

DIELS ALDER REACTION

“There a lot of potential for aggressive expansion”-joker

ANTONY P F

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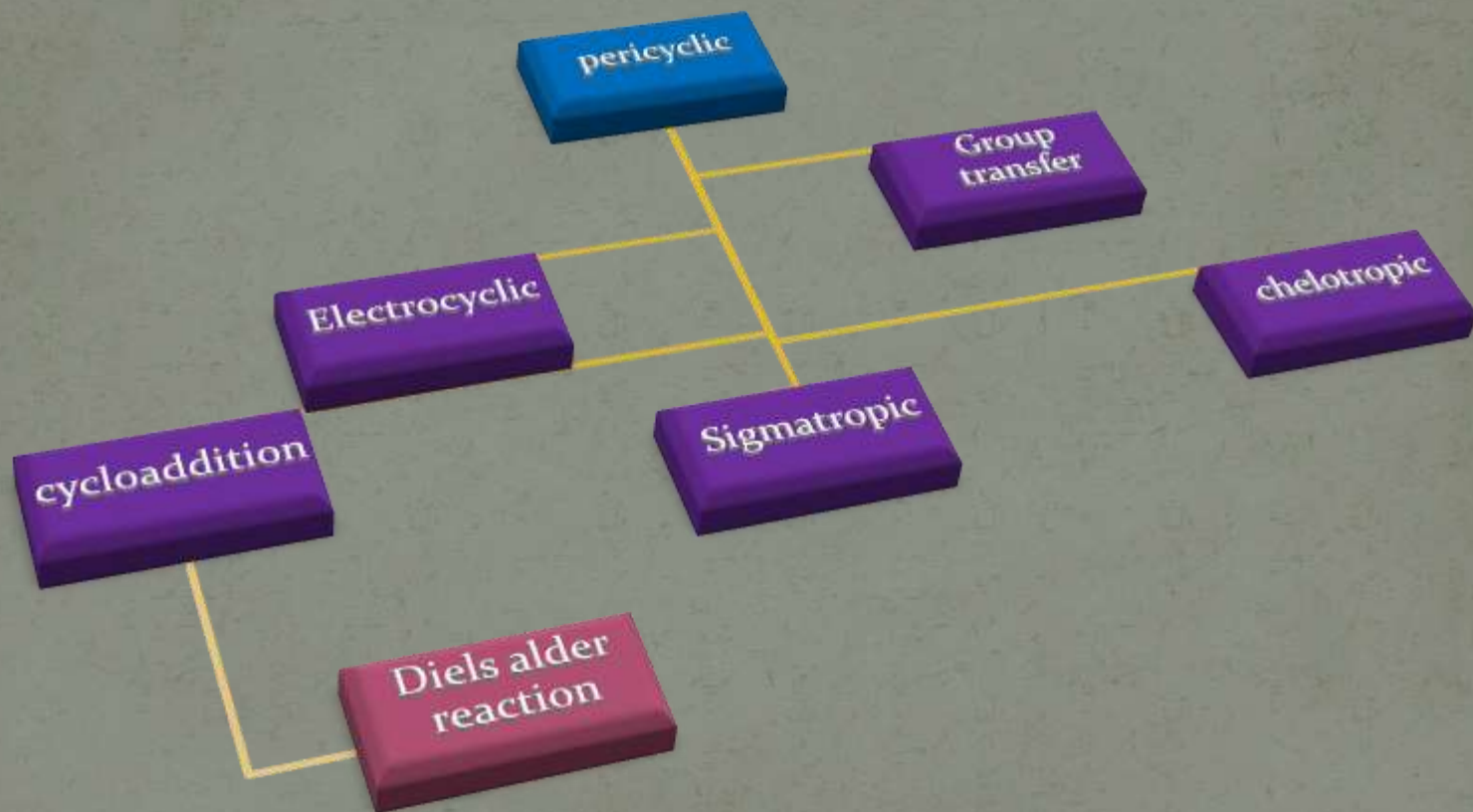
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HISTORY

- ◎ The Diels-Alder reaction is a method of producing cyclical organic compounds (cycloaddition reaction), and is named for Otto **Diels** and Kurt **Alder** who in 1950 received the Nobel Prize for their experiments.

Pericyclic reaction initiated by heat or light and do not need any other reagent or chemical species

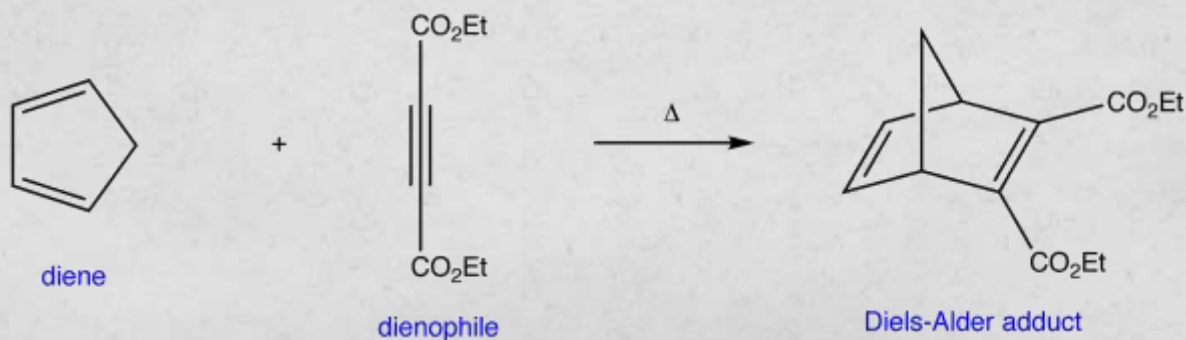


Diels alder reaction



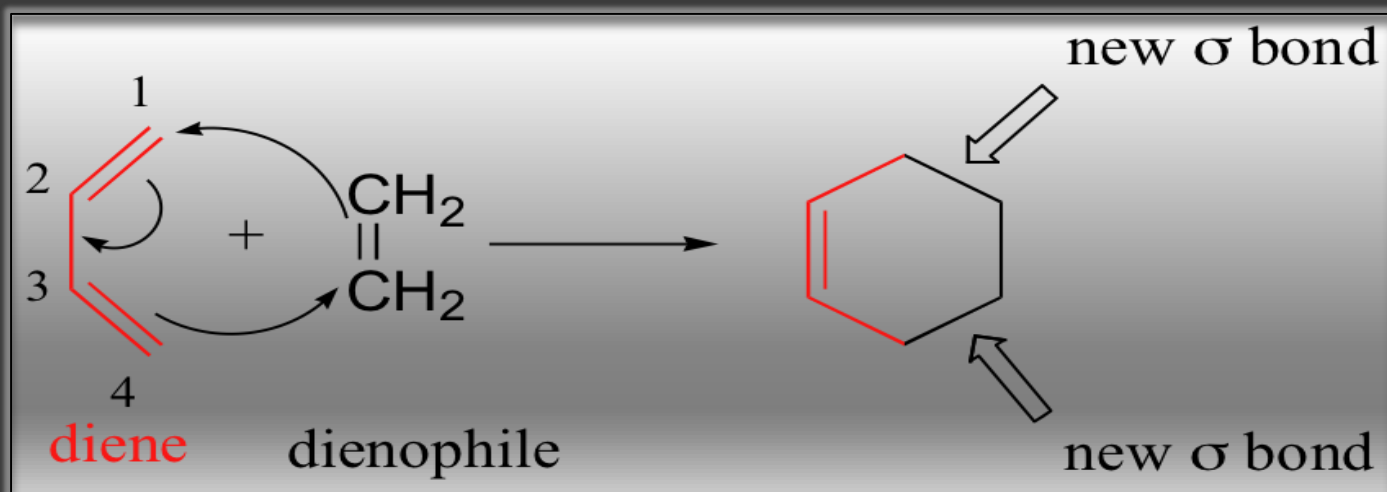
DIELS ALDER REACTION

- Diels alder reaction is a [4+2] cycloaddition reaction
- The Diels-Alder reaction is an addition reaction between a 1,3-diene and an alkene or alkyne (called a dienophile), to form a new ring.
- dienophile: Diene-loving



- **Diene** : diene are electron rich compound. In the presence of **electron releasing** groups such as alkyl, phenyl, or alkoxy groups may further enhance the reactivity of diene
- **Dienophile**: the most common dienophiles are the electron poor alkenes and alkyne. A good dienophile generally has one or more **electron-withdrawing** groups (CHO, COOH, CN) pulling electron density away from the Π bond

