



# **CHEM F111 : General Chemistry**

## **Semester II: AY 2017-18**

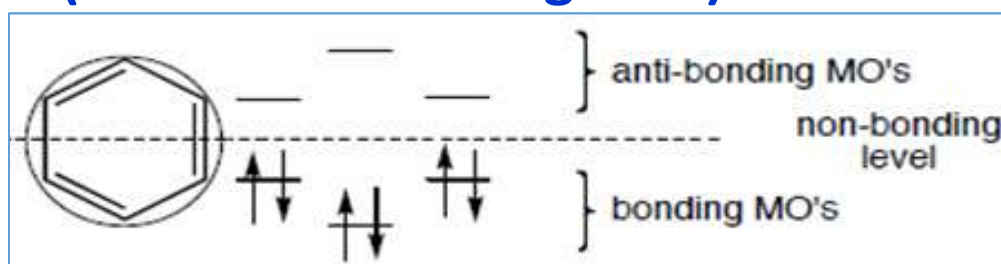
### **Lecture 36 (20-04-2018)**

# Summary of Lecture 35

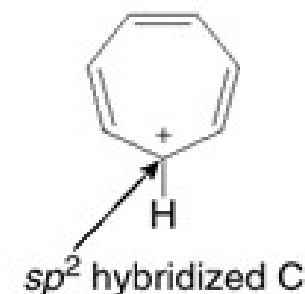
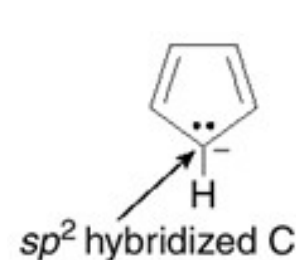
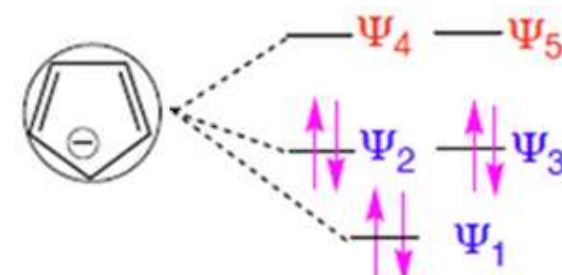
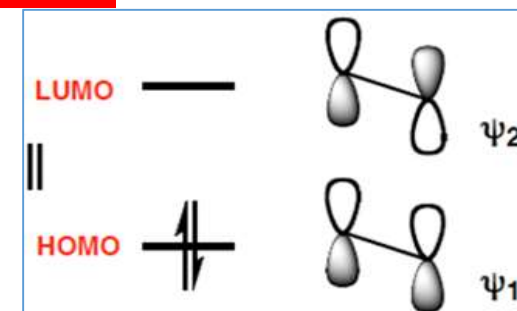


❑ Construction of molecular orbitals for acyclic conjugated compounds

❑ **Construction of  $\pi$  -Mos of cyclic conjugated (Frost-Musulin diagrams)**



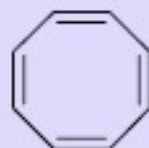
1. A molecule must be cyclic.
2. A molecule must be planar.
3. A molecule must be completely conjugated.
4. A molecule must satisfy Hückel's  $(4n+2)$  rule .



[4] Annulene



[6] Annulene



[8] Annulene



[10] Annulene



# Chemical and Physical Properties of Conjugated Molecules



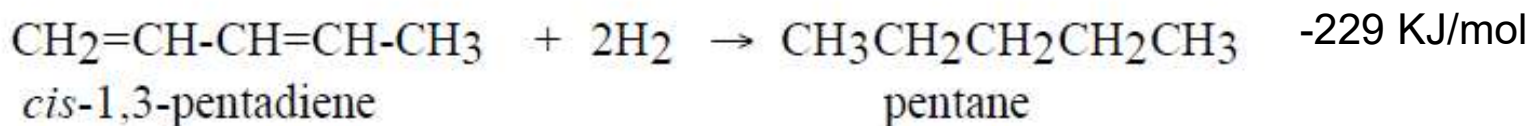
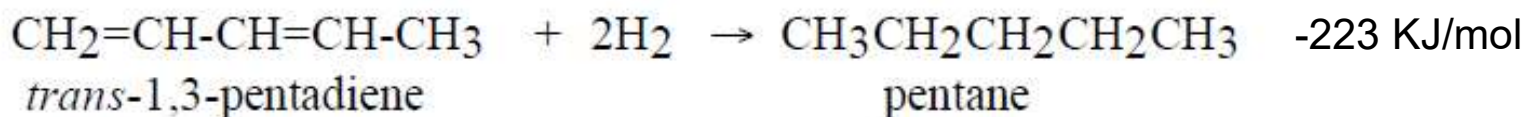
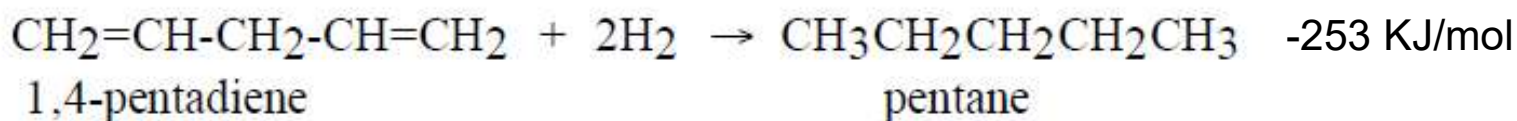
Delocalization means possibility of new orbital overlap and additional stabilization of the system.

Delocalization has important effects on both the stability and chemical reactions of this conjugated molecule.

Molecules with conjugated multiple bonds are generally more stable than comparable molecules with unconjugated multiple bonds.

We can see this extra stability due to conjugation when we compare heats of hydrogenation of related conjugated and unconjugated systems.

