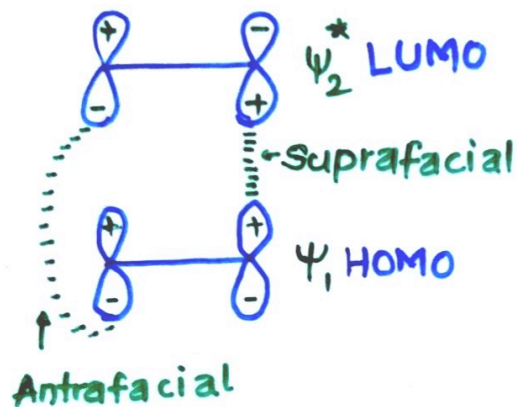


The above reaction is possible or not is determined by (FMO) Frontier molecular orbital method.

Consider the HOMO and LUMO of ethene molecule.

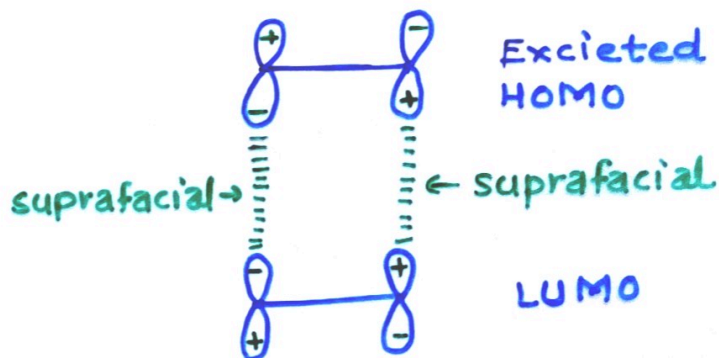


(1) Thermal way



Thermally forbidden

(2) Photochemical way

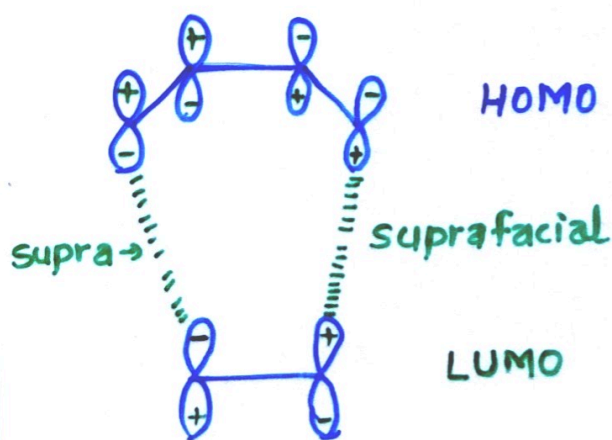


photochemically allowed.

(4+2) cycloaddition Reaction:-

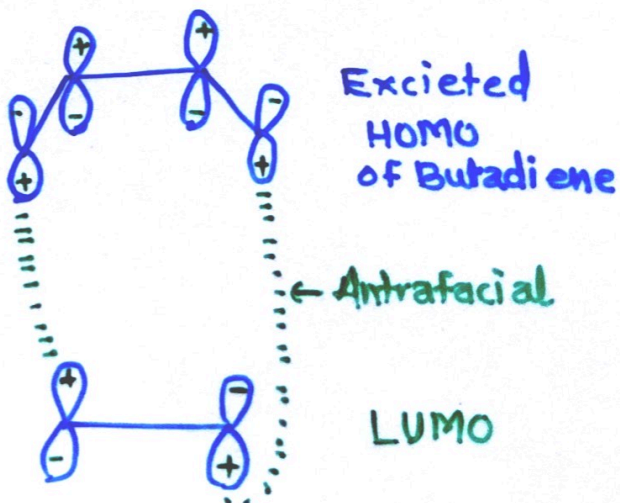
The Diels-Alder reaction may also be analysed by a similar consideration of molecular orbitals of ethylene and butadiene.

(1) Thermal way



Thermally allowed

(2) photochemical way



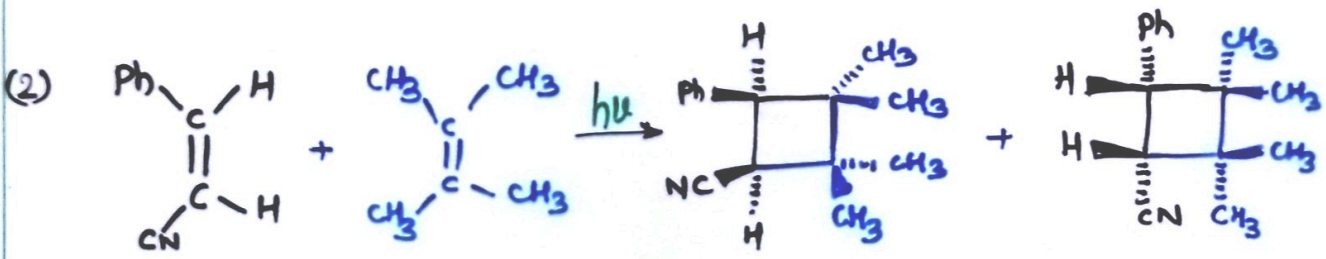
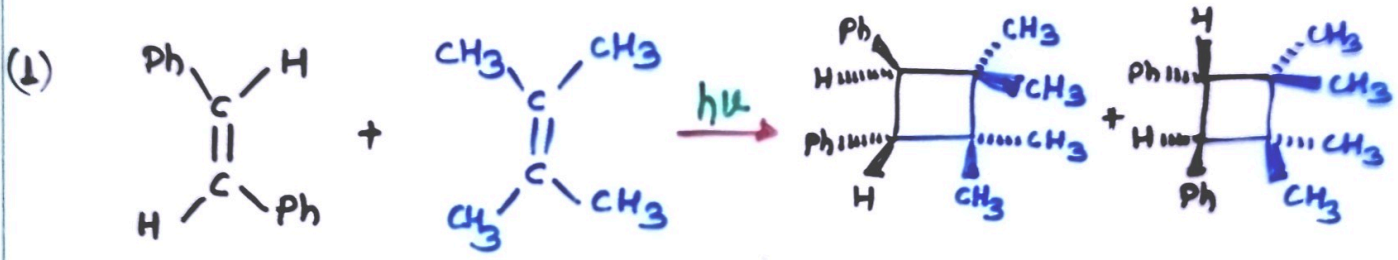
Photochemically forbidden Reaction.