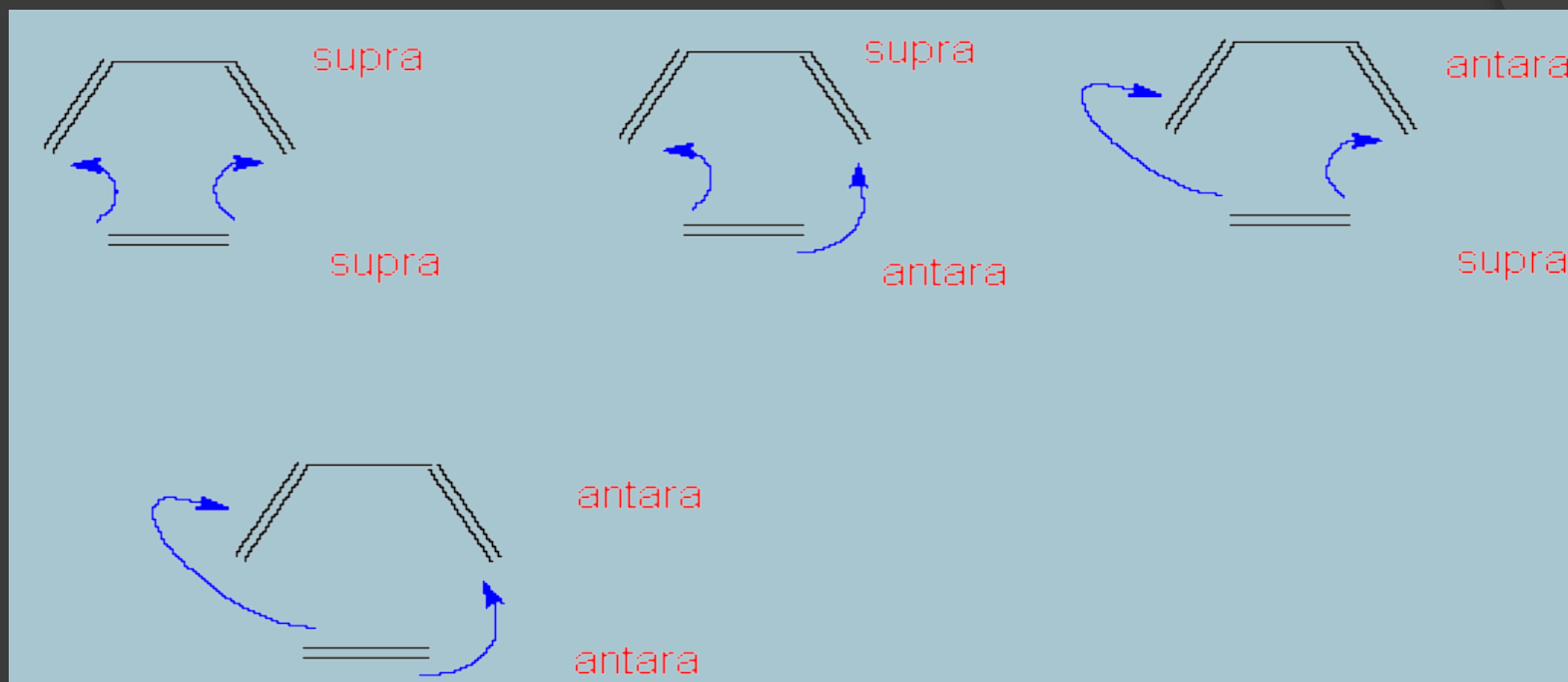
MECHANISUM



All Diels-Alder reactions have the following features in common:

- 1. They are initiated by heat; that is, the Diels-Alder reaction is a thermal reaction.**
- 2. They form new six-membered rings.**
- 3. Three π bonds break, and two new C—C σ bonds and one new C—C π bond forms.**
- 4. All old bonds are broken and all new bonds are formed in a single step**

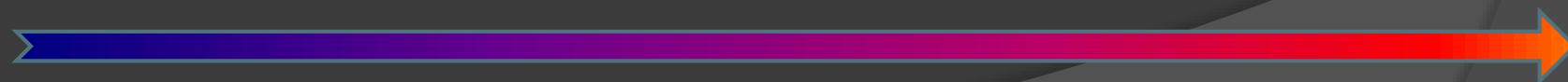
CLASSIFICATION OF ORBITAL INTERACTION



S-S

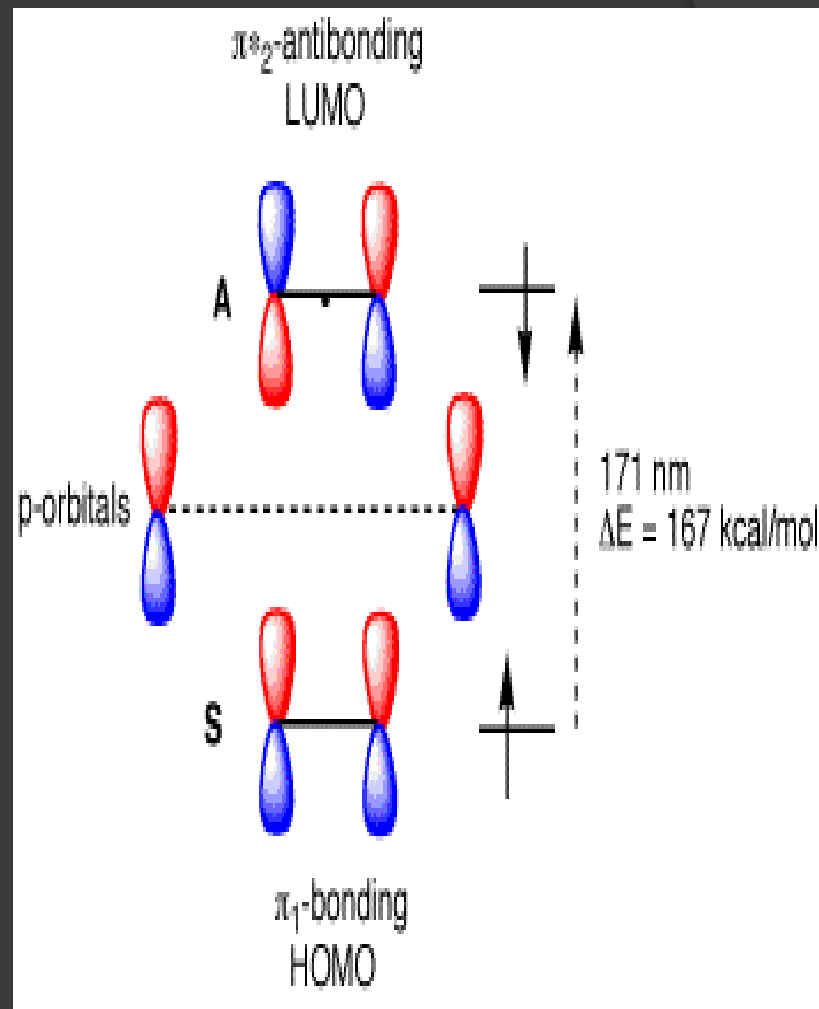
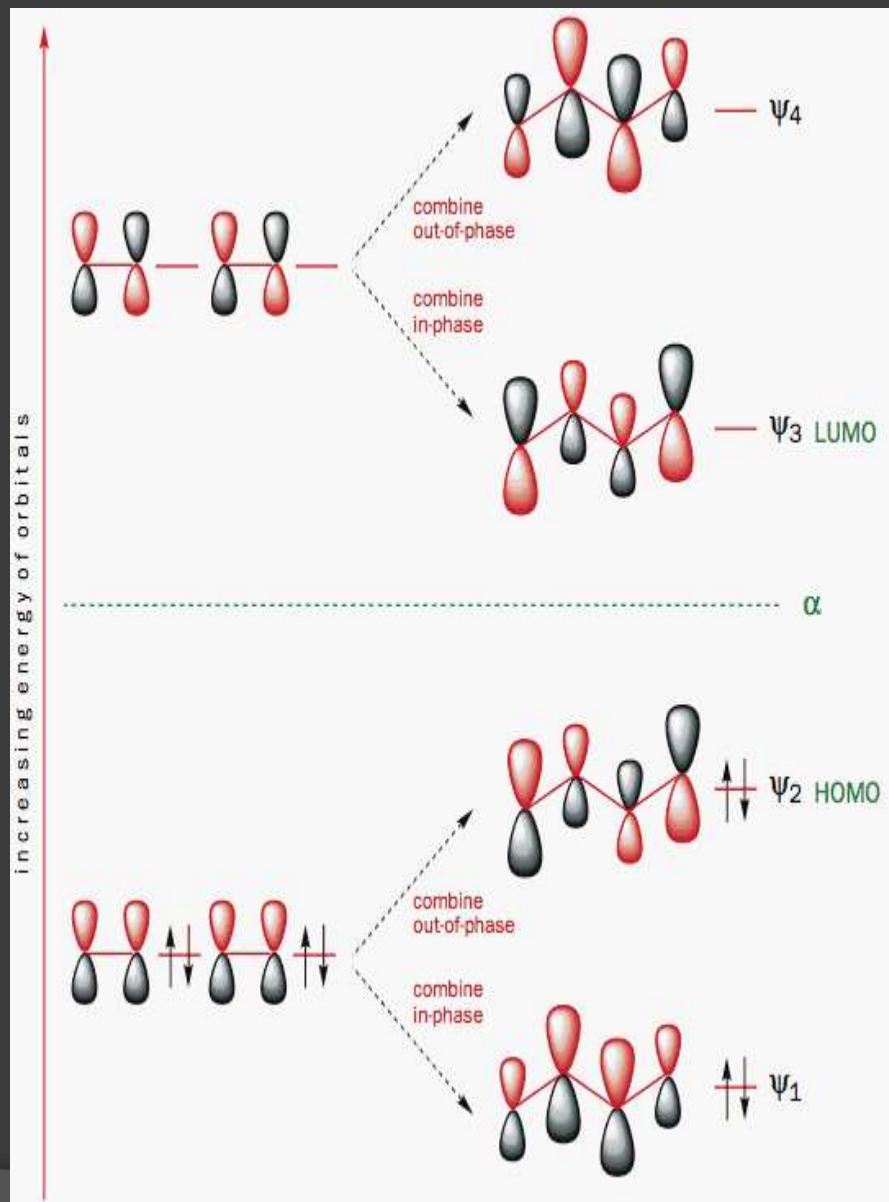
S-A=A-S