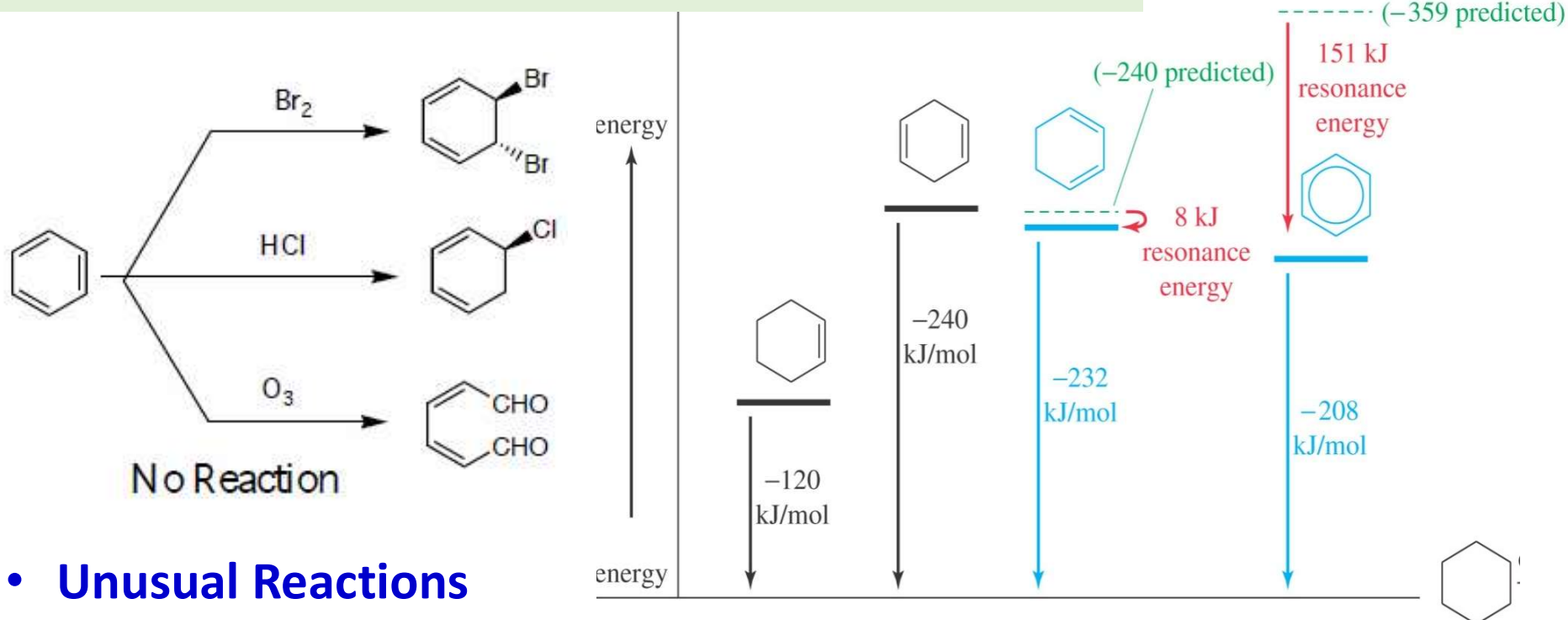
The extra stability (in terms of energy) gained through delocalization is called *delocalization energy or resonance energy*.



# Aromatic vs. Unsaturated Compounds



- Unusual Stability: Based on heats of hydrogenation



- Unusual Reactions

Alkene + KMnO<sub>4</sub> → diol (addition)

Benzene + KMnO<sub>4</sub> → **no reaction**.

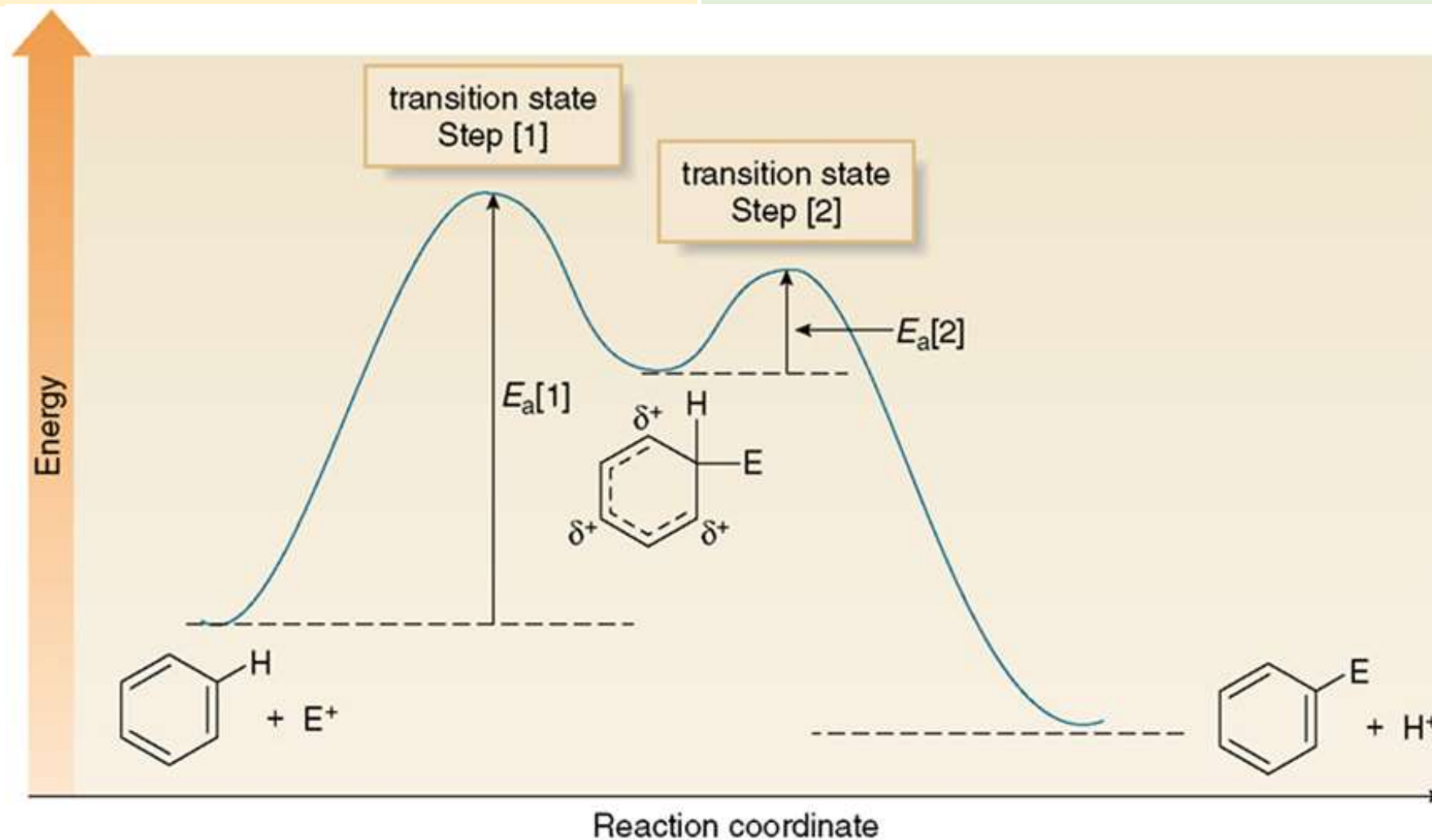
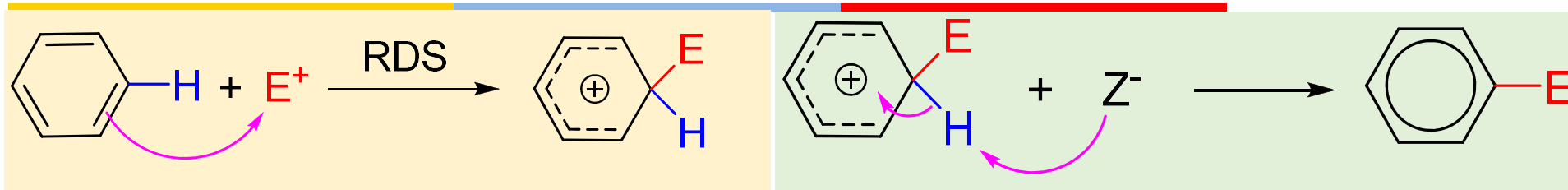
Alkene + Br<sub>2</sub>/CCl<sub>4</sub> → dibromide (addition)

Benzene + Br<sub>2</sub>/CCl<sub>4</sub> → **no reaction**.