Woodward-Hoffmann Rules for Cycloaddition Reaction:-

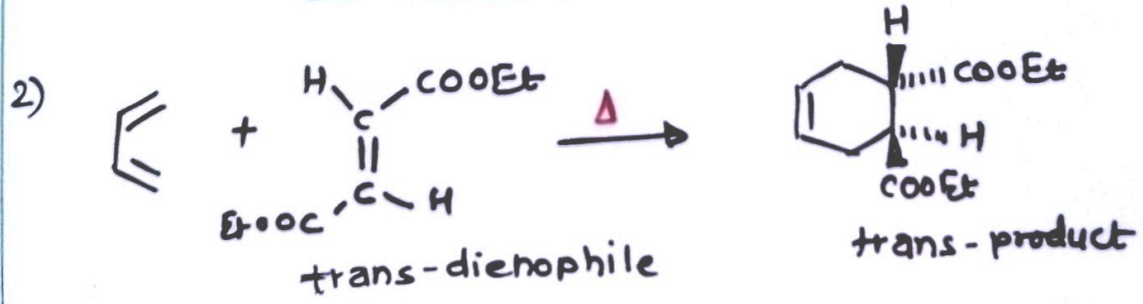
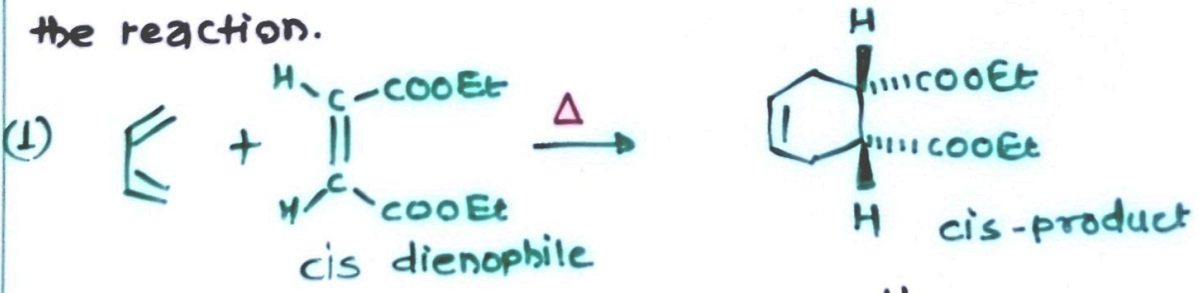
$i+j$	Thermal	photochemical
$4n$	supra, antra antra, supra	supra, supra antra, antra
$4n+2$	supra, supra antra, antra	supra, antra antra, supra

Stereochemistry of cycloaddition Reaction:-

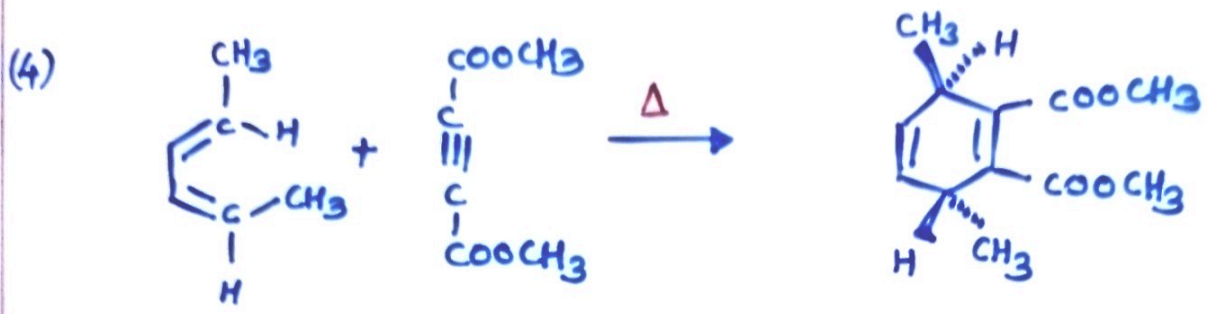
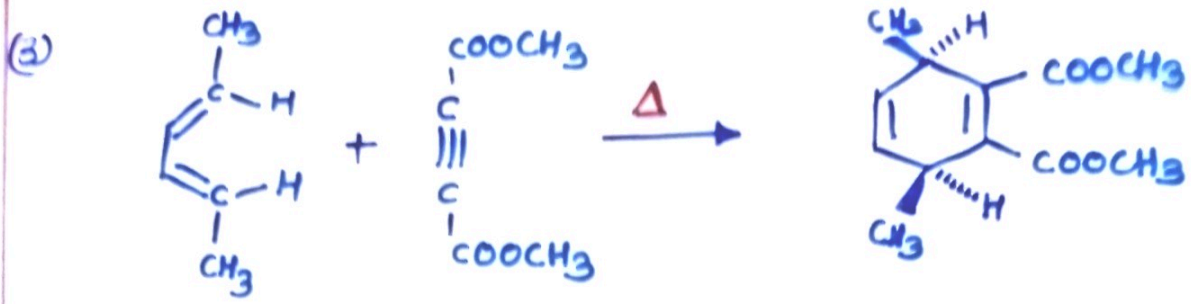
Stereochemistry of (2+2) cycloaddition Reaction is maintained in photochemical reaction but not in thermal reaction.



