

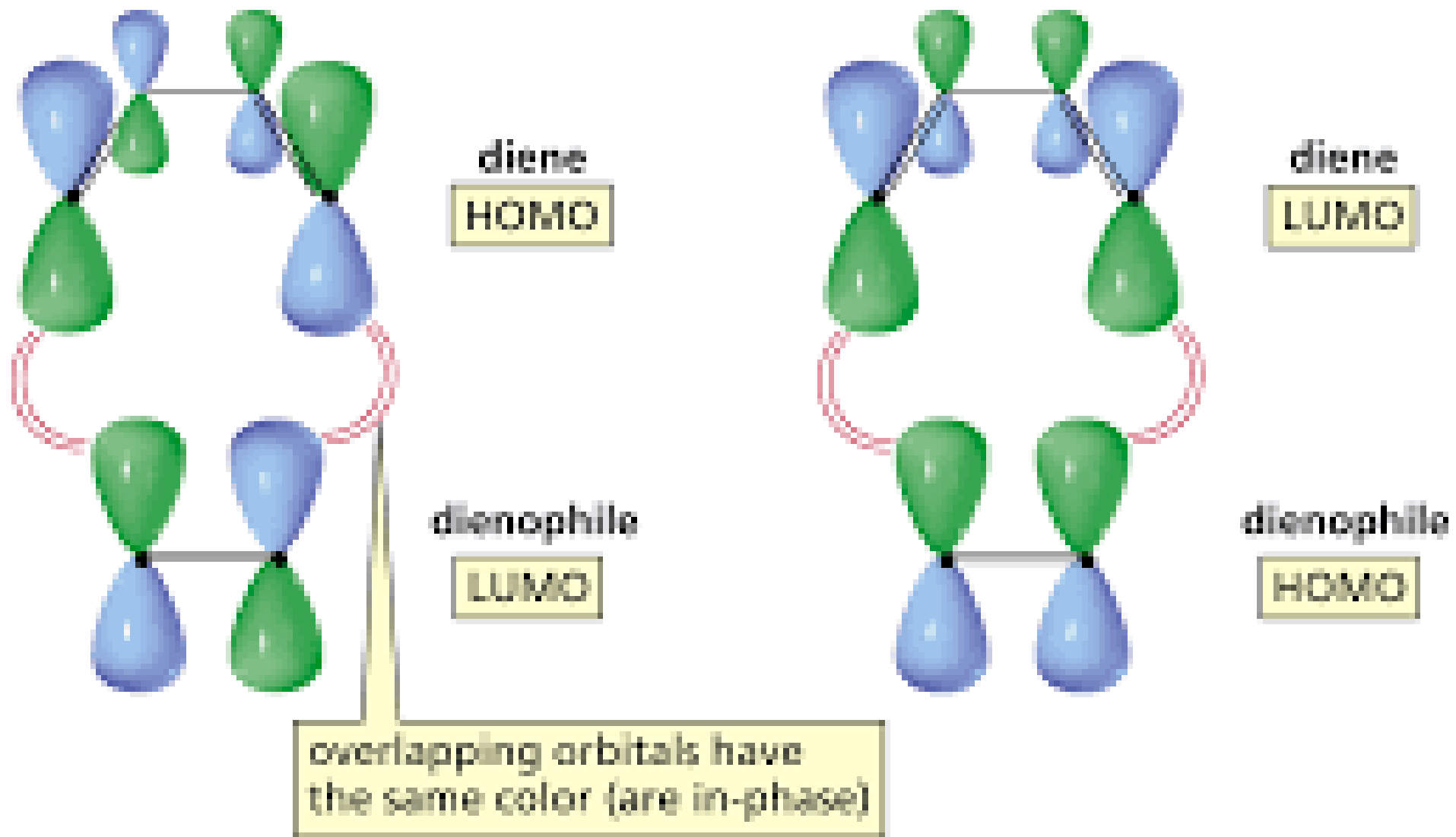
**Department of Chemistry, B. N. College Bhagalpur**

<http://bncollegebgp.ac.in/>

8 May 2020

Dept. of Chem. B. N. College BGP\_ Dr. Ambika Kr.

# Topic: Diels-Alder Reaction





Otto Diels

# Diels-Alder Reaction



Kurt Alder

- Method for synthesis of 6-membered ring
- One-step, concerted reaction
- Termed [4+2] cycloaddition reaction where  $4\pi$  and  $2\pi$  electrons react.



# Diels-Alder Reaction

- Discovered by O. Diels and K. Alder in 1928.
- Occur between a conjugated diene and substituted alkene (dienophile) to form cyclohexene ring system.
- Concerted reaction (single step), can be accelerated by heating or using some catalysts.
- [ 4+2 ] cycloaddition reaction.
- In retro Diels-Alder reaction, the six membered ring is break down to regenerate the diene and dienophile using high temperature usually.
- Stereoselective reaction ( mainly one product formed).



# Diels-Alder Reaction

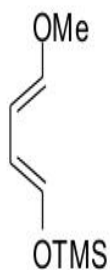
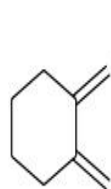
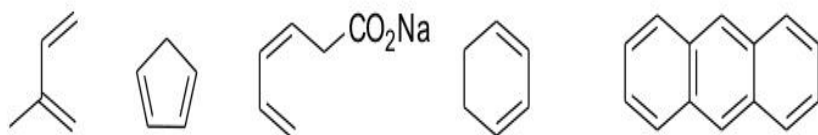
- Stereospecific reaction ( reactants can keep their stereochemistry).
- No transition states or charged intermediates.
- All electrons moving in same time to form two new  $\sigma$  bonds.
- 100 % economic ( No. of reactants atoms = No. of products atoms).
- If one or more of diene or dienophile atoms are not carbon ,the reaction is hetero-Diels-Alder reaction.

Diels-Alder reaction is the best known [4 + 2] cycloaddition reaction. This reaction is thermally allowed reaction. Diels-Alder reaction is photochemically forbidden. Since Diels-Alder reaction is the most common [4 + 2] cycloaddition reaction, let us first discuss the general description of this reaction.

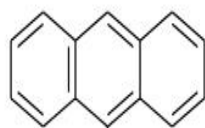
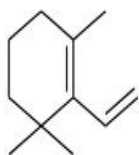
Diels-Alder reactions occur between a conjugated **diene** and an **alkene (or alkyne)**, usually called the **dienophile**.

# The dienes

- Can be cyclic , acyclic carrying many kinds of substituents.
- Must have *s-cis* conformation.
- +I substituted dienes are more reactive than others.