A-A



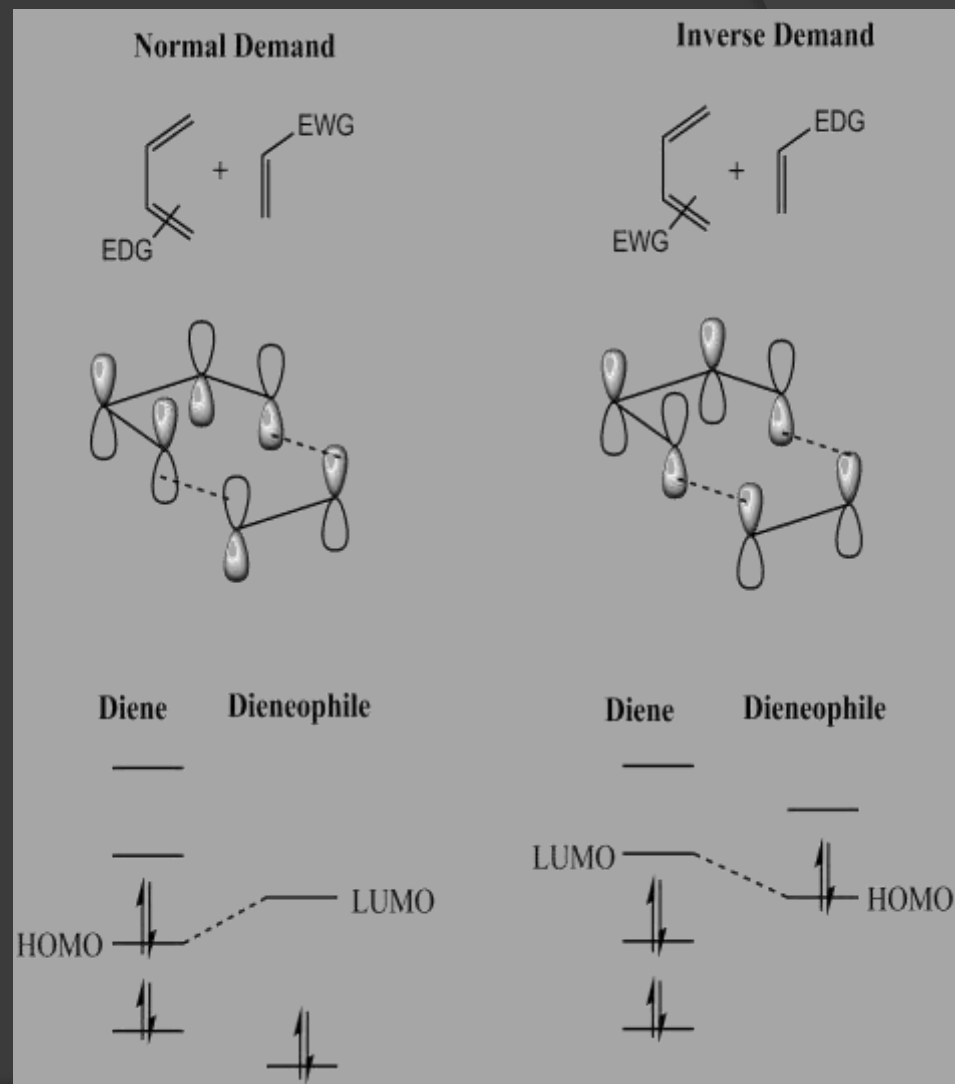
Energy increasing order

ORBITALS OF ETLYENE AND BUTA DI ENE



INTERACTION OF ORBITALS

Diels alder reaction initiated by thermally, in the case of thermal reaction we consider the interaction between HOMO of diene and LUMO of dienophile or LUMO-HOMO interaction



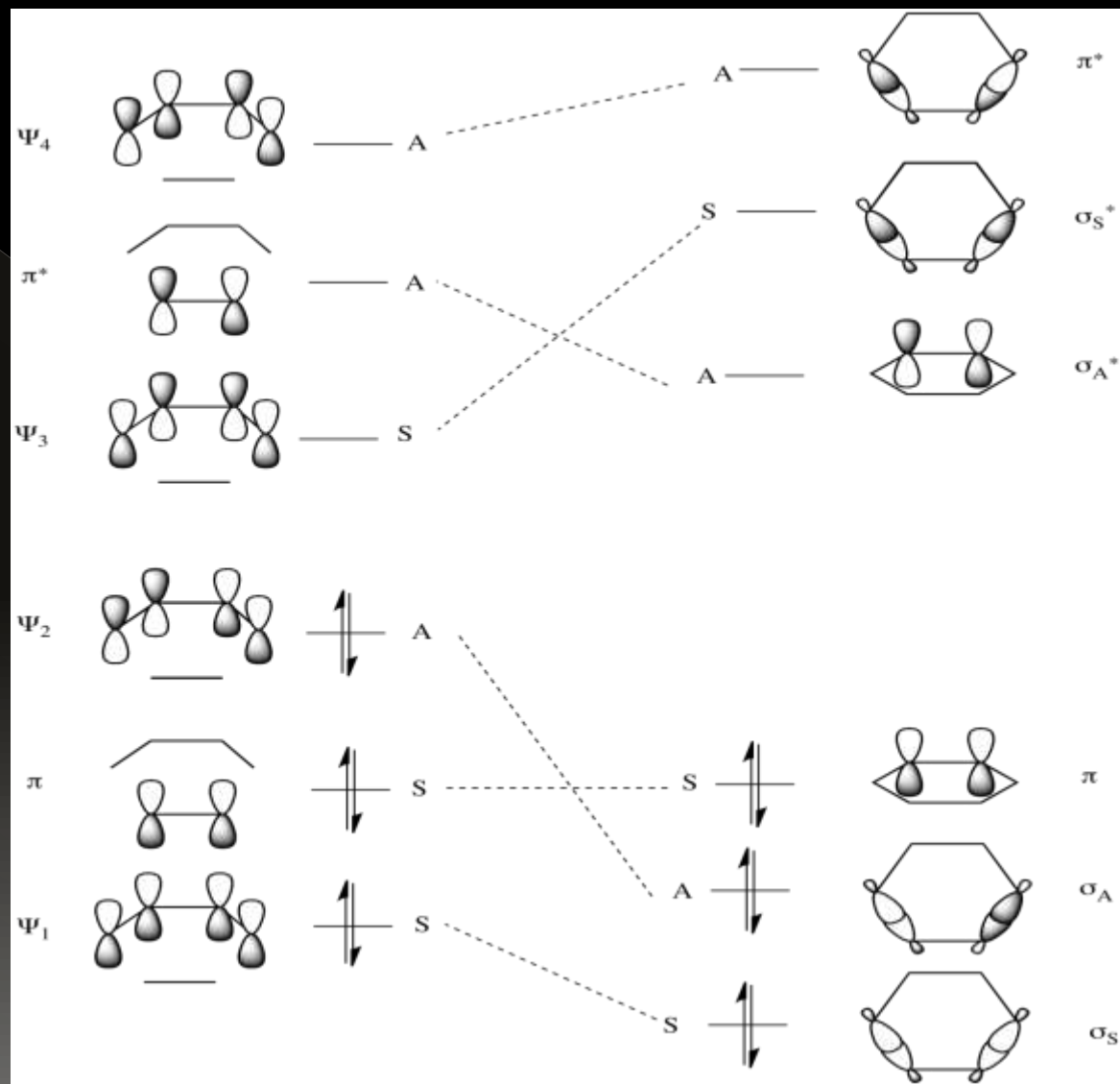
Depending upon nature and interaction of system we can predict whether the reaction is thermal or photochemical

system	thermal	photochemical
$4n+2$	S-S	S-A
$4n$	S-A	S-S

Diels alder reaction $4n+2$ systems supra-supra interaction so that the reaction is thermally allowed reaction

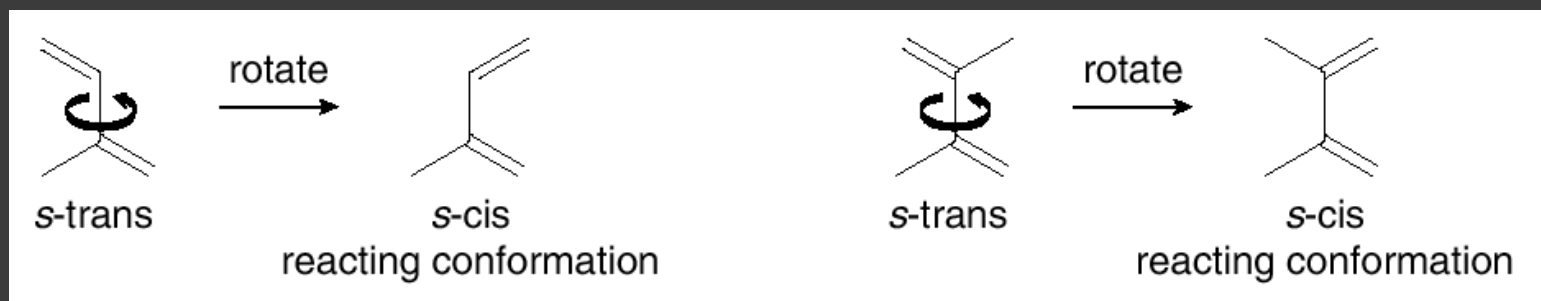
CORRILATION DIAGRAM

Ground state orbitals of reactants correlate with the ground state orbitals of product. Therefore the Diels alder reaction is thermally allowed



Several rules govern the Diels-Alder reaction.