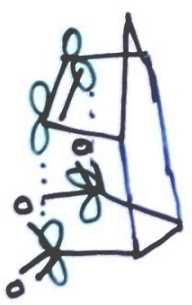
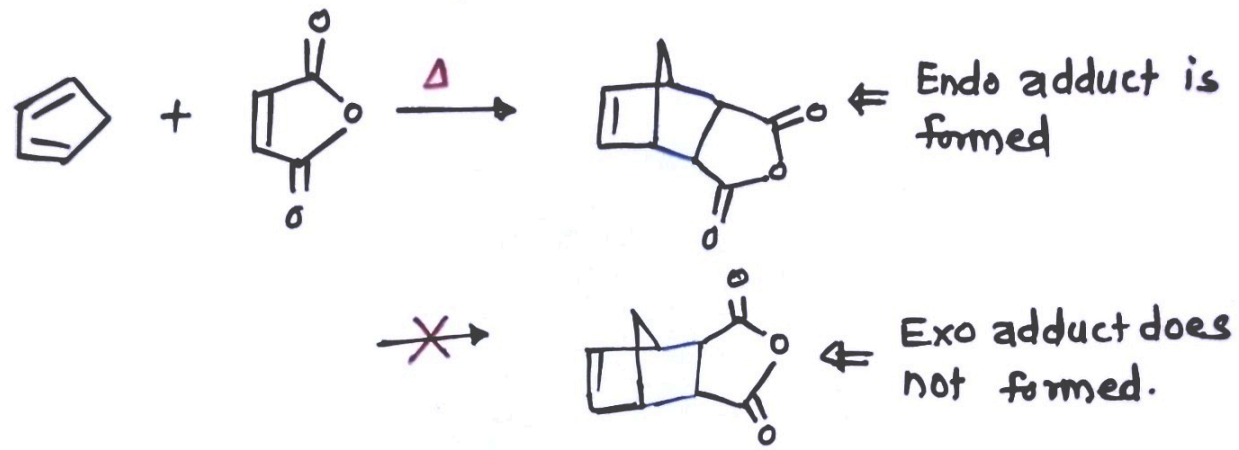
Stereochemistry of (4+2) cycloaddition:- this reaction is stereospecific and stereochemistry is maintained through the reaction.



In above reactions stereochemistry of dienophile is retained.

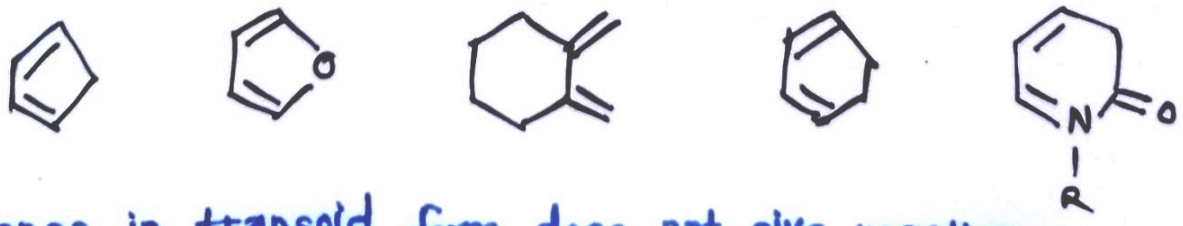


In above examples stereochemistry of diene is retained.
 Endo Rule :- The Diels Alder reaction take place generally to give endo adduct as major product.

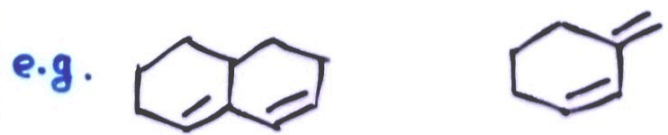


secondary interaction between π -system is possible in endo adduct but in exo adduct π -system interaction is not possible so it can not formed.

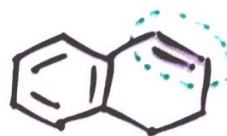
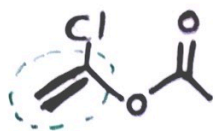
* some dienes which can give Diels-Alder Reactions &



* Dienes in transoid form does not give reaction.