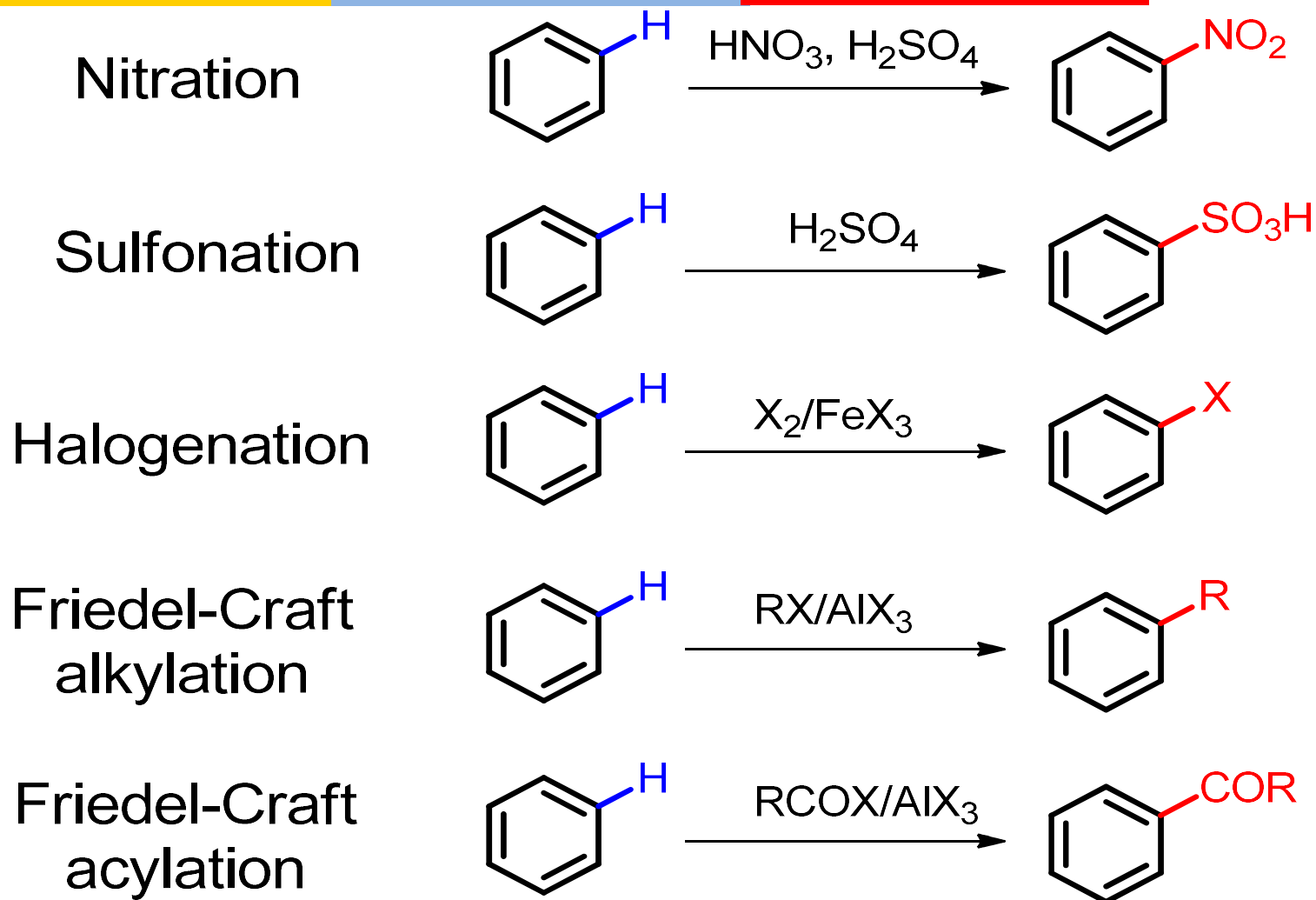
Benzene (aromatic compounds) react with Br<sub>2</sub> in presence of catalyst (FeBr<sub>3</sub> etc.) to form **bromobenzene**.

It's a substitution reaction. Double bonds remain. Aromatic compounds behave differently than unsaturated compounds.

# General Electrophilic Aromatic Substitution Mechanism



# Substitution Reactions of Benzene (aromatic compounds)



The first step in **electrophilic aromatic substitution** is formation of electrophile that attacks the aromatic ring (electron rich) and forms a carbocation, for which three resonance structures can be drawn.