1. The diene can react only when it adopts the *s-cis* conformation.

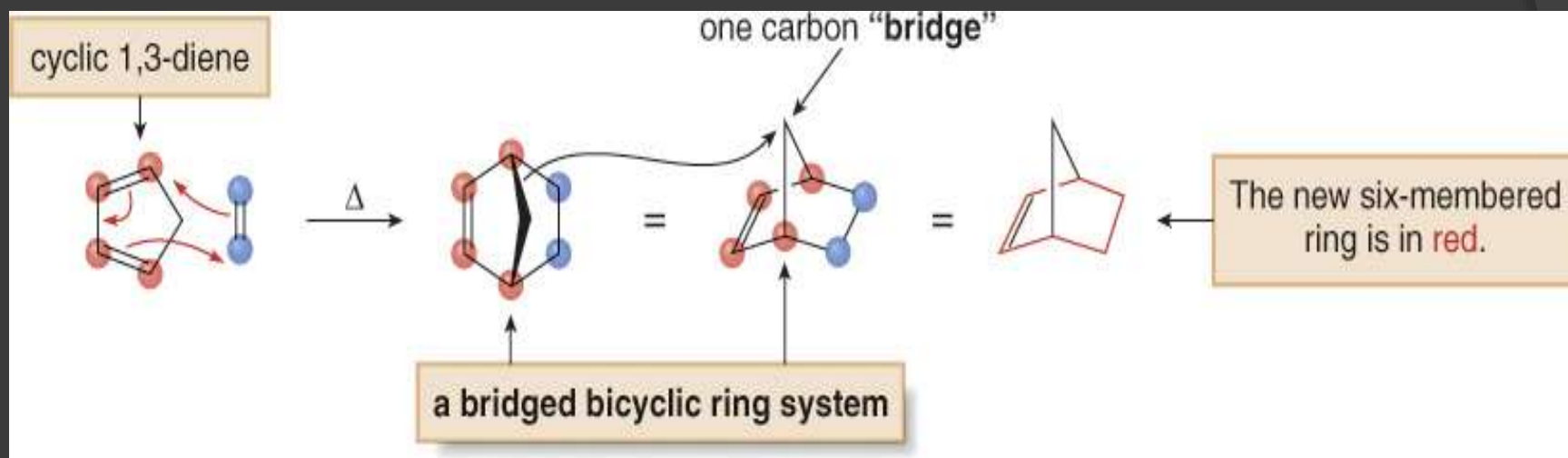


This rotation is prevented in cyclic alkenes. When the two double bonds are constrained to an *s-cis* conformation, the diene is unusually reactive. When the two double bonds are constrained in the *s-trans* conformation, the diene is unreactive.



2. When endo and exo products are possible, the endo product is preferred. (alder rule)

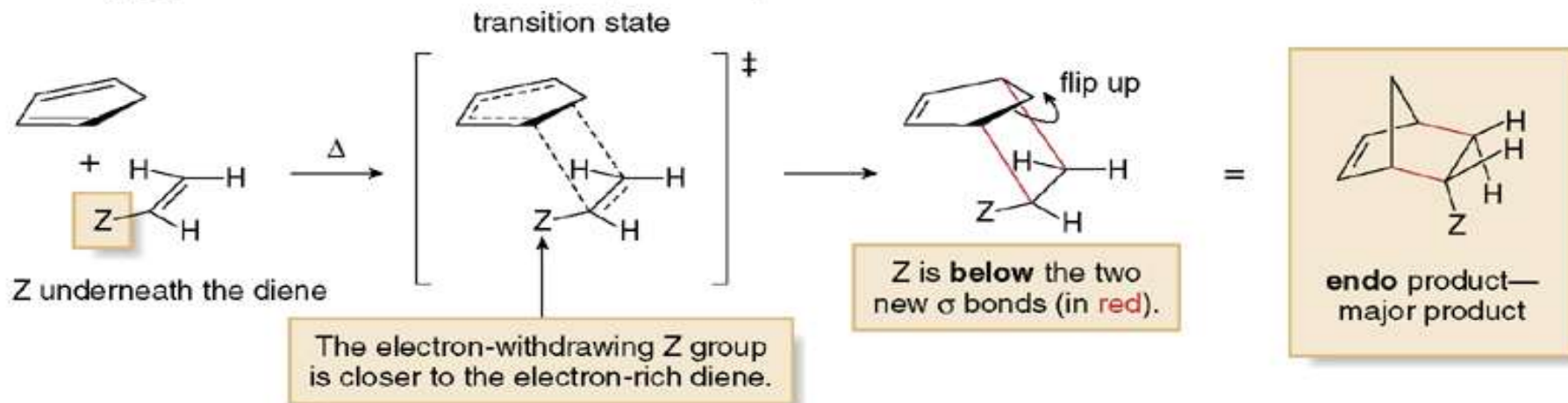
• Consider the reaction of 1,3-cyclopentadiene with ethylene. A new six-membered ring forms and above the ring there is a one atom “bridge.”



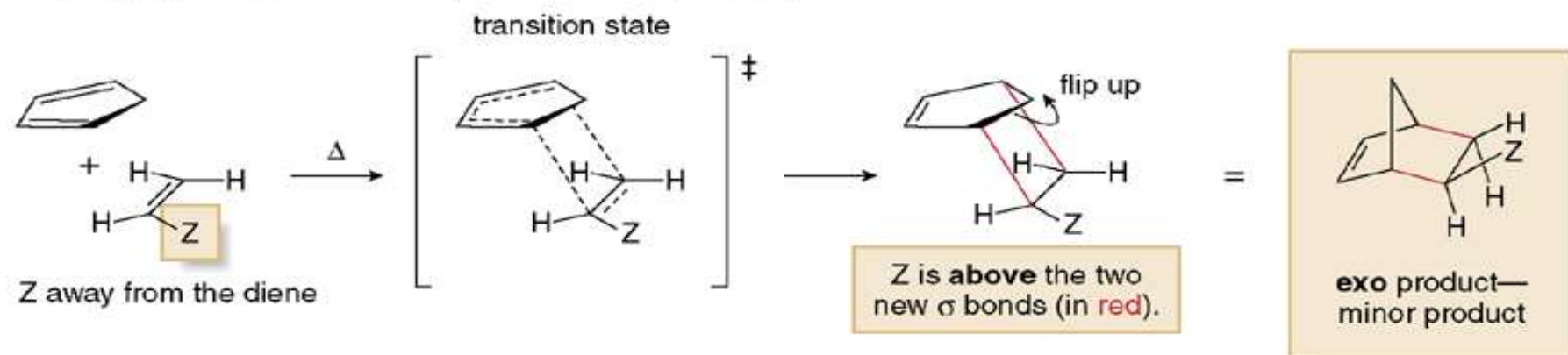
In transition state the electron withdrawing group(z) is more closer to diene, the product become more stable. In the case of bridge carbon ring system endo product more stable then exo

•When cyclopentadiene reacts with a substituted alkene as the dienophile ($\text{CH}_2=\text{CHZ}$), the substituent Z can be oriented in one of two ways in the product.

Pathway [1] With Z oriented under the diene, the endo product is formed.

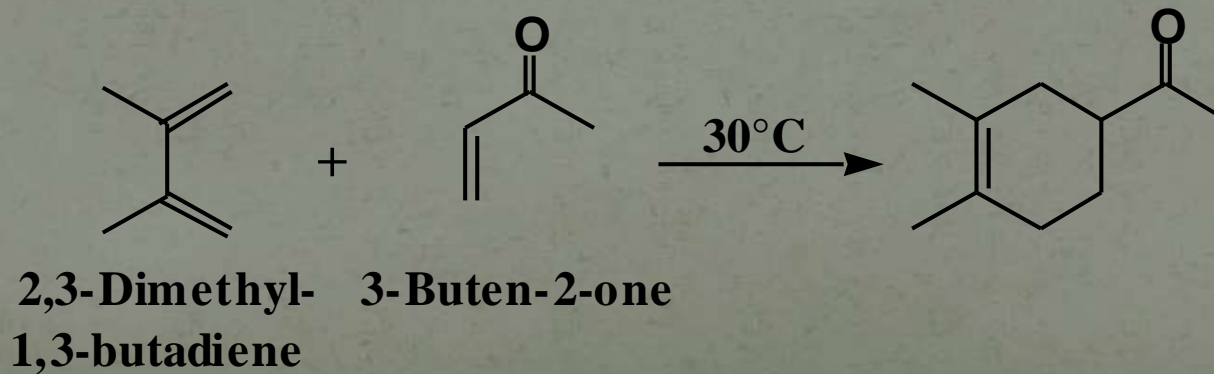
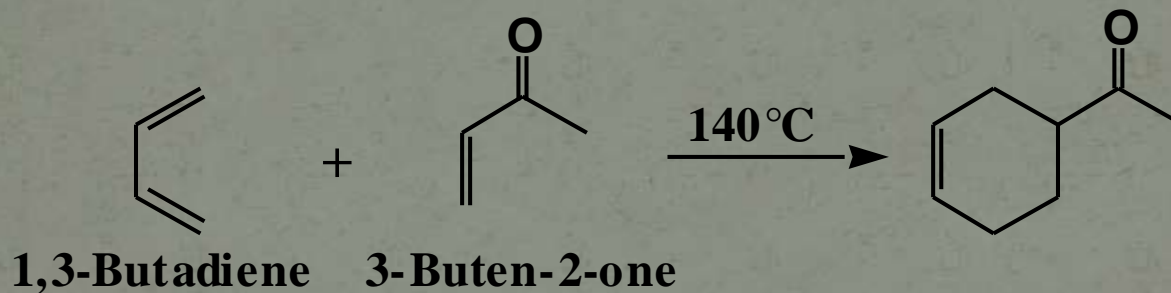
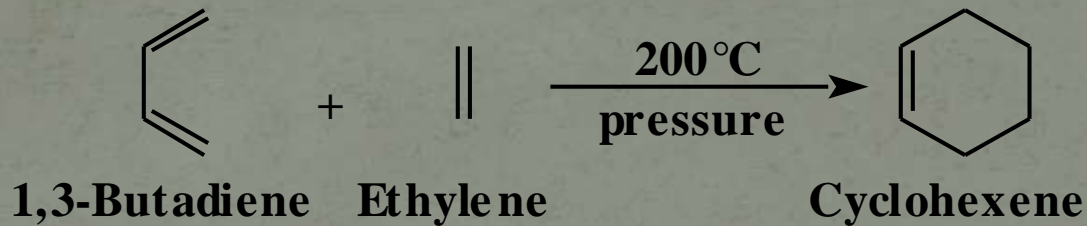