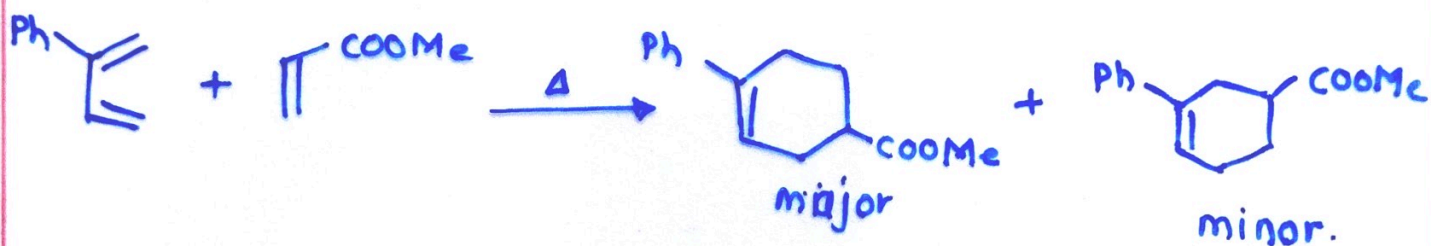
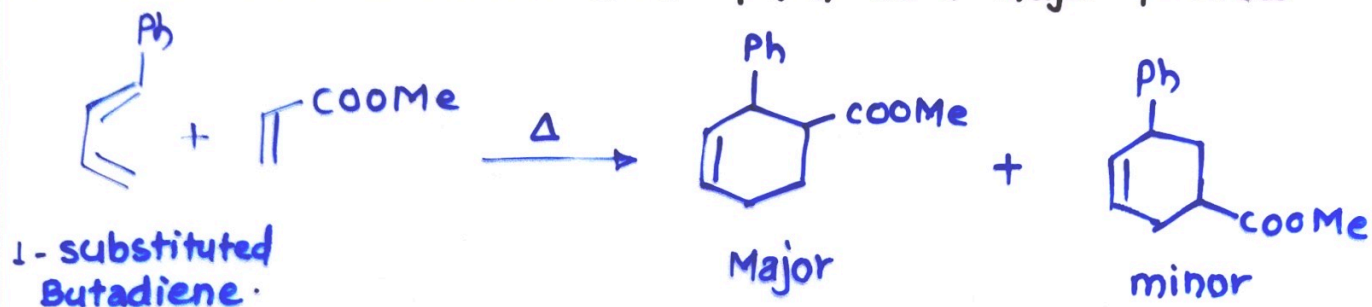
some dienophiles:-



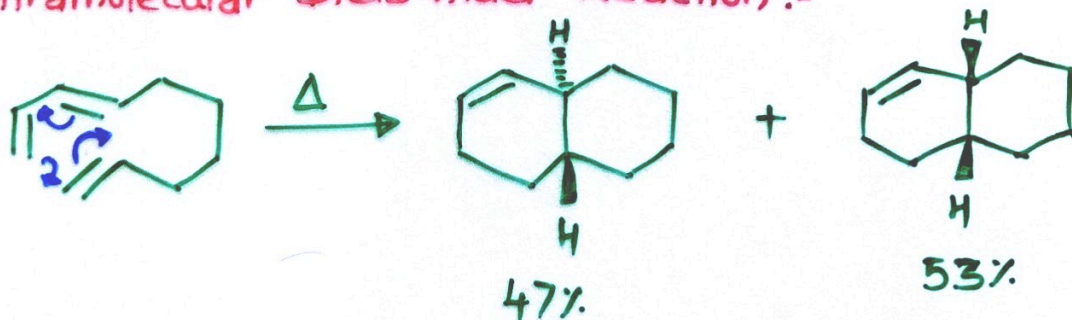
Regioselectivity of Diels Alder Reaction:-

Cycloaddition of an unsymmetrically substituted diene and dienophile lead to regioisomer.

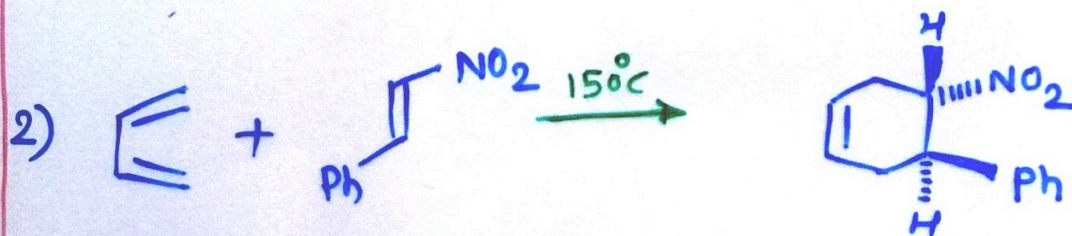
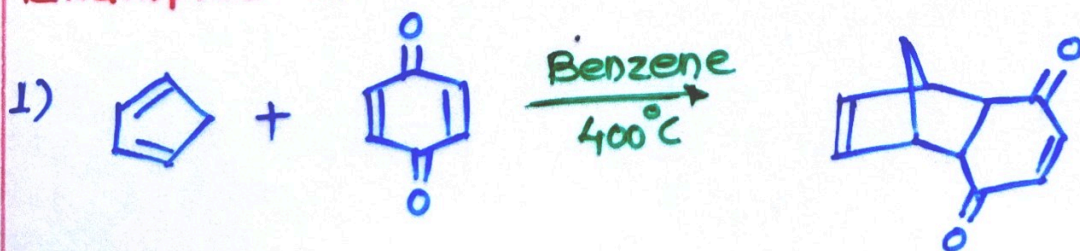
- 1- substituted butadiene give ortho as a major product
- 2- substituted butadiene give para as a major product.