# Electrophile generation in EAS reactions



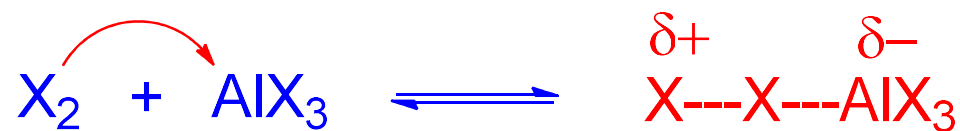
Nitration



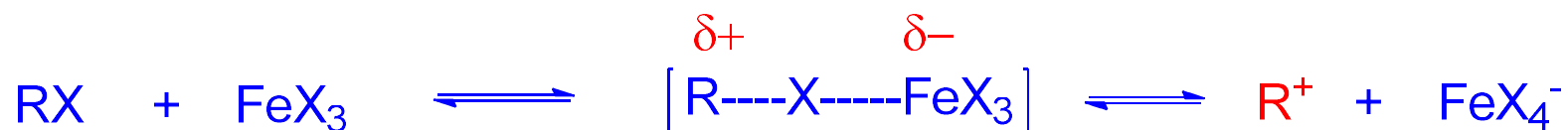
Sulfonation



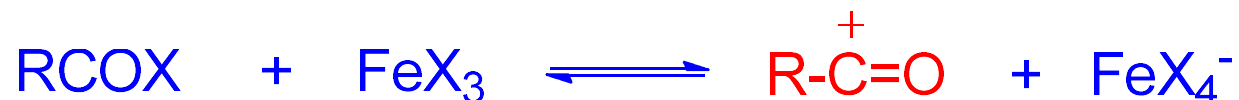
Halogenation



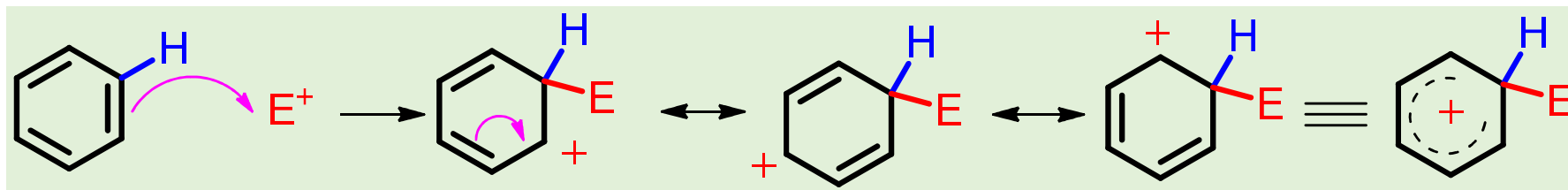
Friedel-Crafts Alkylation/Acylation



(carbocation, can rearrange to form more stable carbocation)

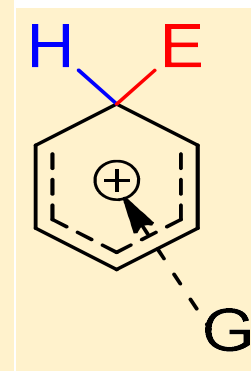


# Reactivity of Substituted Benzene in EAS



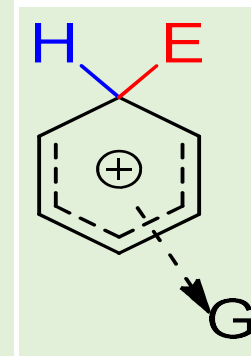
Electron donating groups activate the benzene ring to electrophilic aromatic substitution.

1. electron donating groups increase the electron density in the ring and make it more reactive with electrophiles.
2. electron donation stabilizes the intermediate carbocation, lowers the  $E_{\text{act}}$  and increases the rate.



Electron withdrawing groups deactivate the benzene ring to electrophilic aromatic substitution.

1. electron withdrawing groups decrease the electron density in the ring and make it less reactive with electrophiles.
2. electron withdrawal destabilizes the intermediate carbocation, raising the  $E_{\text{act}}$  and slowing the rate.



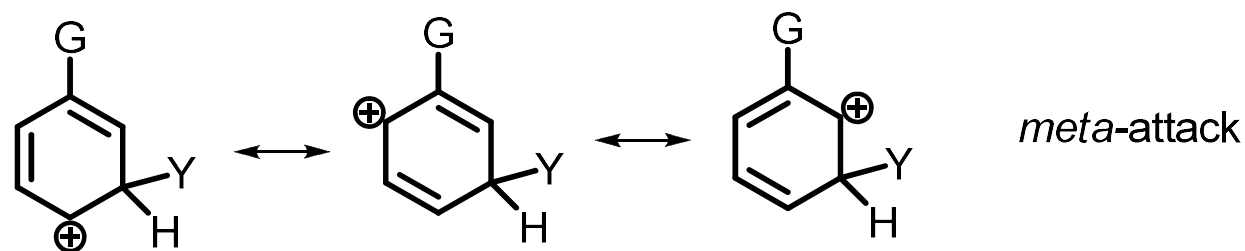
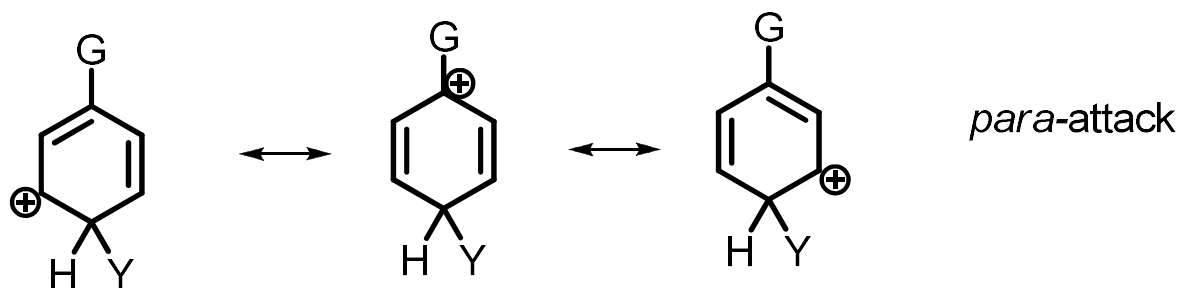
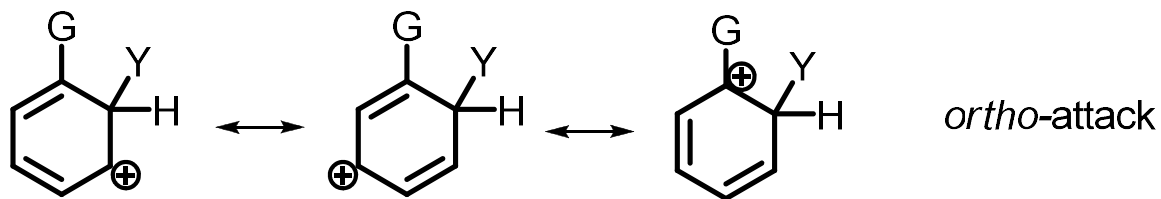


# Orientation in EAS reactions



## Resonance – delocalization via resonance

- electron-donating resonance effect is observed whenever an atom **G** having a lone pair of electrons is directly bonded to a benzene ring.
- electron-withdrawing resonance effect is observed with substituents having the general structure  $G(-Y=Z)$ , where  $Z$  is more electronegative than  $Y$ .