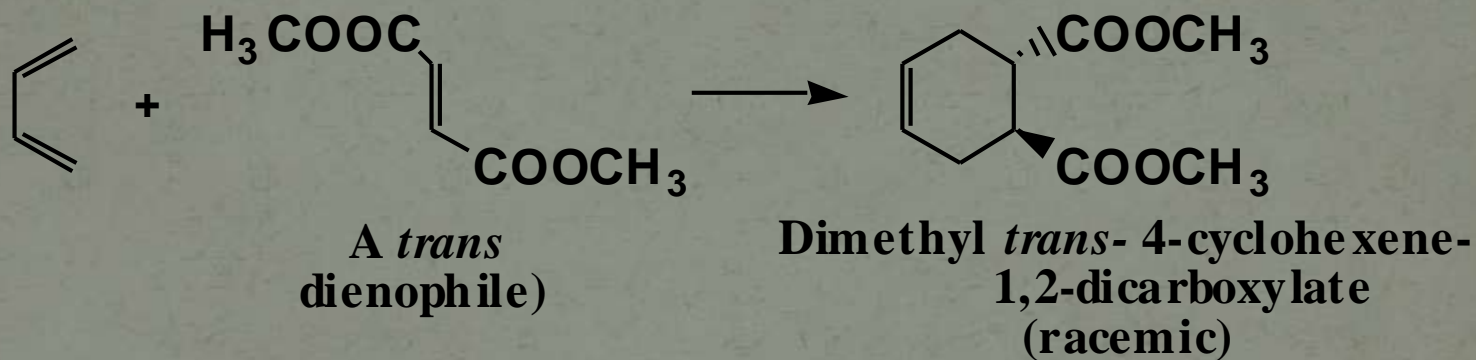
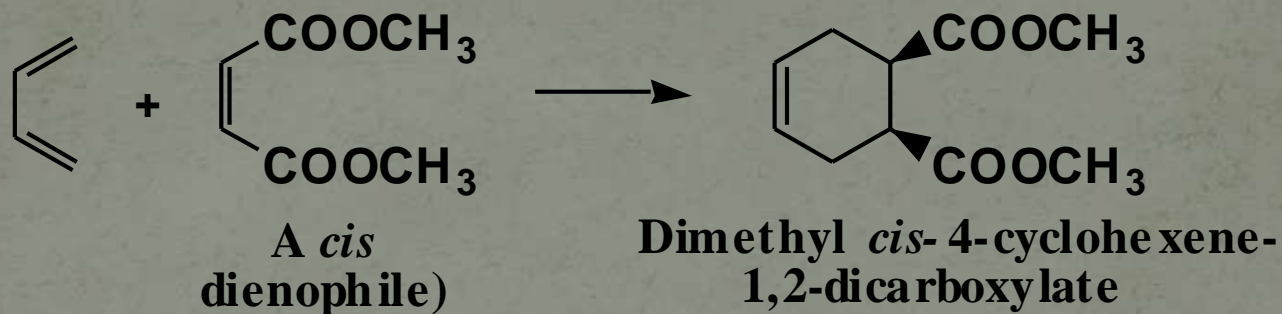
Pathway [2] With Z oriented away from the diene, the exo product is formed.



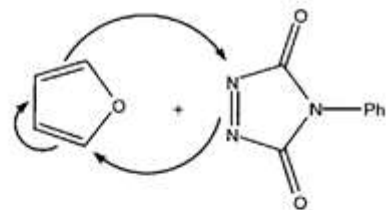
EXAMPLE

ACYCLIC COMPOUND

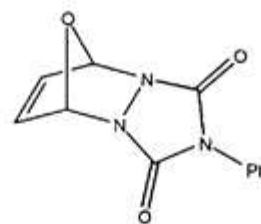




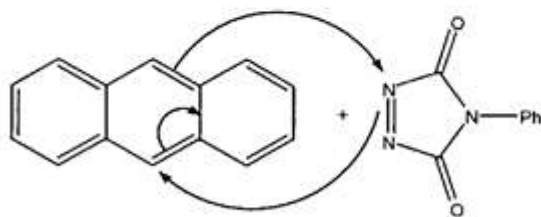
CYCLIC COMPOUND



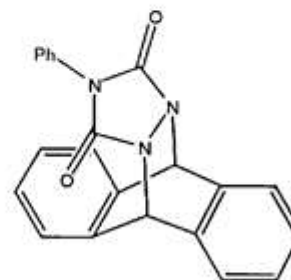
furan (1) N-PTD (3)
(red)



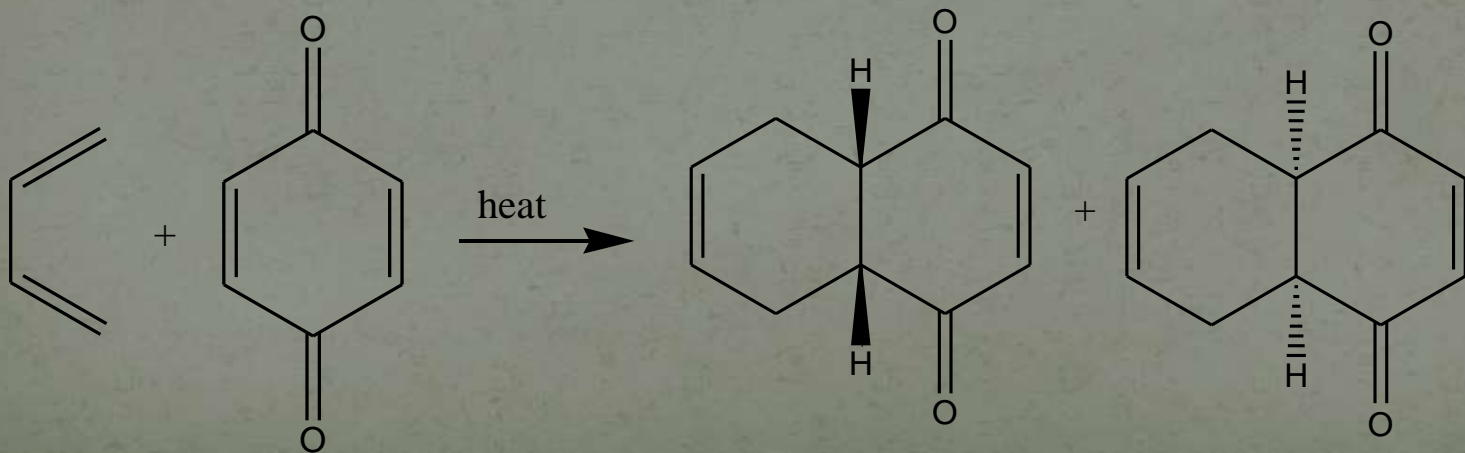
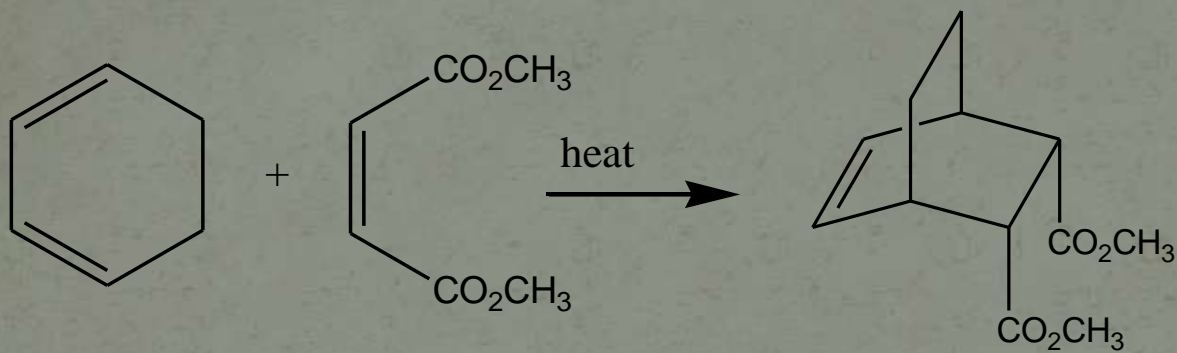
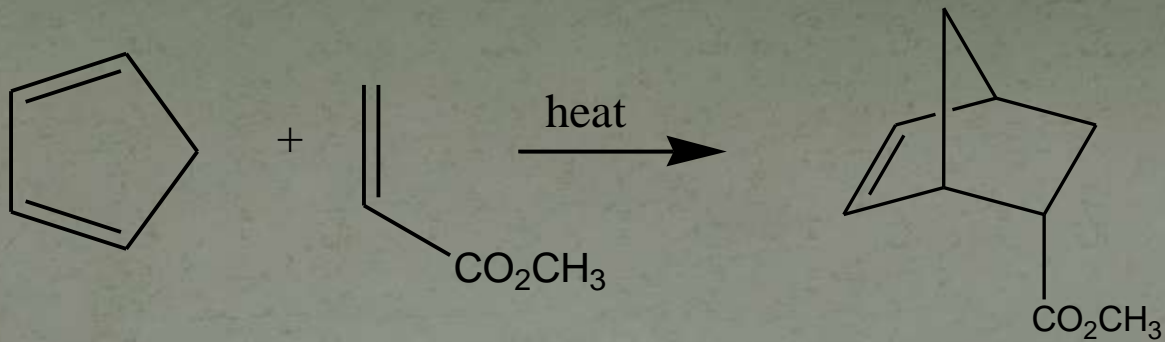
cycloadduct
(colorless)