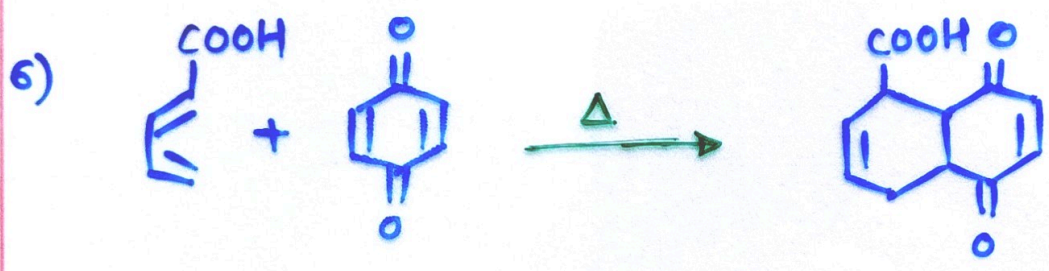
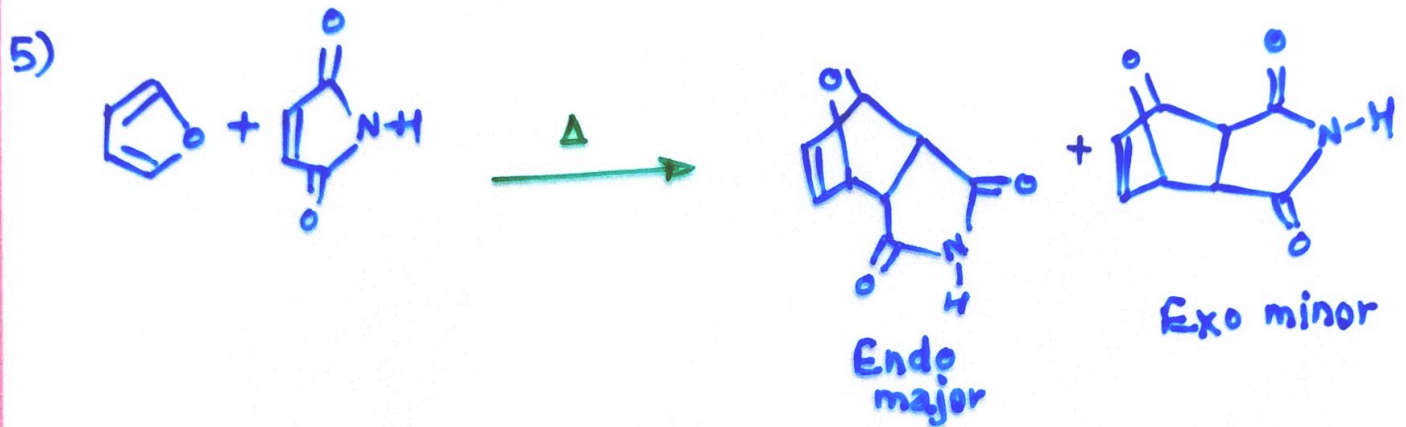
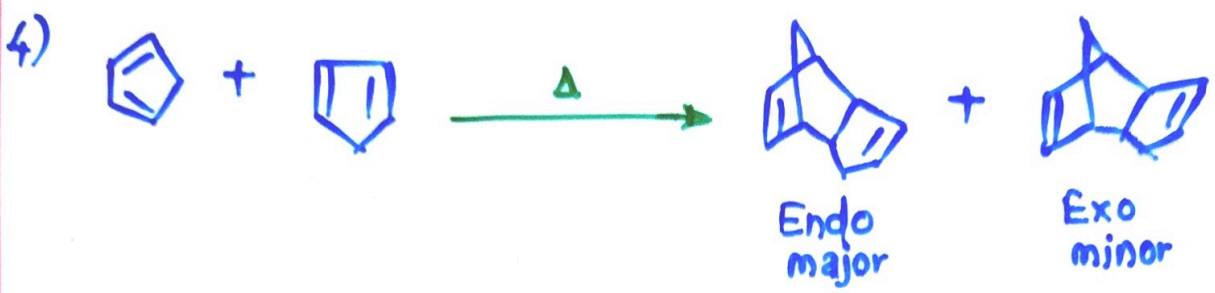