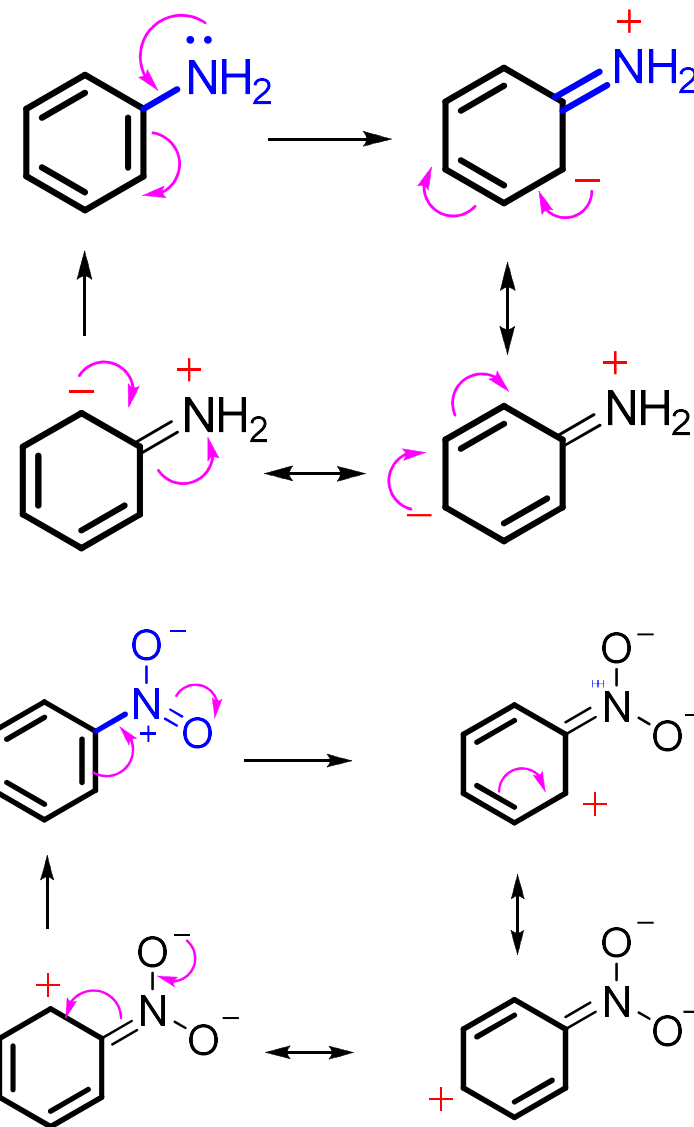
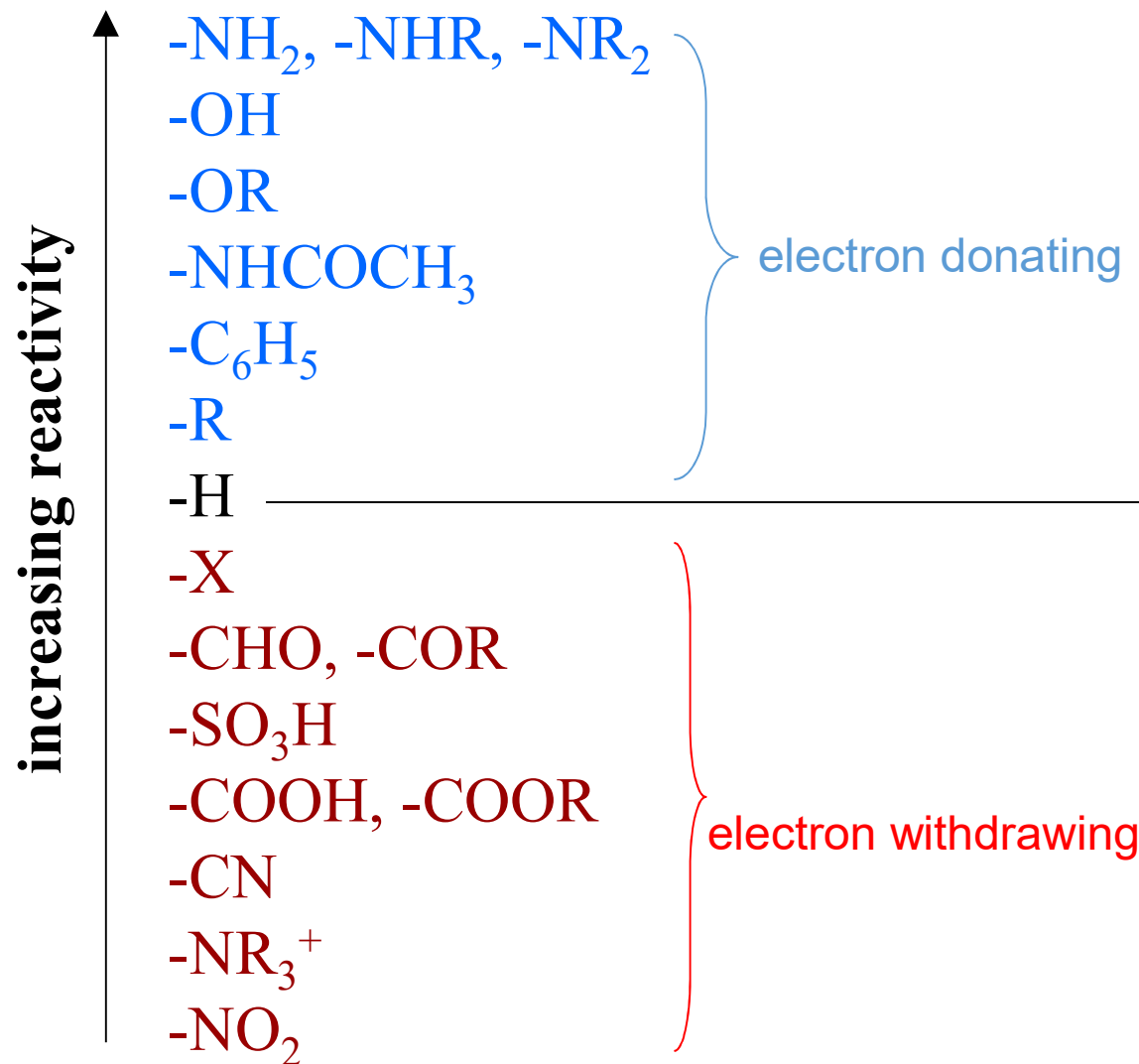
If **G** is an electron **donating group**, following two structures from *ortho* and *para* attack are especially **stable**.

If **G** is an **electron withdrawing group**, following two structures from *meta* attack are especially **unstable**.

# Common Substituent Groups & Effect on EAS Reactions



How the substituent groups on a benzene ring will affect the reactivity and orientation?



## Limitations of Friedel-Crafts alkylation



The intermediate carbocation may rearrange to more stable carbocation prior to alkylation.