anthracene (2) N-PTD (3)
(red)



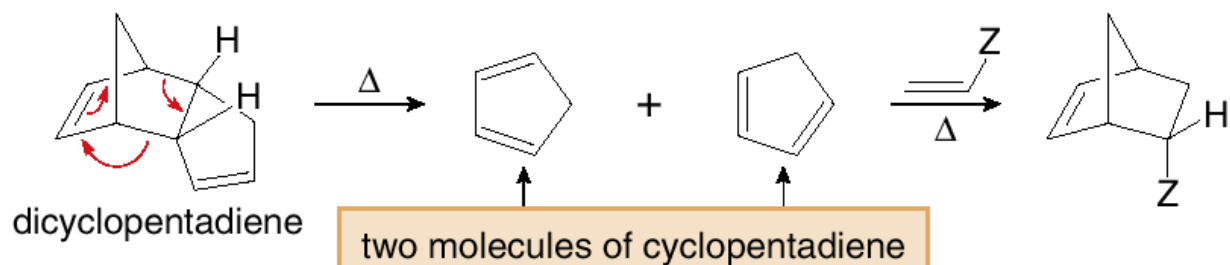
cycloadduct
(colorless)



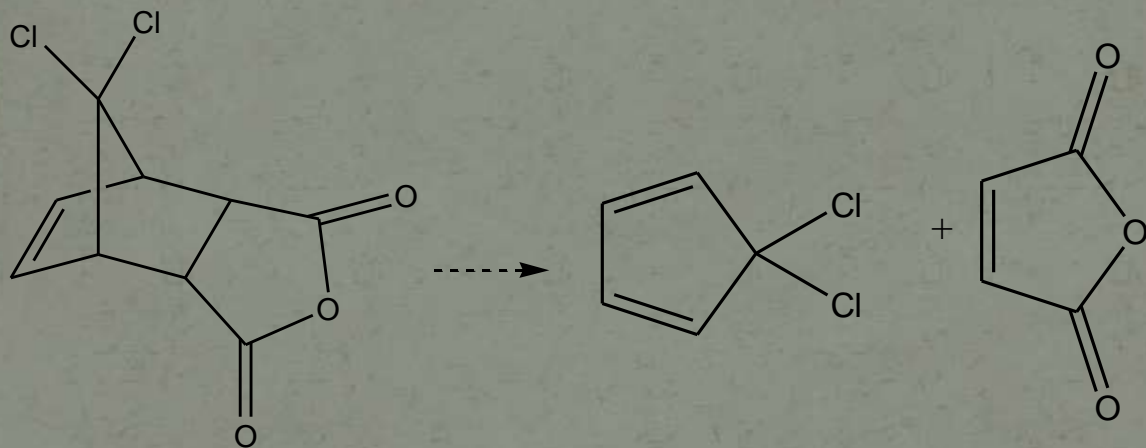
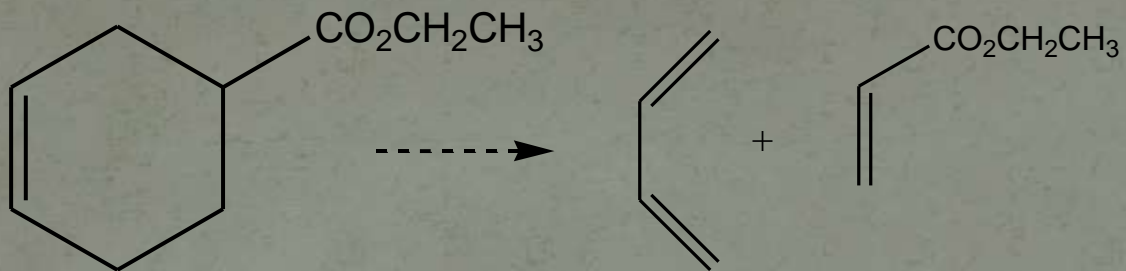
The Retro Diels-Alder Reaction

- When heated, dicyclopentadiene undergoes a **retro Diels-Alder reaction**, and two molecules of cyclopentadiene are re-formed.
- If the newly produced cyclopentadiene is immediately treated with a different dienophile, it reacts to form a new Diels-Alder adduct with this dienophile.
- This is how cyclopentadiene used in Diels-Alder reactions is produced.

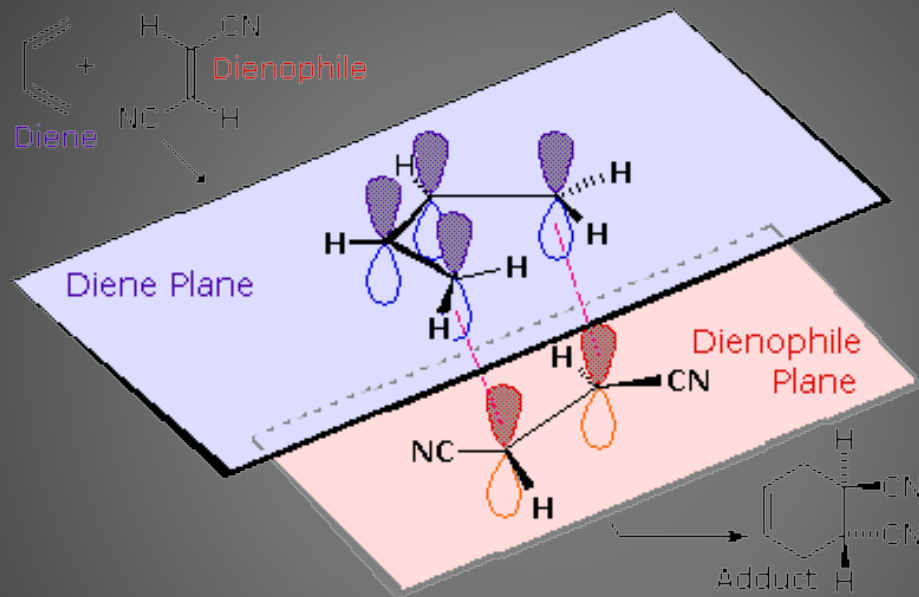
Retro Diels–Alder reaction



This diene can now be used with a different dienophile.



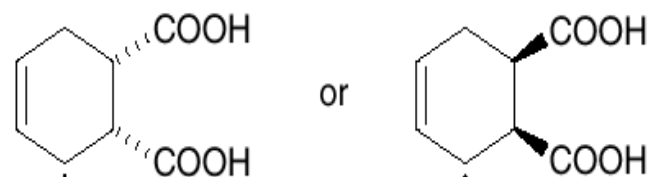
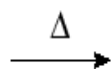
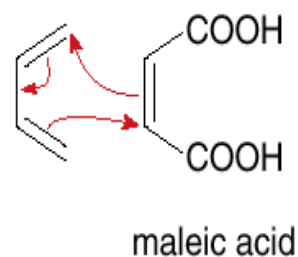
STEREO CHEMISTRY



The diels alder reaction is stereospecific. Substituents that are cis in dienophile remain cis in product. It is same in the case of trans.

The stereochemistry of the dienophile is retained.