Intramolecular Diels Alder Reaction:-

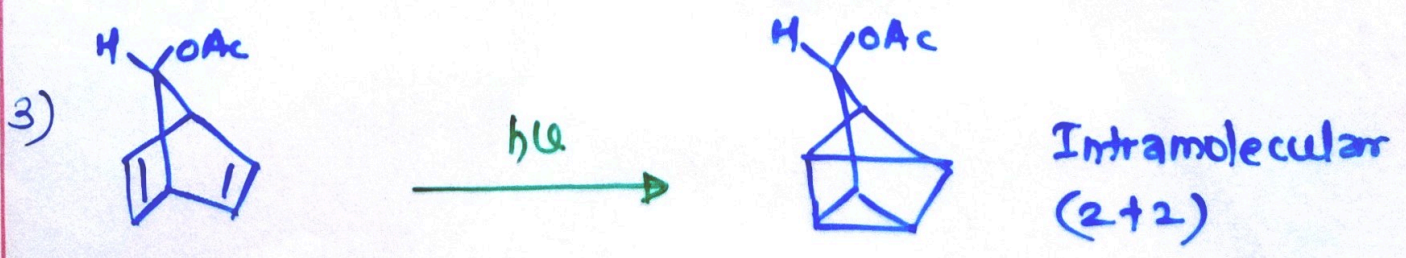
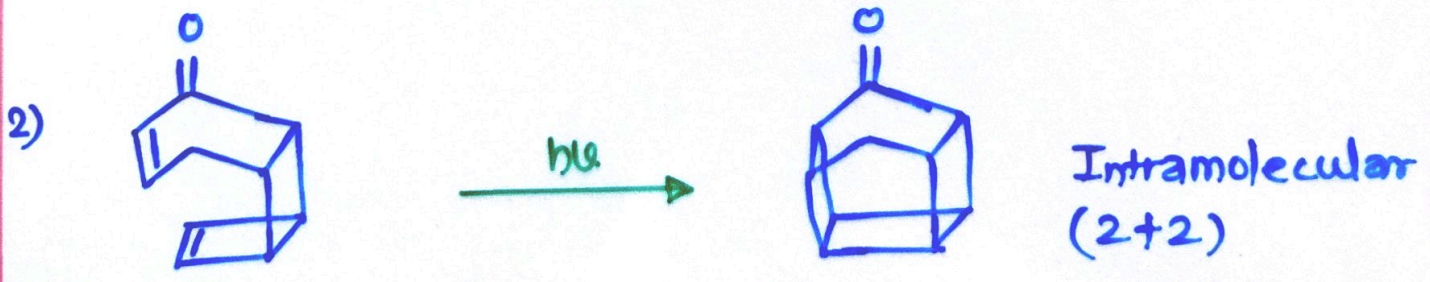
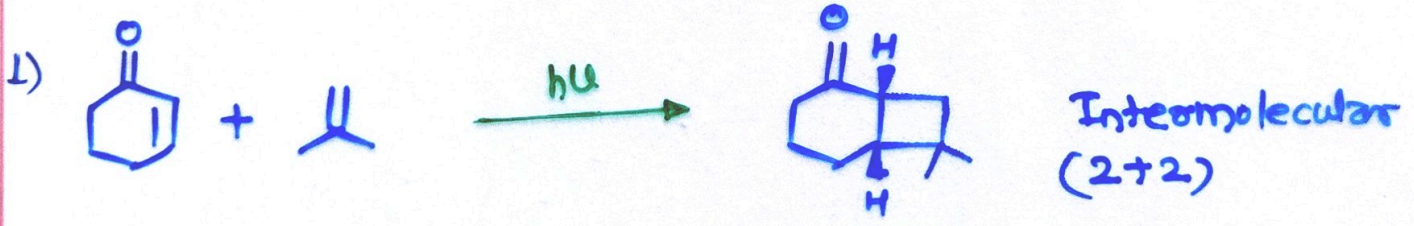


Examples of Diels Alder Reaction:-



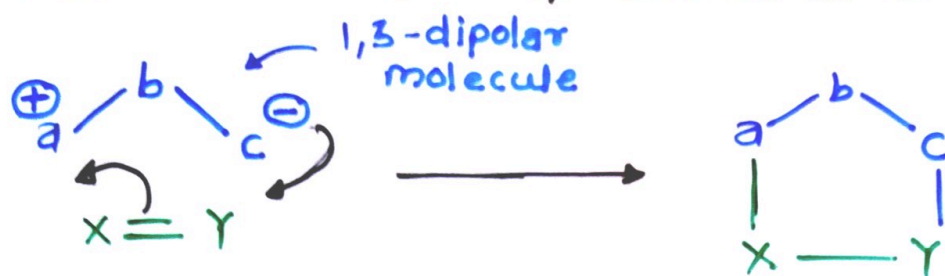


Examples of (2+2) cycloaddition:-



1,3-Dipolar cycloaddition Reaction:-

Dipolar cycloaddition reactions are useful for both synthesis of heterocyclic compounds and for C-C bond formation. These reactions are represented as given below.

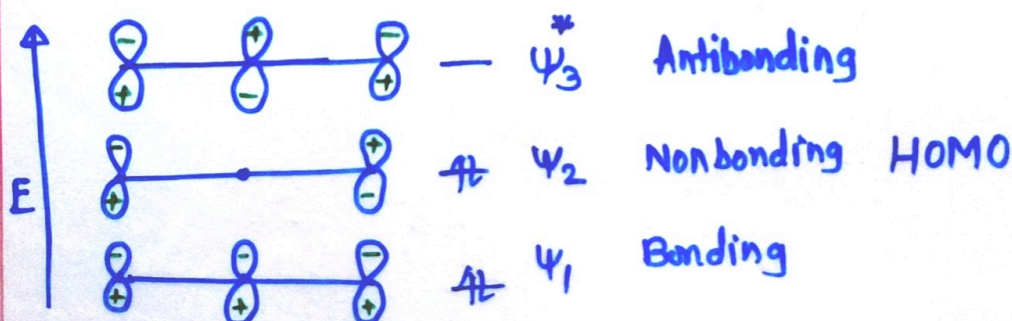


The species $\overset{\oplus}{a}-b-\overset{\ominus}{c}$ is called 1,3-dipolar molecule and $X=Y$ is called dipolarophile. The 1,3-dipolar molecule is isoelectronic with allylcarbanion and has four electrons in the pi system. All 1,3-dipoles contain 4 pi electrons in three p orbitals of a, b, and c.