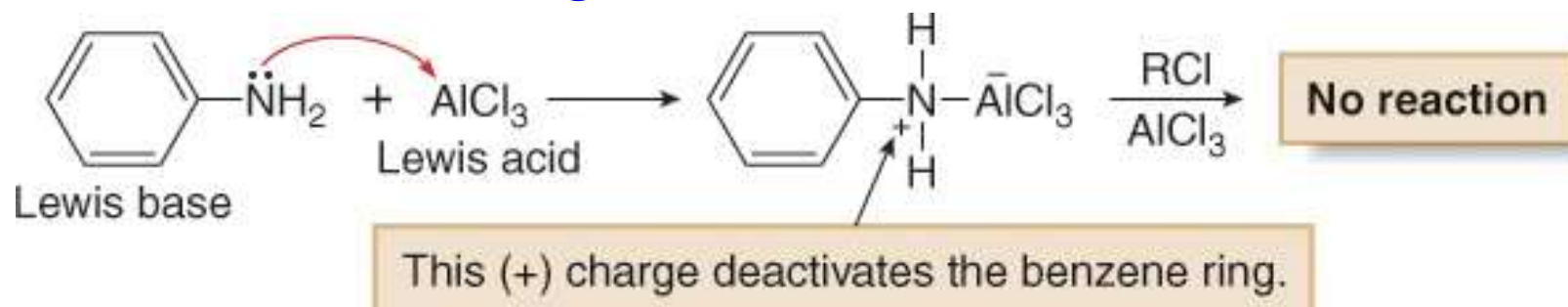
e.g. In case of alkylation with n-butylbromide.

Electron withdrawing groups make benzene ring much less reaction towards Friedel-crafts alkylation.

Aryl and vinyl halides can not be used in Friedel-Crafts alkylation as they do not form stable carbocation.

Polyalkylation frequently occur in in Friedel-Crafts alkylation as alkylbenzene is more electron rich than benzene.

Formation of complex between  $\text{NH}_2$  group and the  $\text{AlCl}_3$  catalyst in anilines deactivates the ring towards Friedel-Crafts reactions.



# Orientation in EAS reactions



Electron donating groups stabilize the intermediate carbocations for *ortho-* and *para-* in EAS more than for *meta-*. The  $E_{\text{act's}}$  for *ortho-/para-* are lower and the rates are faster.

**Electron donating groups direct *ortho-/para-* in EAS.**

Electron withdrawing groups destabilize the intermediate carbocations for *ortho-* and *para-* in EAS more than for *meta-*. The  $E_{\text{act's}}$  for *ortho-/para-* are higher and the rates are slower.

**Electron withdrawing groups direct *meta-* in EAS.**

The halogen atom is unusual in that it is highly electronegative but also has unshared pairs of electrons that can be resonance donated to the carbocation.

**Halogens are electron withdrawing but are *ortho/para* directing in EAS.**

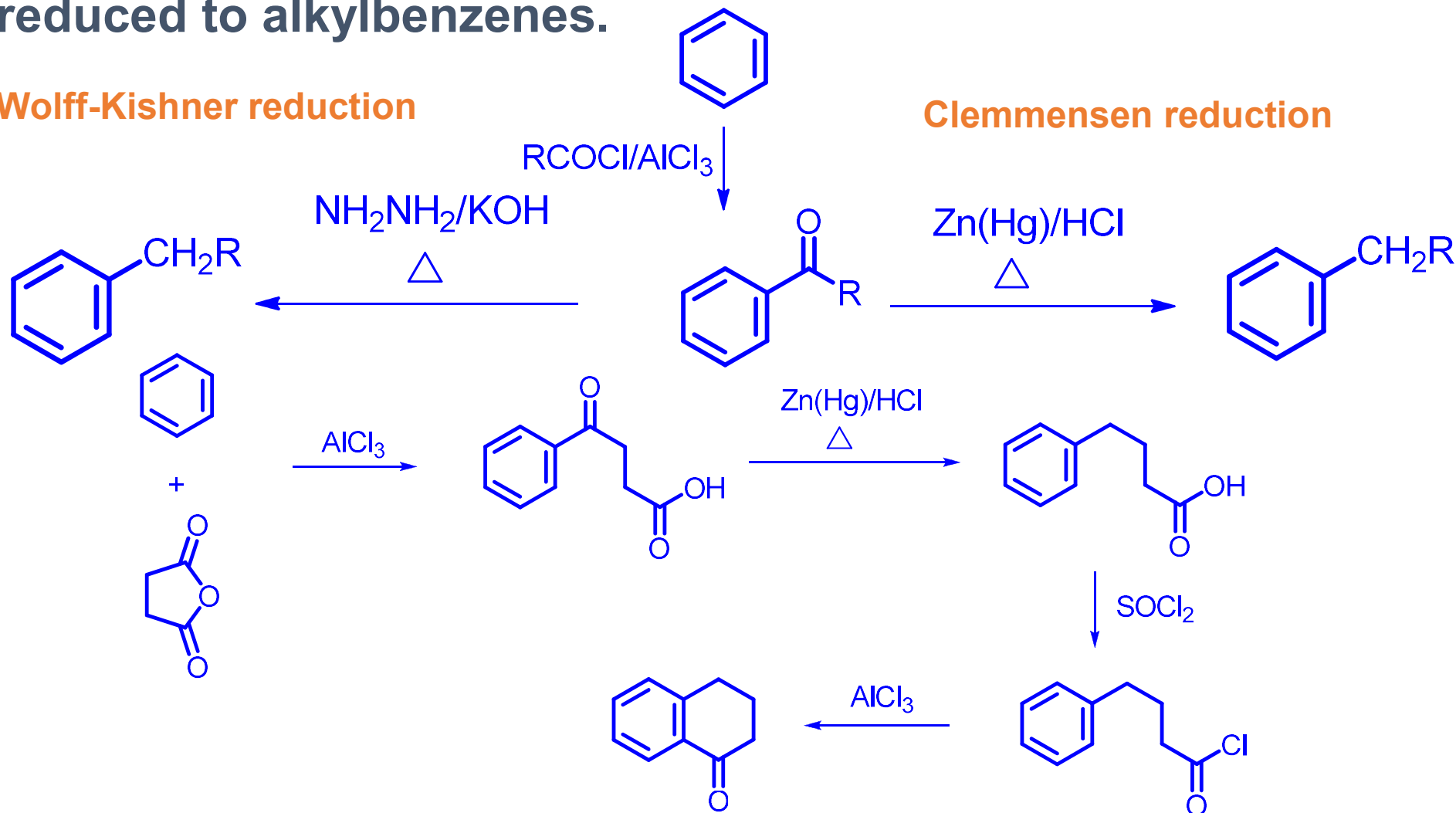
# Alternative to Friedel-Crafts alkylation



To avoid polyalkylation in Friedel-Crafts alkylation ketones formed as products of Friedel-Crafts acylation can be reduced to alkylbenzenes.