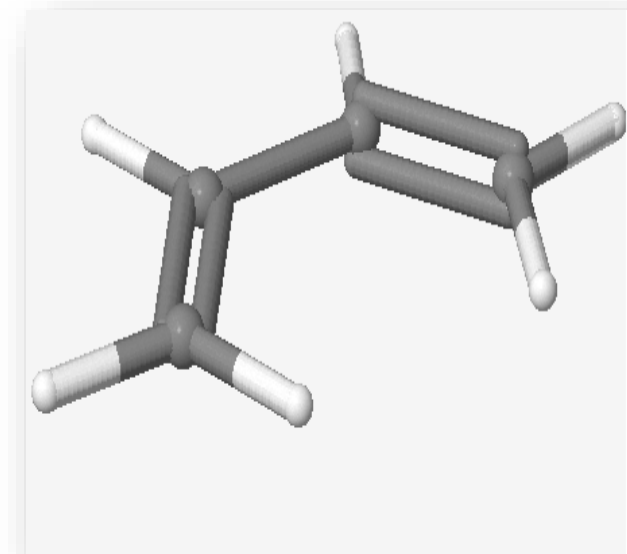


Danishefsky diene

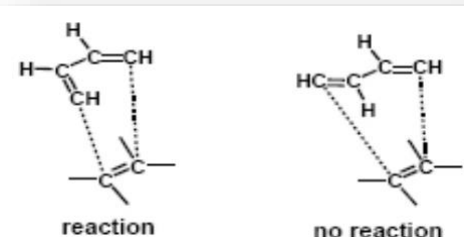
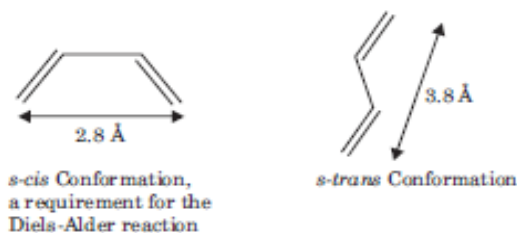
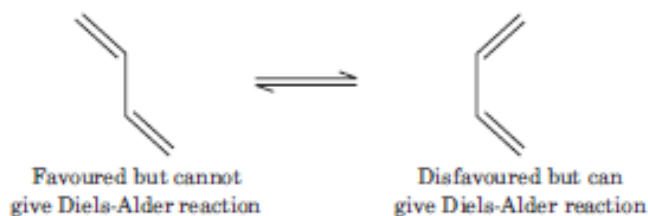


R

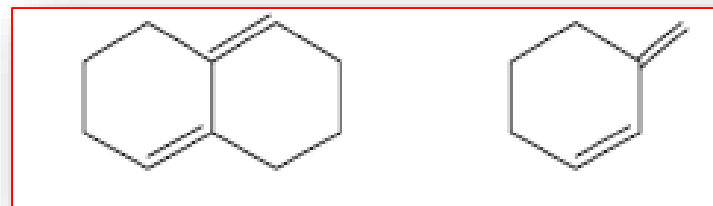
R= Me, OMe, CH(Me)OMe



**The diene** component of the Diels-Alder reaction can be open-chain or cyclic but it must have *s-cis* conformation. Butadiene normally prefers the *s-trans* conformation with the two double bonds as far away from each other as possible for steric reasons. The barrier to rotation about the central  $\sigma$  bond is small (about 30 kJ/mole at 25°C) and rotation to the less favourable but reactive *s-cis* conformation is rapid.



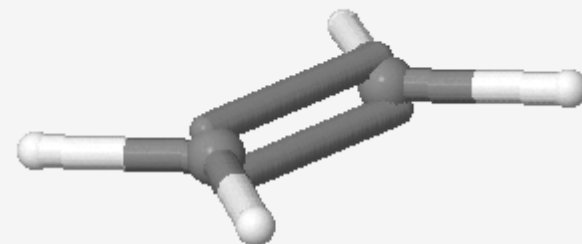
This explains why dienes such as those given on right side **will not serve as dienes** in the Diels-Alder reaction.





# The dienophiles

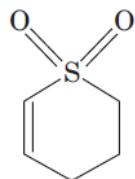
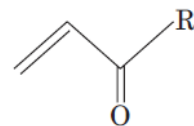
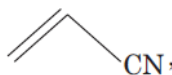
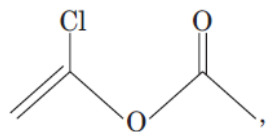
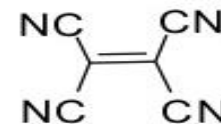
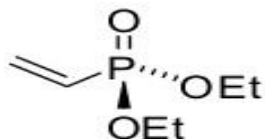
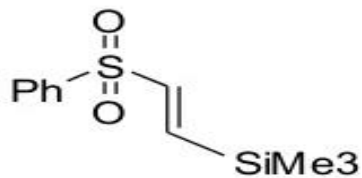
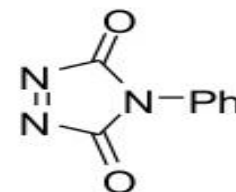
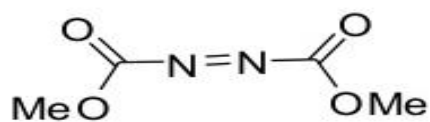
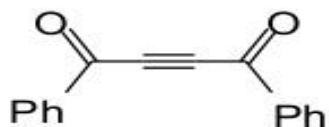
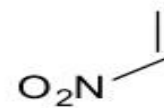
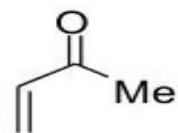
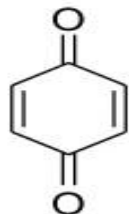
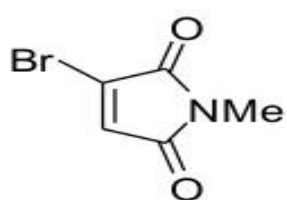
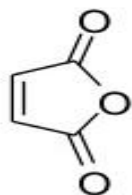
- Wide range of dienophiles can be used including cyclic, acyclic and hetero compounds.
- Perfect dienophiles are alkenes conjugated to electron withdrawing groups such as carbonyl, nitro, cyano, halogens...*etc*
- -I groups increase the rate of D.A reaction.
- D.A reaction between alkene and diene without any substituents can take place but with low yield.



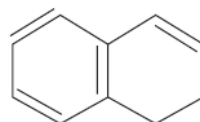
The most common **dienophiles** are the electron-poor alkenes and alkynes. Since electron-poor alkenes and alkynes are prone to react with a diene, these are called dienophiles (lover of dienes). Thus the simple alkenes and alkynes such as ethylene and acetylene are not good dienophiles. A good dienophile generally has one or more electron-withdrawing groups pulling electron density away from the  $\pi$  bond.

Dienophiles that do undergo the Diels-Alder reaction include conjugated carbonyl compounds, nitro compounds, nitriles, sulphones, arylalkenes, arylalkynes, vinyl ethers, vinyl esters, haloalkenes and dienes.