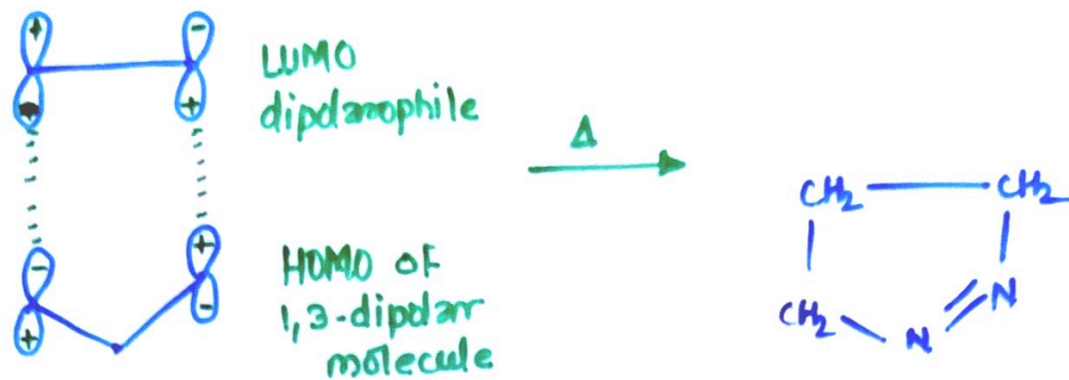
Some typical 1,3-dipolar species are given in the table.

Name	Structure.
1) Azoxy	$-\overset{\oplus}{N}-\overset{\ominus}{N}-O^{\ominus} \leftrightarrow -N=\overset{\oplus}{N}-O^{\ominus}$
2) Nitrosoides	$-\overset{\oplus}{N}-\overset{\ominus}{O}-O^{\ominus} \leftrightarrow -N=\overset{\oplus}{O}-O^{\ominus}$
3) Ozone	$\overset{\oplus}{O}-\overset{\ominus}{O}-O^{\ominus} \leftrightarrow O=\overset{\oplus}{O}-O^{\ominus}$
4) Nitrous oxide	$\overset{\oplus}{N}=\overset{\ominus}{N}-O^{\ominus} \leftrightarrow N\equiv N-O^{\ominus}$
5) Carbonyl oxide	$\overset{\oplus}{C}-\overset{\ominus}{O}-O^{\ominus} \leftrightarrow \overset{\oplus}{C}=\overset{\ominus}{O}-O^{\ominus}$
6) Nitroile oxide	$\overset{\oplus}{C}=\overset{\ominus}{N}-O^{\ominus} \leftrightarrow -C\equiv N^{\oplus}-O^{\ominus}$
7) Nitroile amine	$\overset{\oplus}{C}=\overset{\ominus}{N}-\overset{\ominus}{N} \leftrightarrow -C\equiv N^{\oplus}-\overset{\ominus}{N}$
8) Azides	$\overset{\oplus}{N}=\overset{\ominus}{N}-\overset{\ominus}{N} \leftrightarrow N\equiv N^{\oplus}-\overset{\ominus}{N}$