## Wolff-Kishner reduction

## Clemmensen reduction

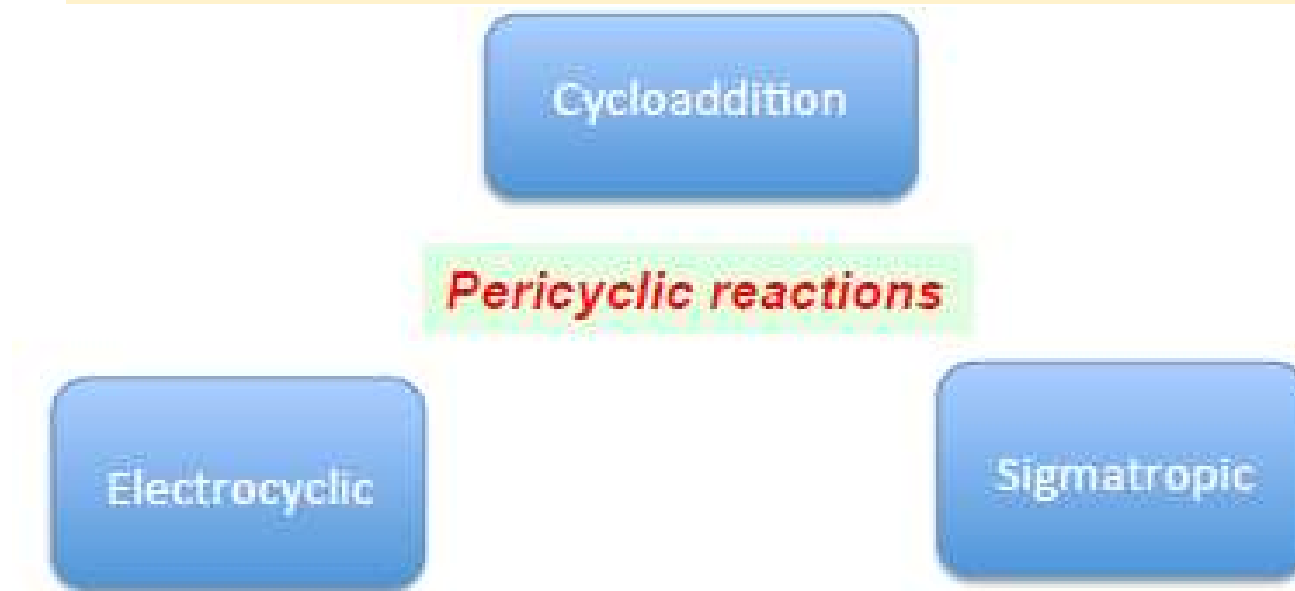


# Pericyclic reactions



- Pericyclic reactions involves a cyclic redistribution of bonding electrons through a concerted process (i. e, without intermediates) and proceed through cyclic transition states.

Two different  $\pi$ -bond-containing molecules react to form a cyclic compound such as [2+2] & [4+2].



An intramolecular reaction in which a new  $\sigma$ -bond is formed between the ends of a conjugated  $\pi$ -system.

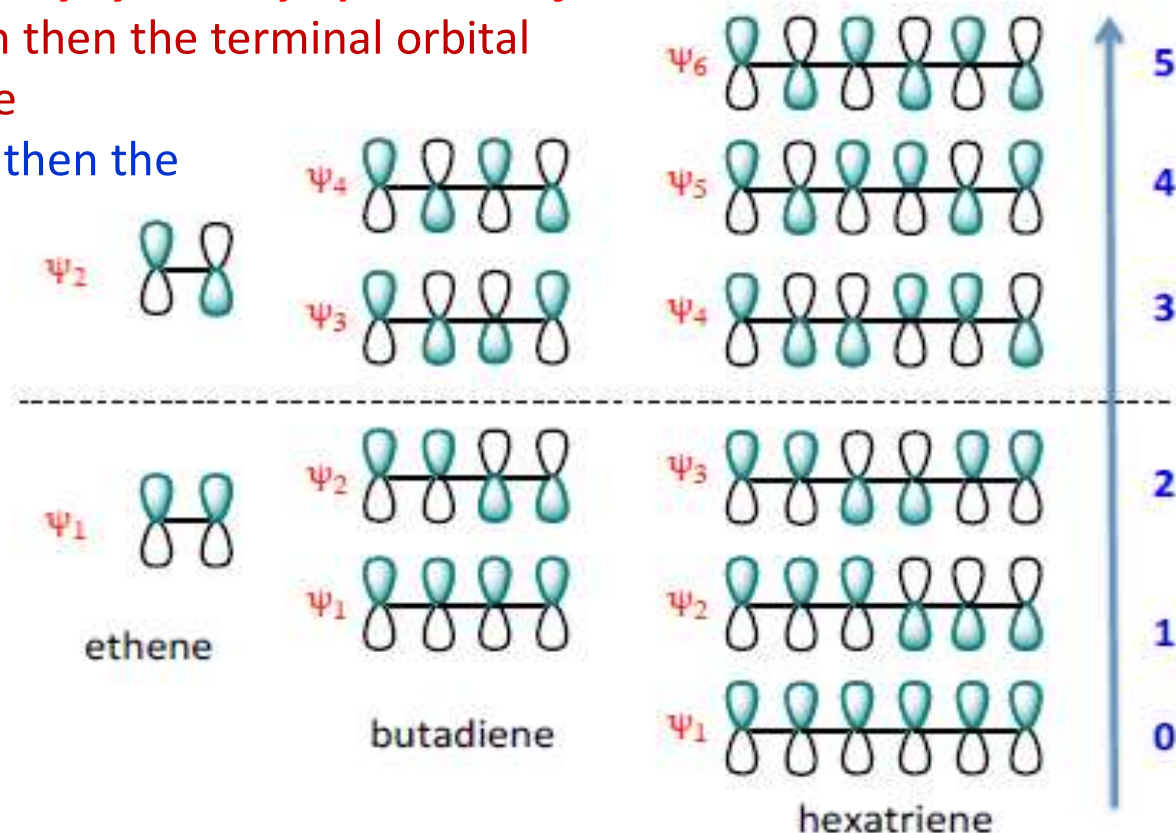
A  $\sigma$  bond is broken in the reactant, a new  $\sigma$  bond is formed in the product, and the  $\pi$  bonds get rearranged.

# MOs of polyconjugated compounds



To draw a molecular orbital diagram:

- i) Count the number of  $\pi$ -orbitals –  $n$
- ii) Count the number of electrons –  $\pi$ —bond = 2, unpaired electron = 1, carbanion = 2, carbocation = 0
- iii) Draw the molecular orbitals as the combination of p-orbitals with an increasing number of NODES from 0 for  $\psi_1$  to  $n-1$  for  $\psi_n$  such that **each MO is symmetric or antisymmetric with respect to any symmetry operation of the molecule.**
- iv) If the number of nodes is even then the terminal orbital coefficients will be same phase
- v) If the number of nodes is odd then the terminal coefficients will be of opposite phase.