# The dienophiles

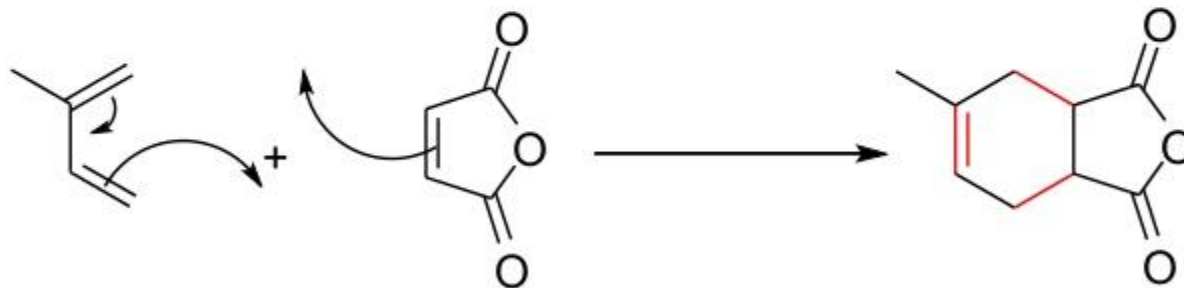


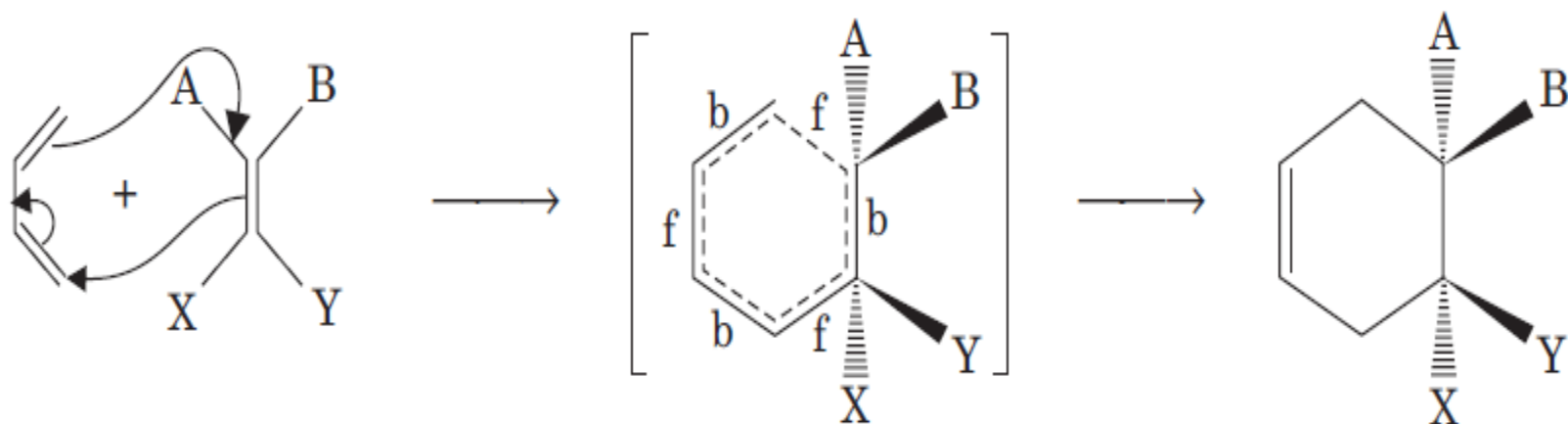
and



# How to know its D.A reaction?

- Since it is {4+2} cycloaddition, the product is, six membered ring, **double bond inside the ring**, conjugate group outside the ring opposite to double bond.

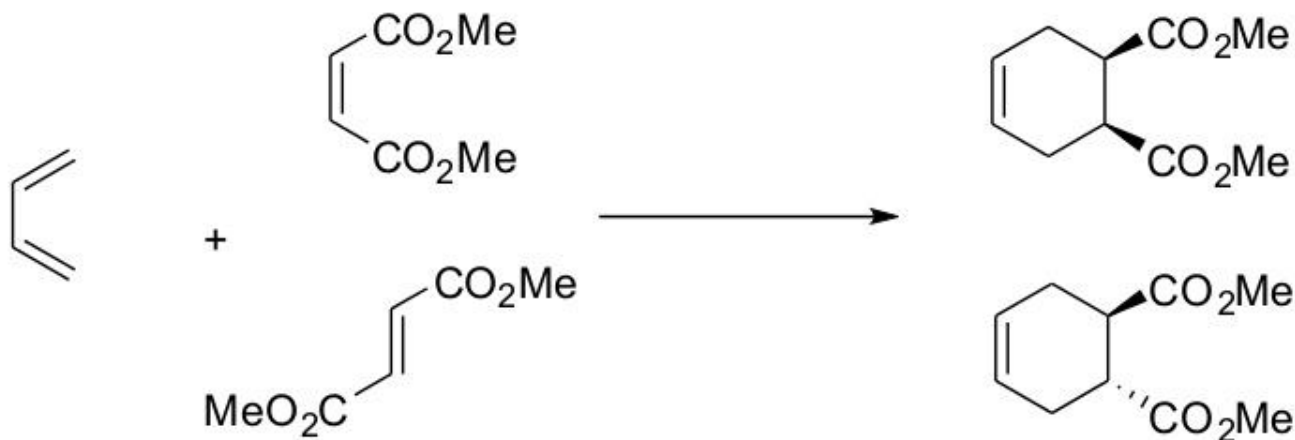




Hypothetical Transition state involved in the mechanism  
(Rxn between butadiene and alkene)

# Stereochemistry

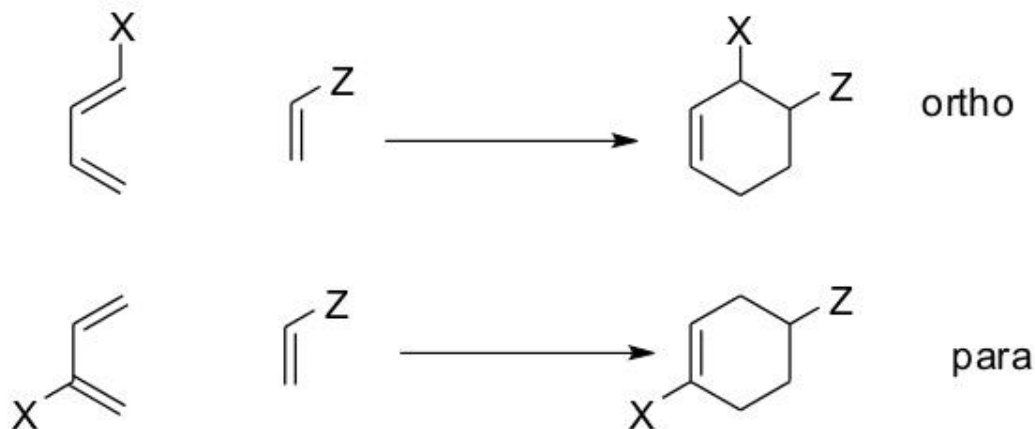
- The stereochemistry of substituents can be retained in the product.
- Cyclic dienes must be in *s-cis* are highly reactive .





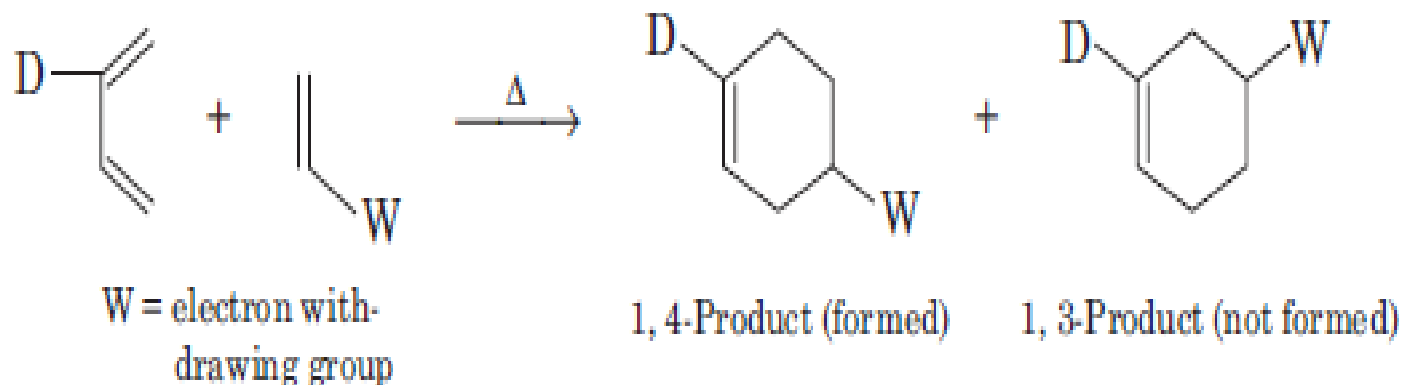
# Regioselectivity

- Diels-Alder reaction can lead to different structural isomers.
- Electronic and steric effects of the substituents.
- Position of these groups is the main factor.
- Usually its *ortho* and *para* directiong.