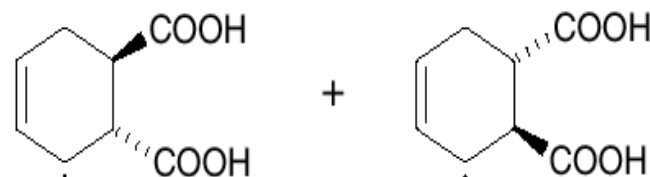
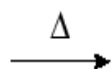
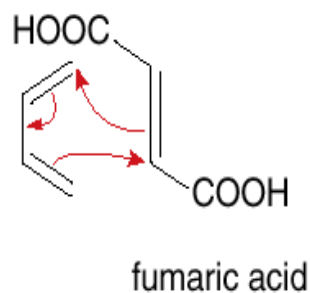
cis dienophile



cis product

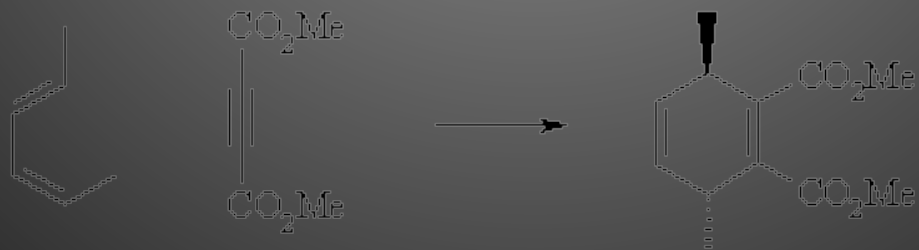
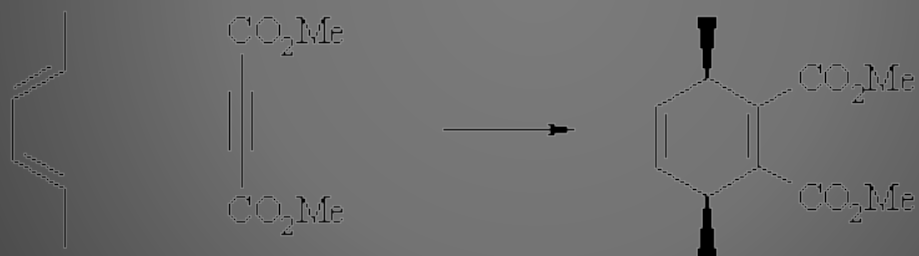
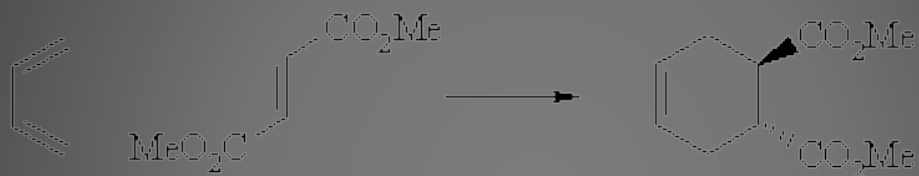
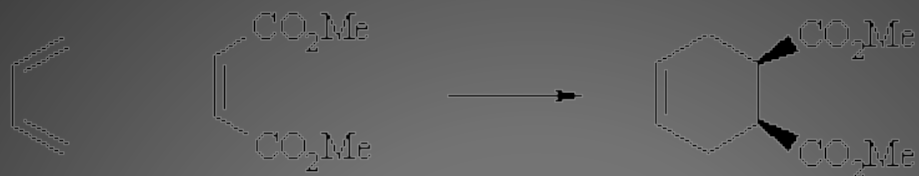
an achiral meso compound

trans dienophile



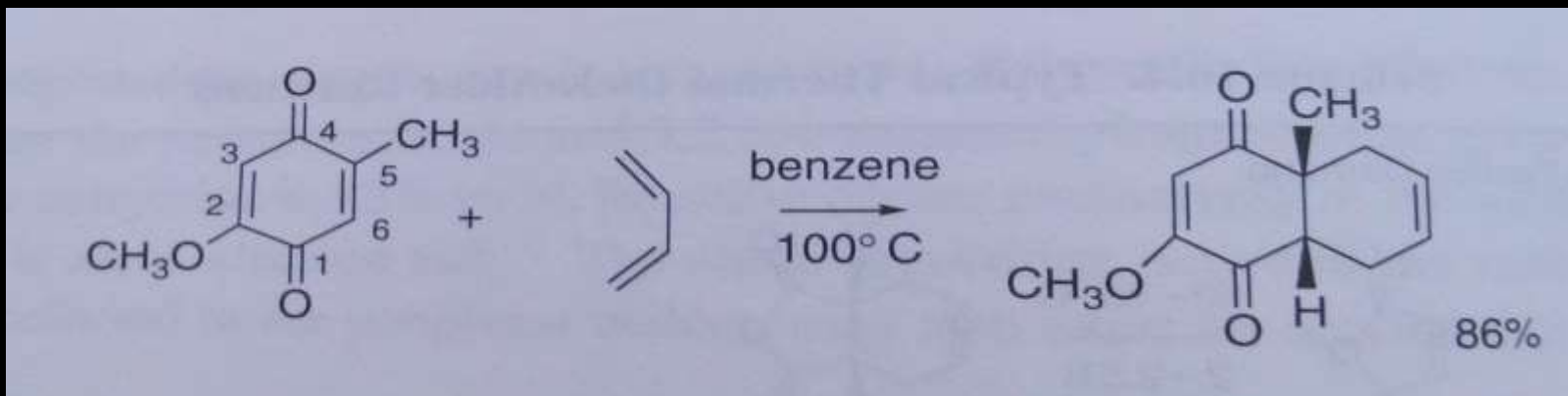
trans product

enantiomers

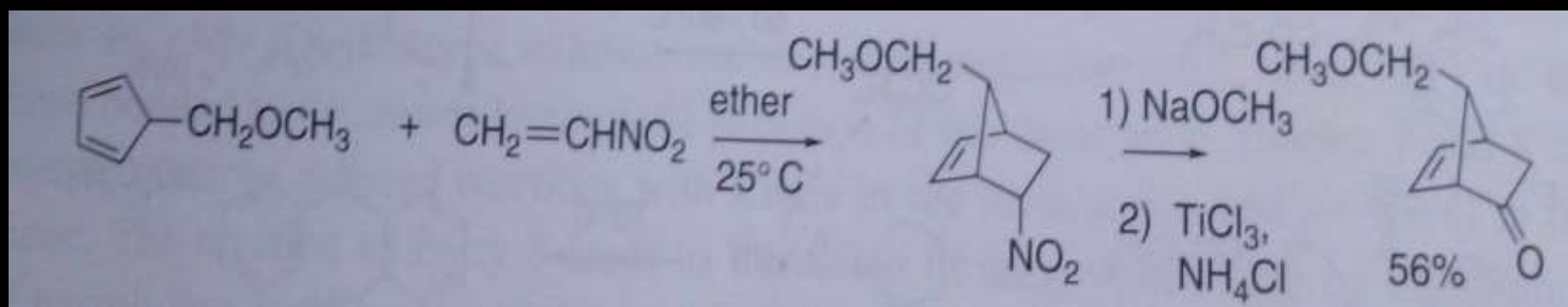
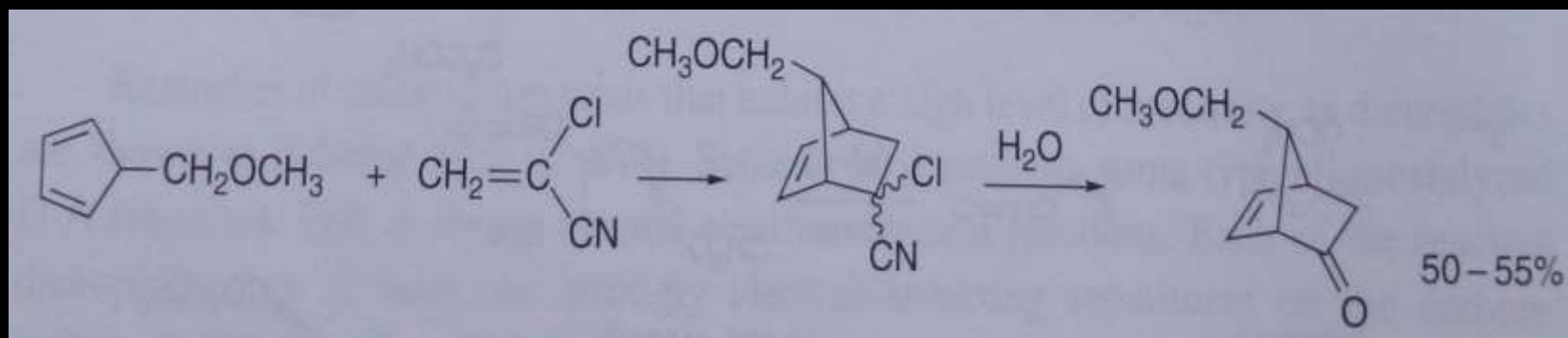