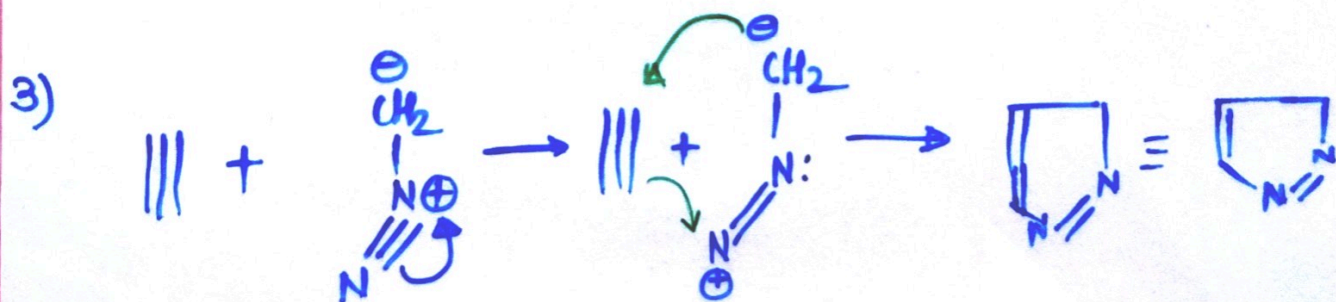
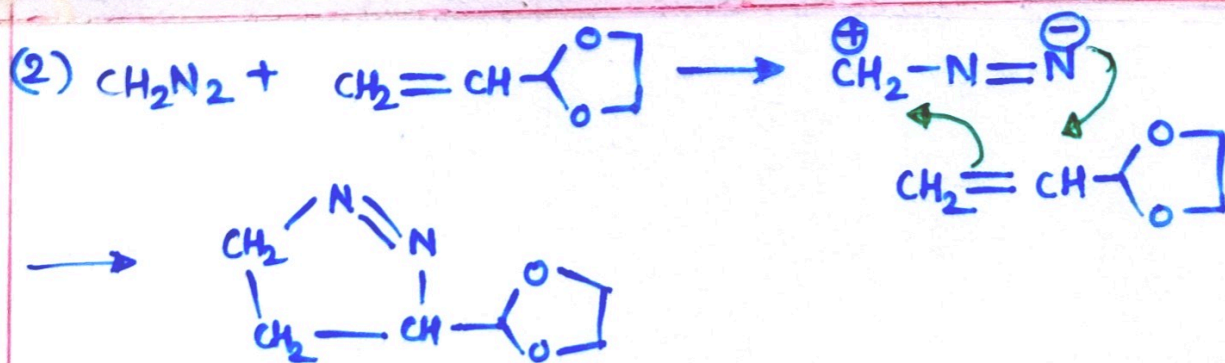
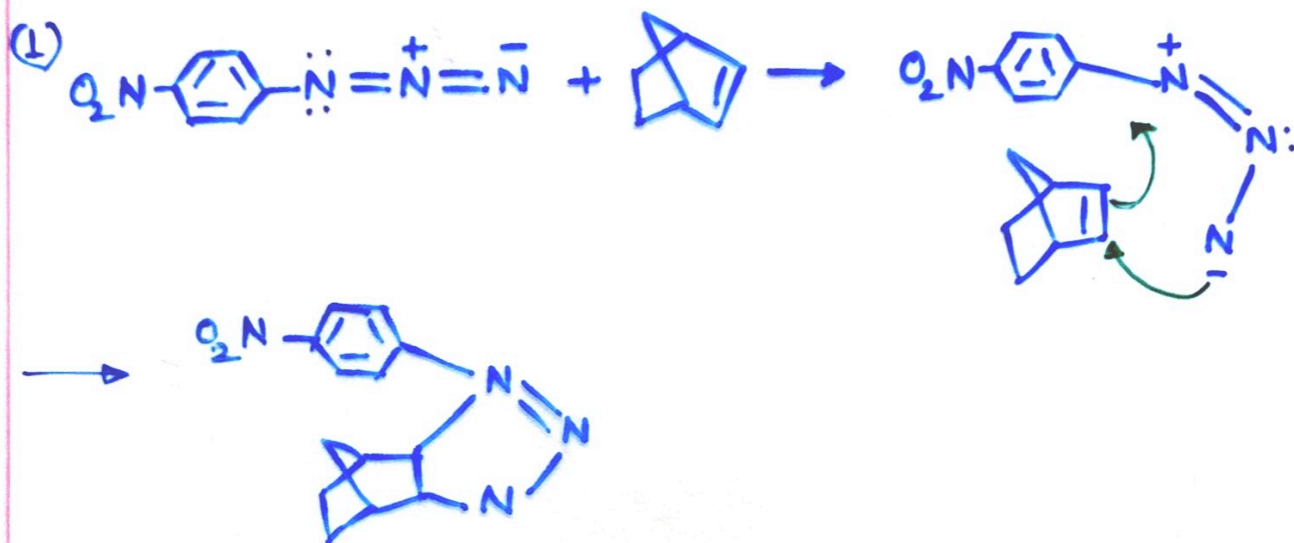
Molecular orbitals of 1,3-dipolar species:-



1,3-dipolar cycloaddition is thermally allowed.



Example:-

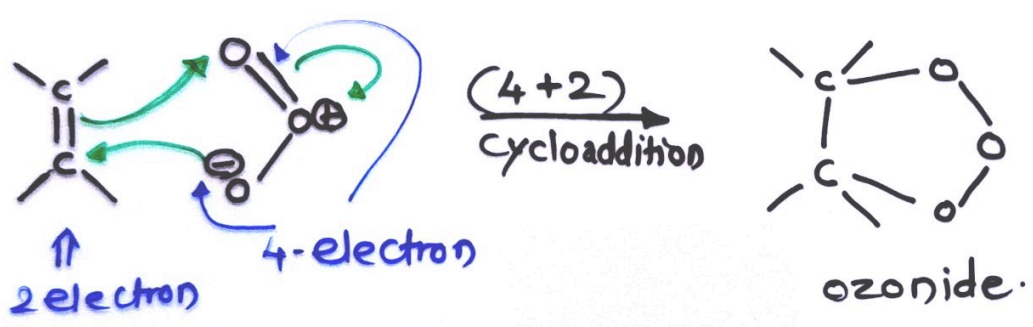
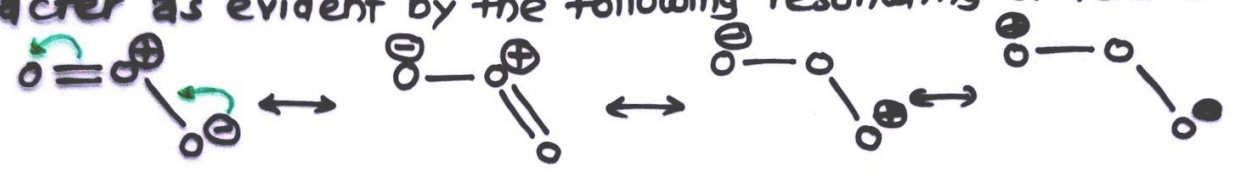


Cycloaddition of alkene with OsO₄:-



Cycloaddition of alkene with ozone:-

Each of three oxygen atoms of ozone has electrophilic character as evident by the following resonating structures.



Chelotropic reactions:-

In chelotropic reaction two σ bonds that terminate at a single atom are made or broken during a concerted reaction.