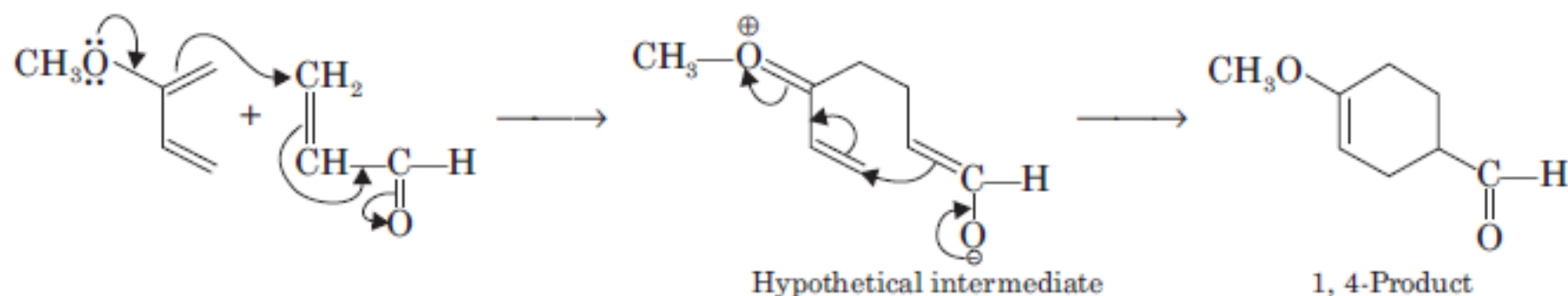


Z= electron-withdrawing group  
x= electron-donating group

**Case I:** When electron-donating group (D) is present on the middle carbon of the diene.

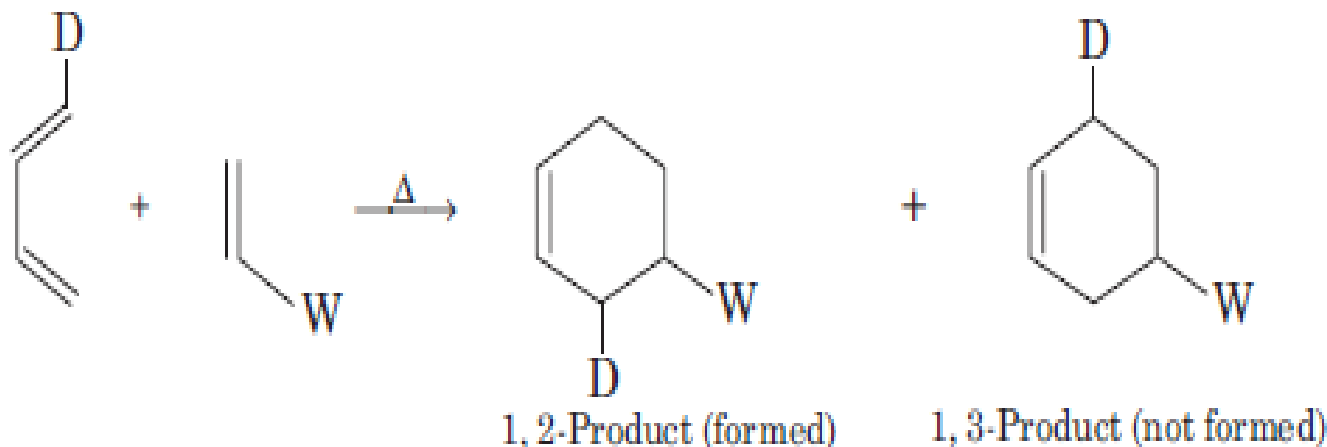


Imaginary flow of electrons in the above case is as follows:

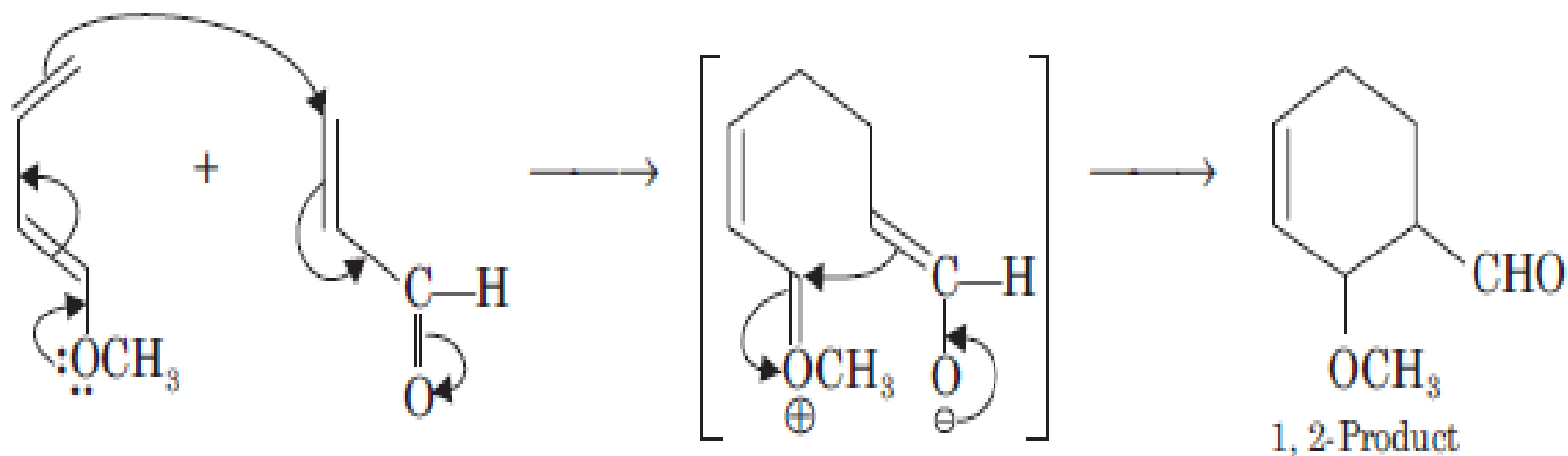


Thus, if electron-donating group is present either at C-2 or at C-3 then in this case product is always 1, 4 and not 1, 3.