APPLICATION

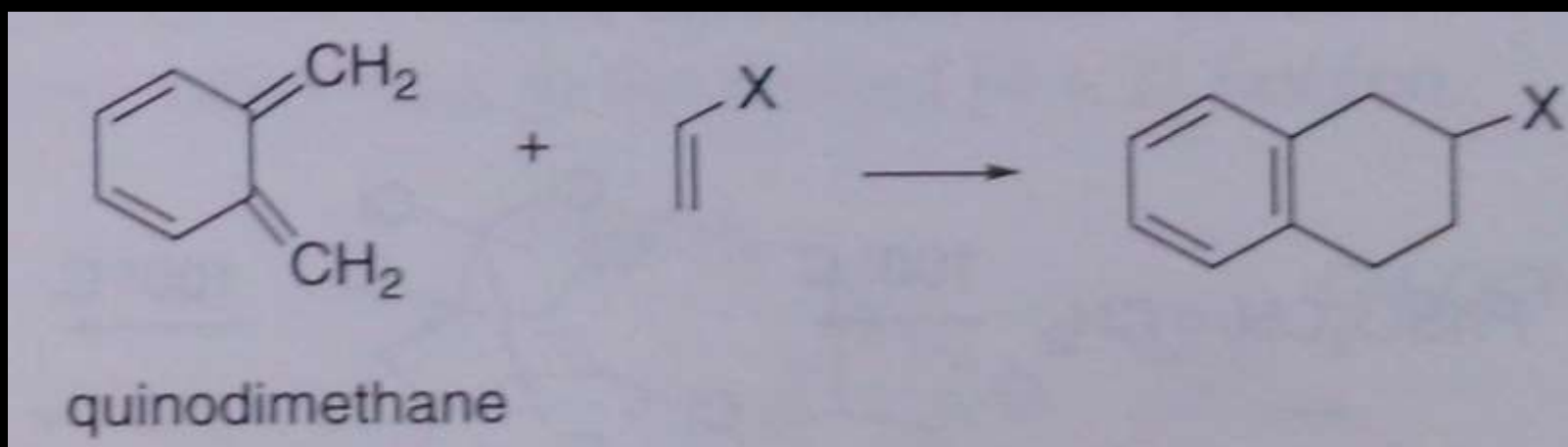
1. Use for the synthesis of steroids



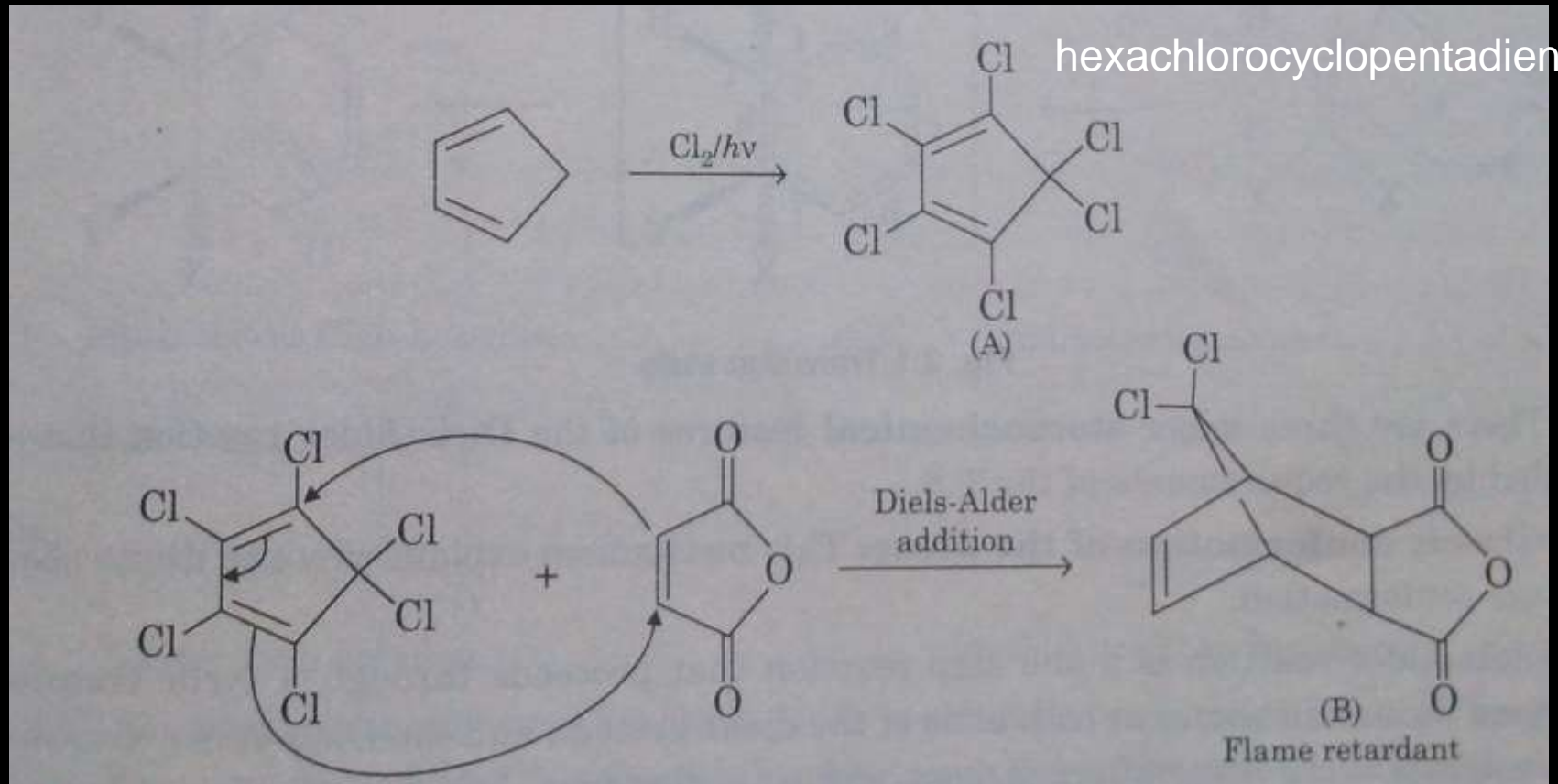
2. Use for the synthetic equivalent of unreactive species



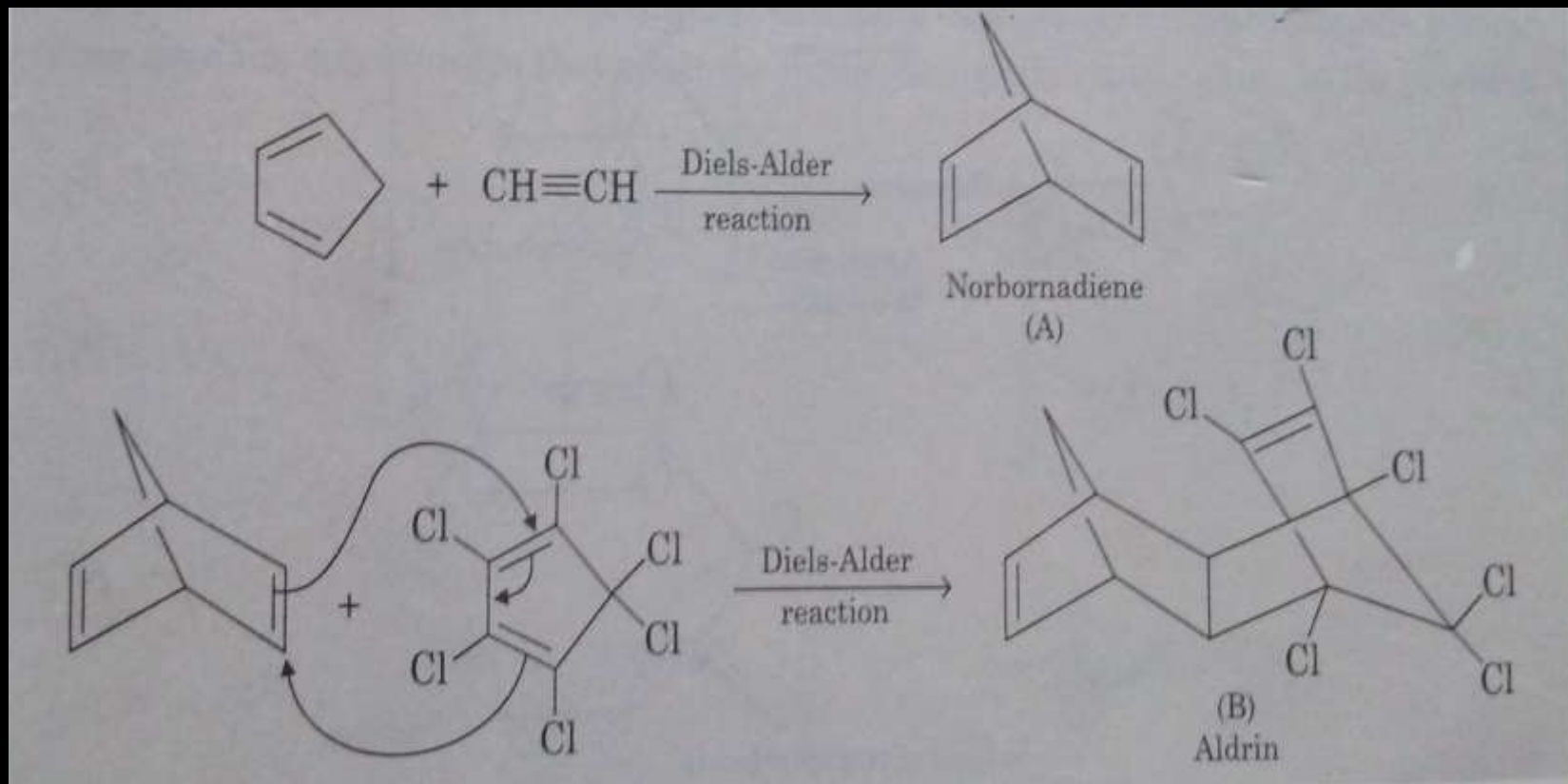
3. Use for the aromatic stabilization



4. Use for the synthesis of flame retardant



5. Use for the synthesis of pesticide





THE END