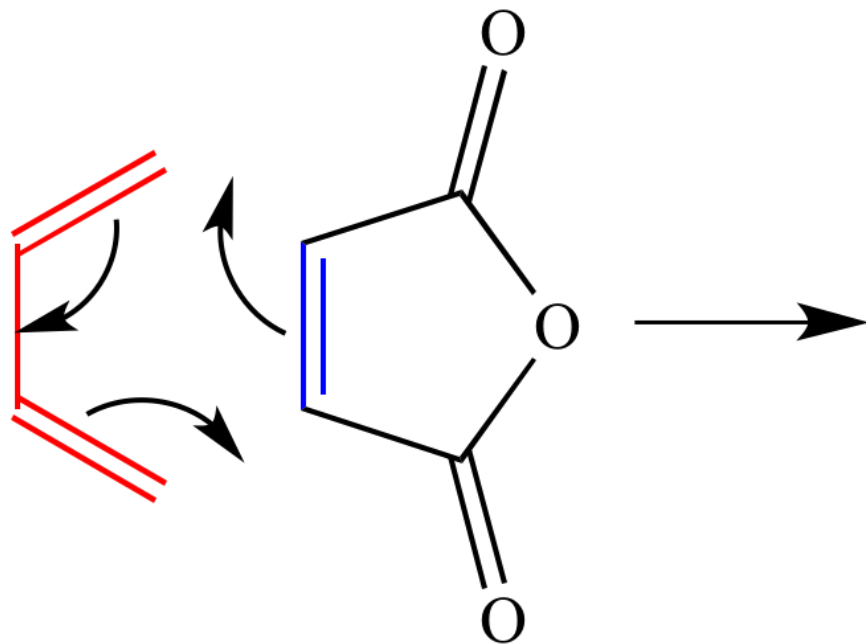
**Case II:** When an electron-donating group is present at terminal carbon of the diene.

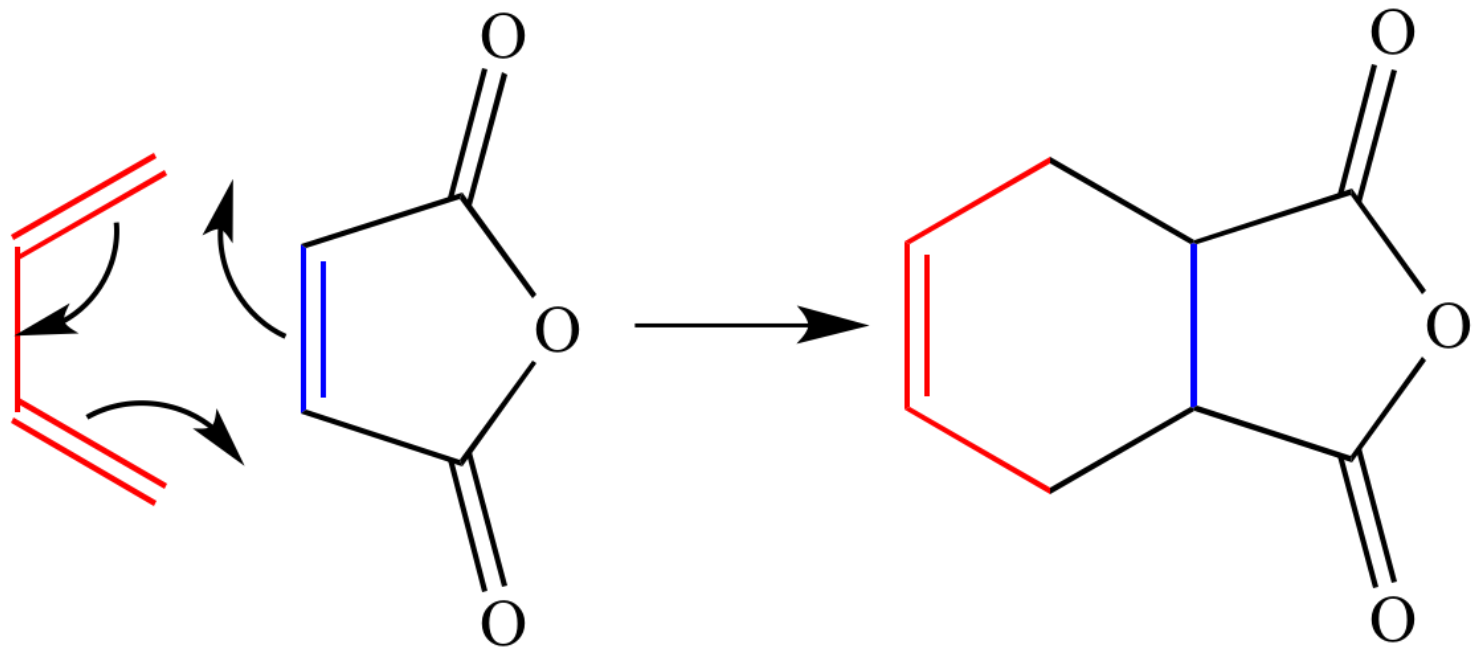


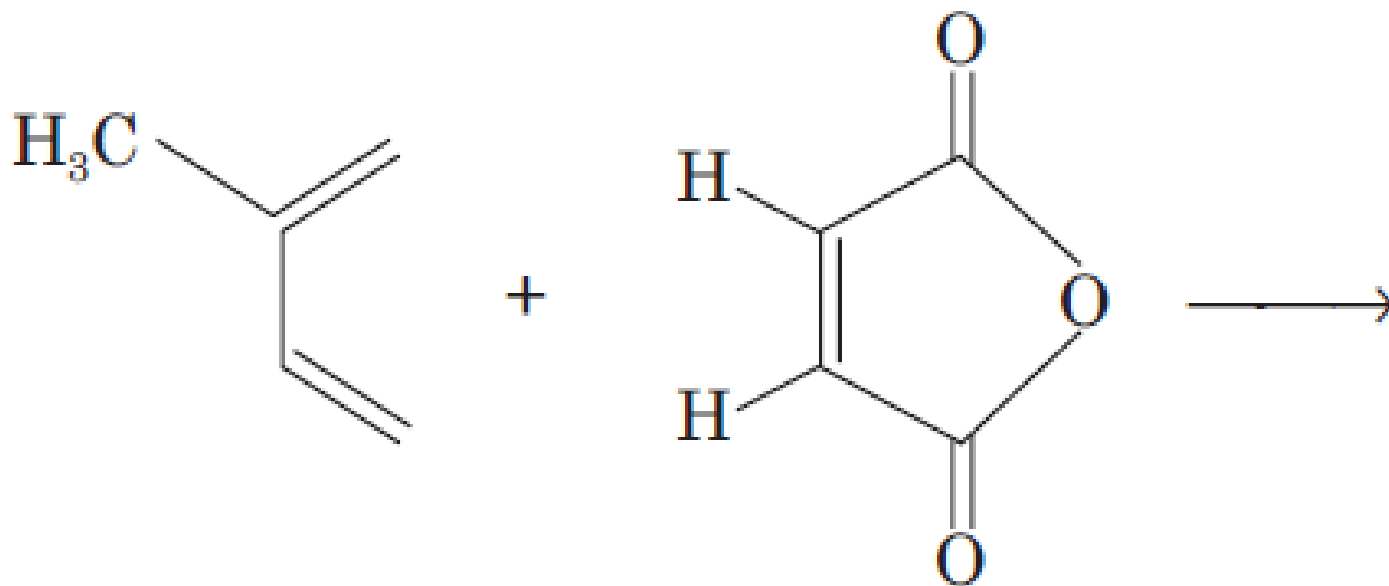
Imaginary flow of electrons in this case is as follows:



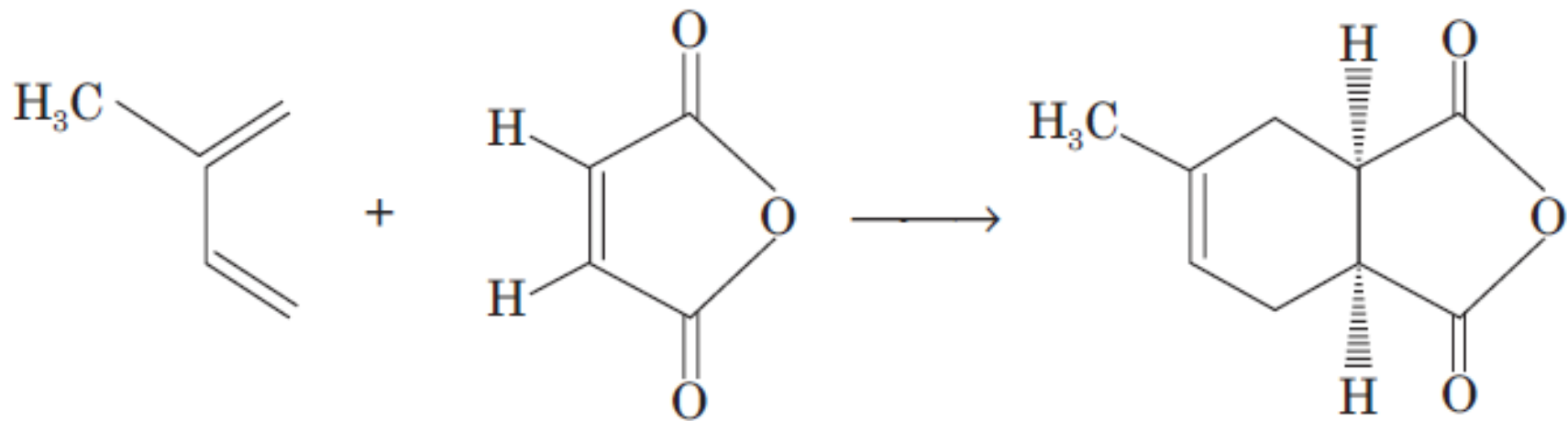
Thus, if electron-donating group is present either at C-1 or C-4 then in this case the product is always 1, 2 and not 1, 3.

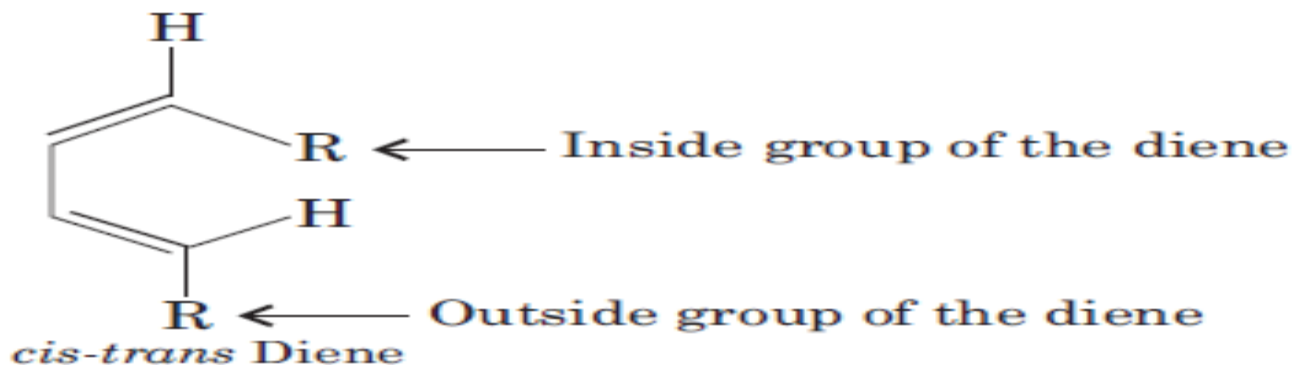
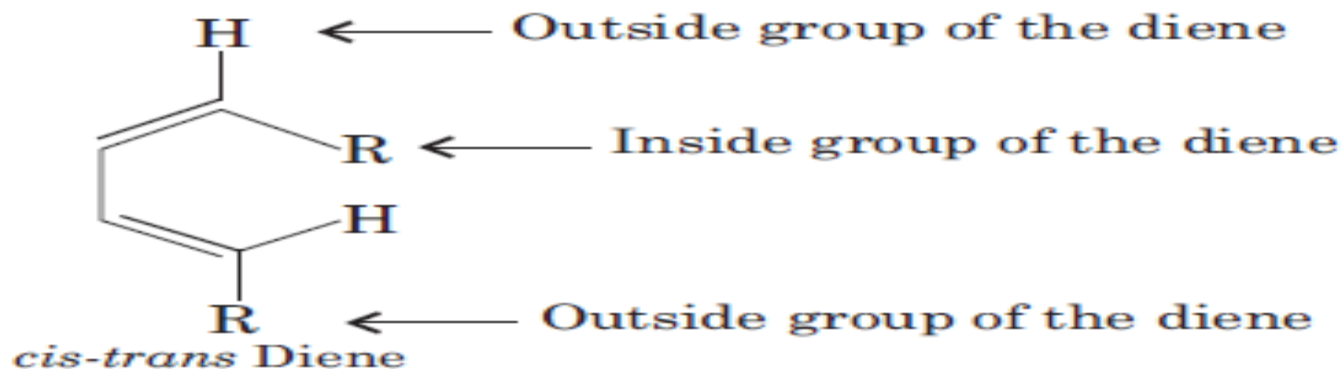
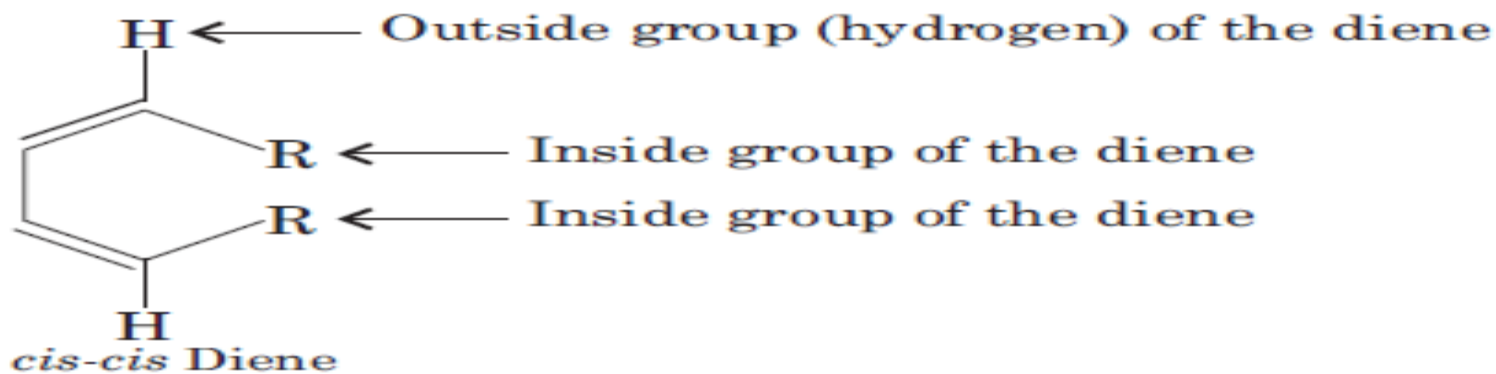


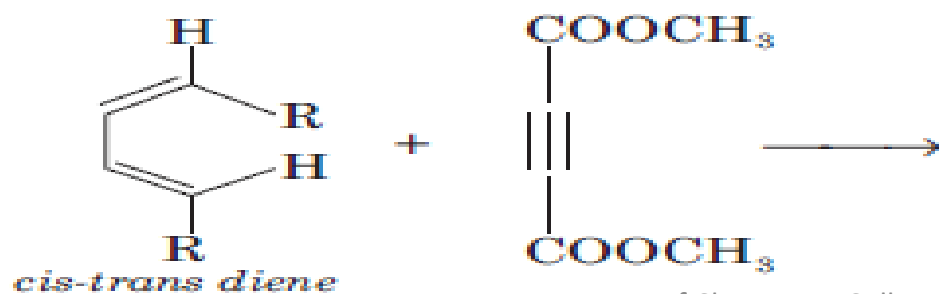
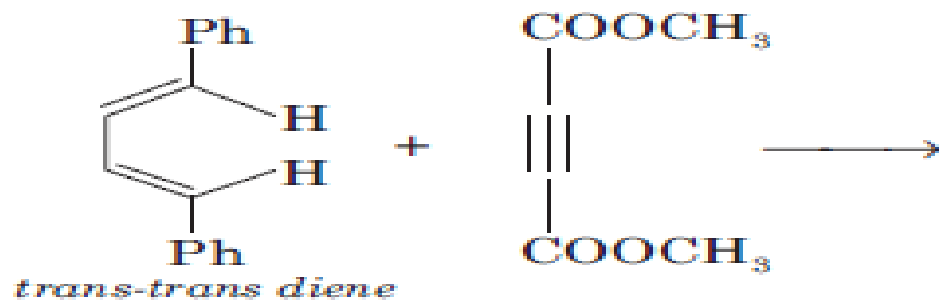
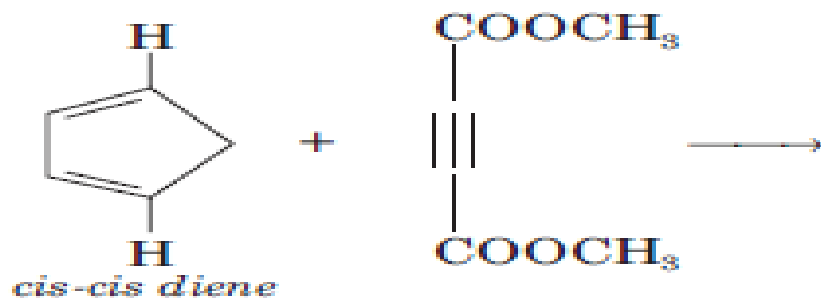
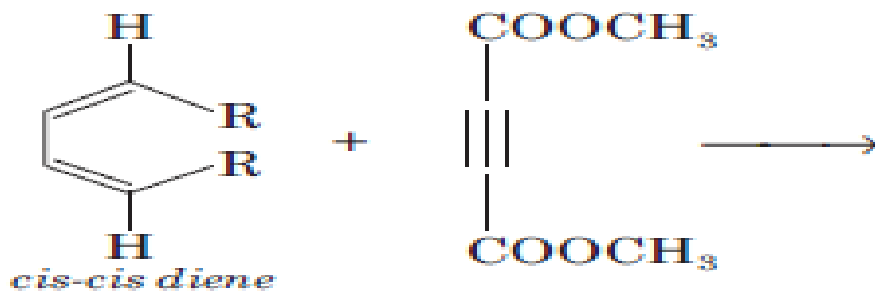


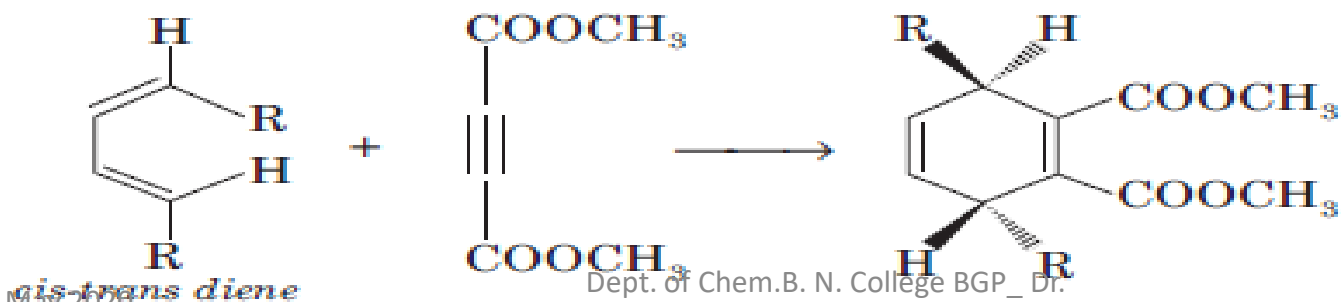
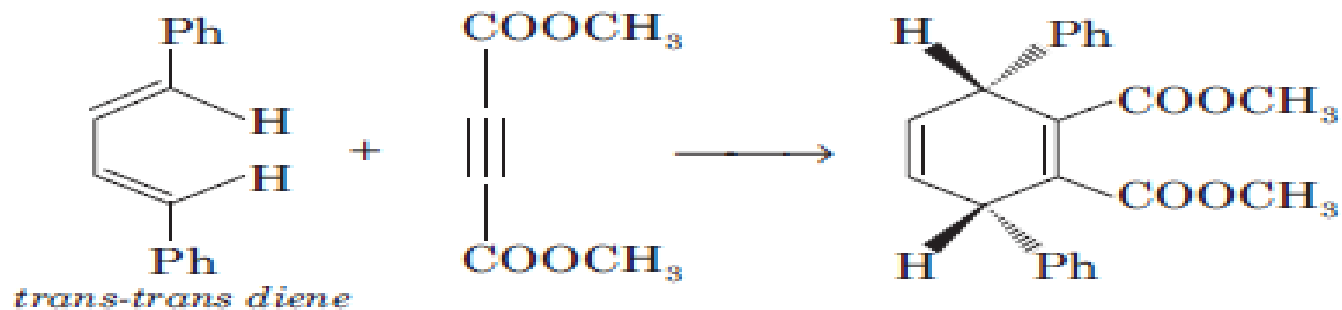
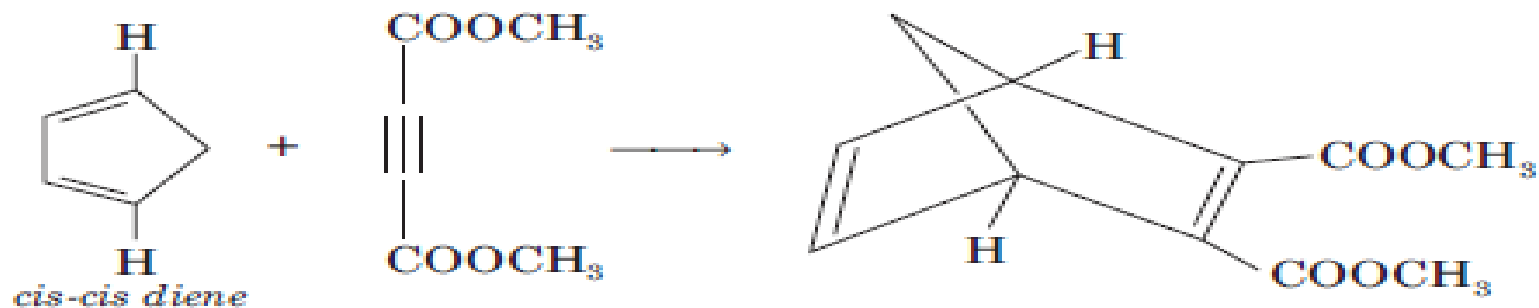
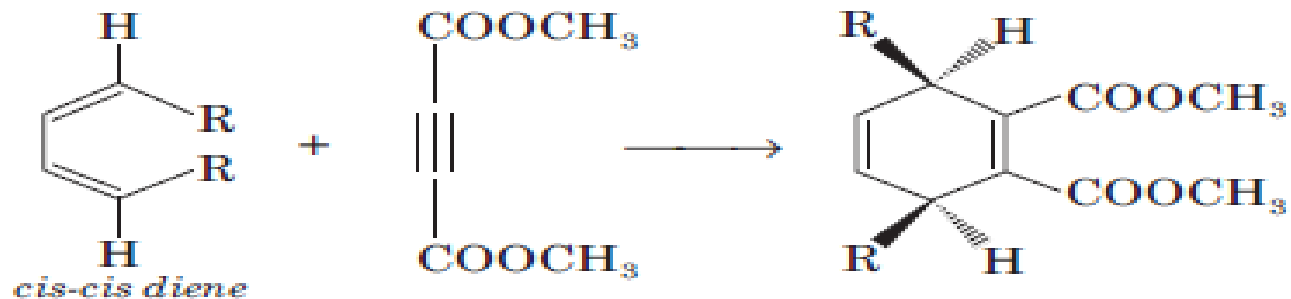


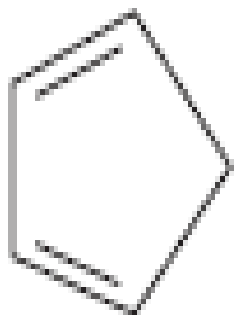




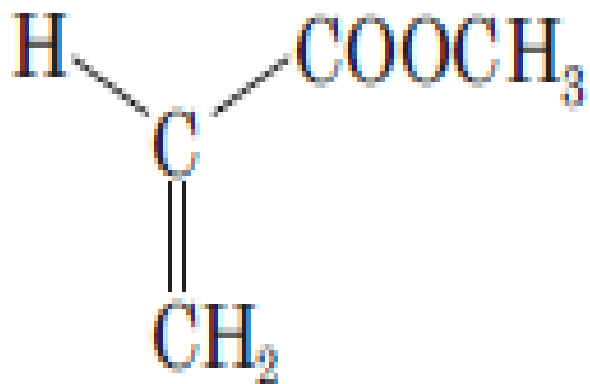


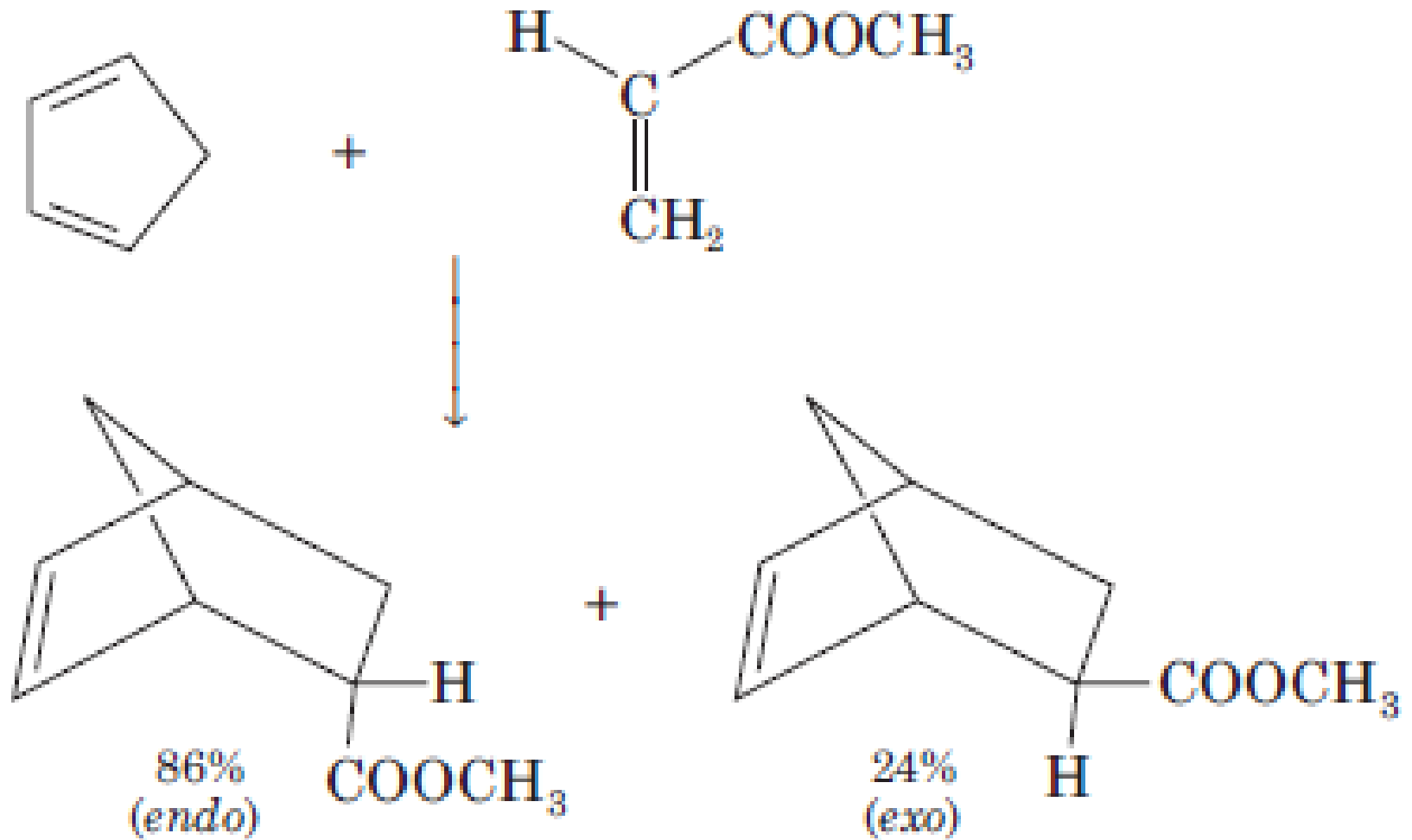






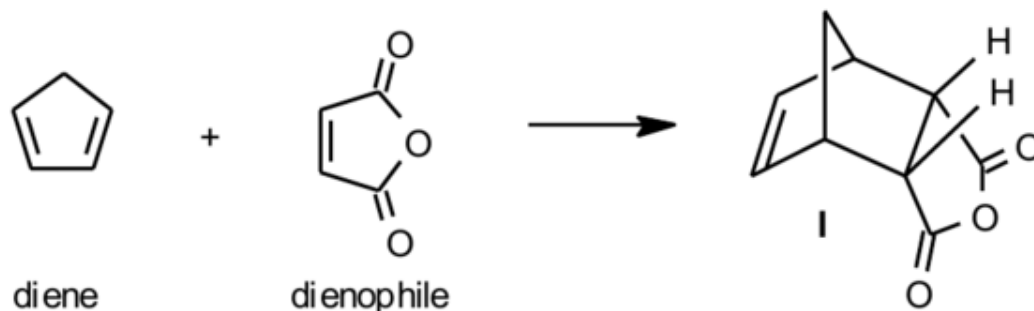
+







# Questions of the Day:



- Diels-Alder reactions are what type of reactions?
- Which structural feature is always formed as the result of Diels-Alder reactions?
- What is a “good diene” (i.e. one that reacts fast in Diels-Alder)?
- What would be a good dienophile?