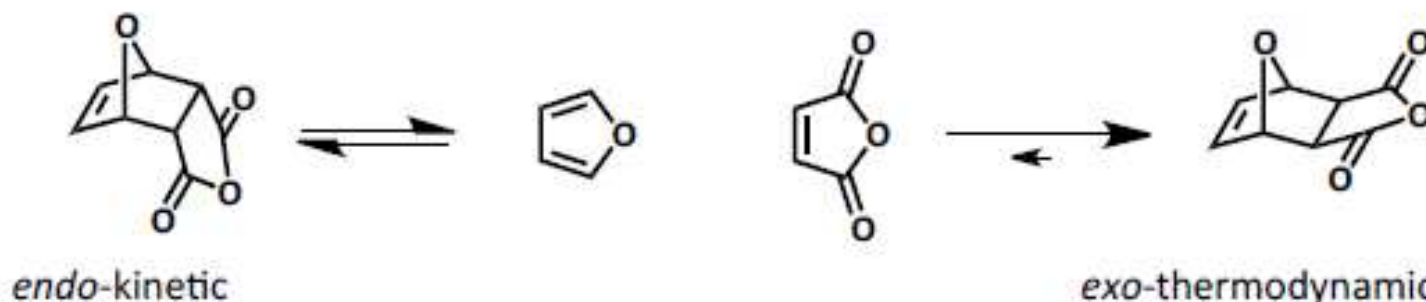




# [4+2] cycloaddition: Diels-Alder reaction



■ In cases where the reaction readily reverses (e.g. Diels Alder reactions with furan) the thermodynamically preferred *exo*-adducts are usually obtained.



Discovered by Professor Otto Diels and his student Kurt Alder in 1928 and received Nobel prize in 1950



Otto Diels (1876-1952)

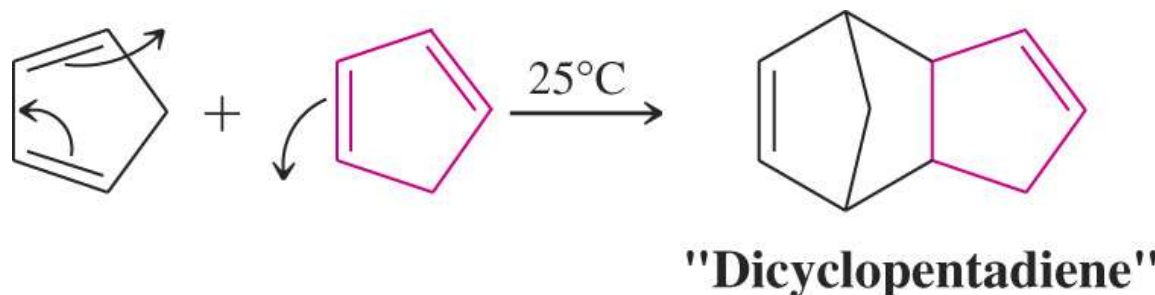


Kurt Alder (1902-1958)

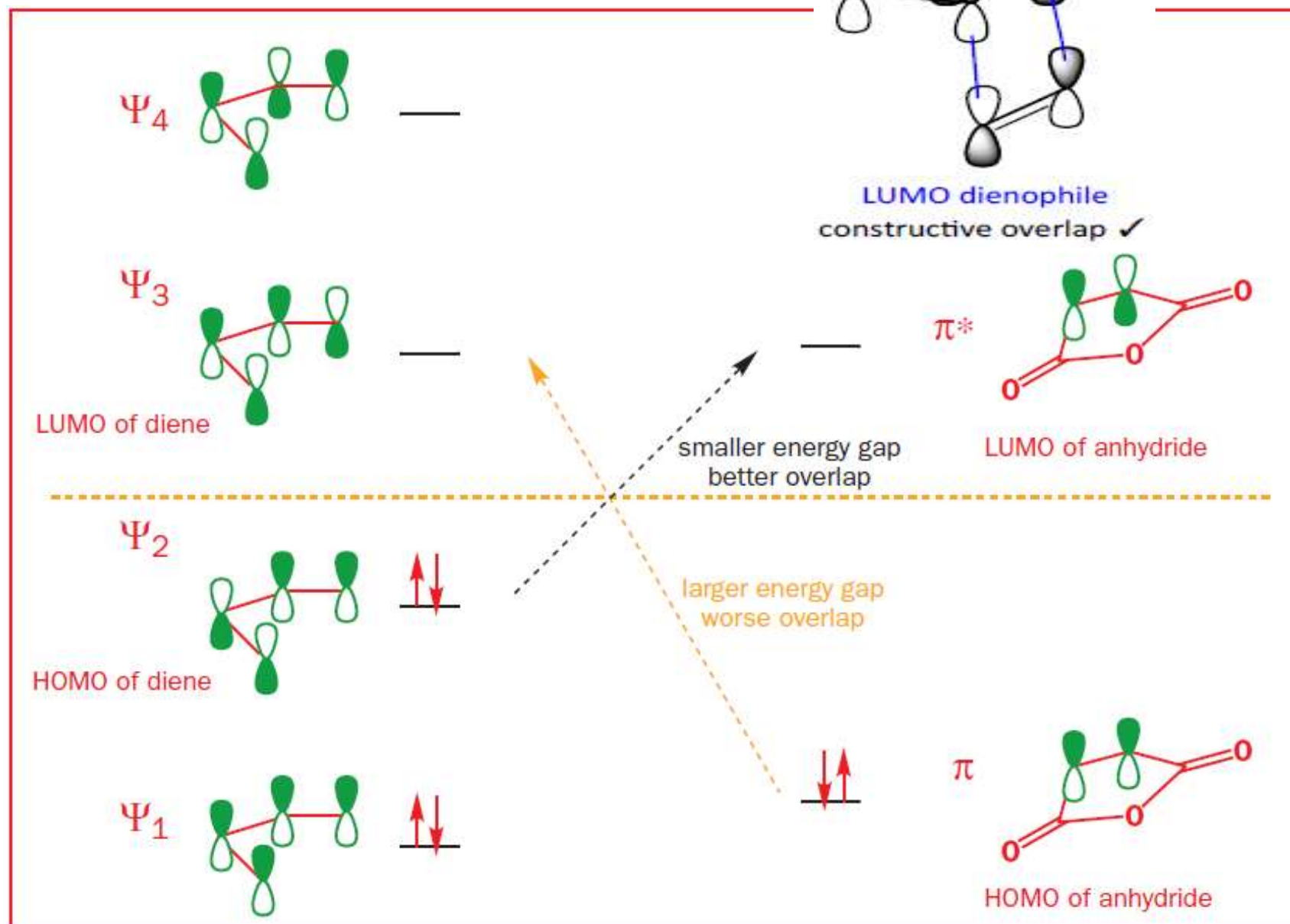
# Diels-Alder Reaction



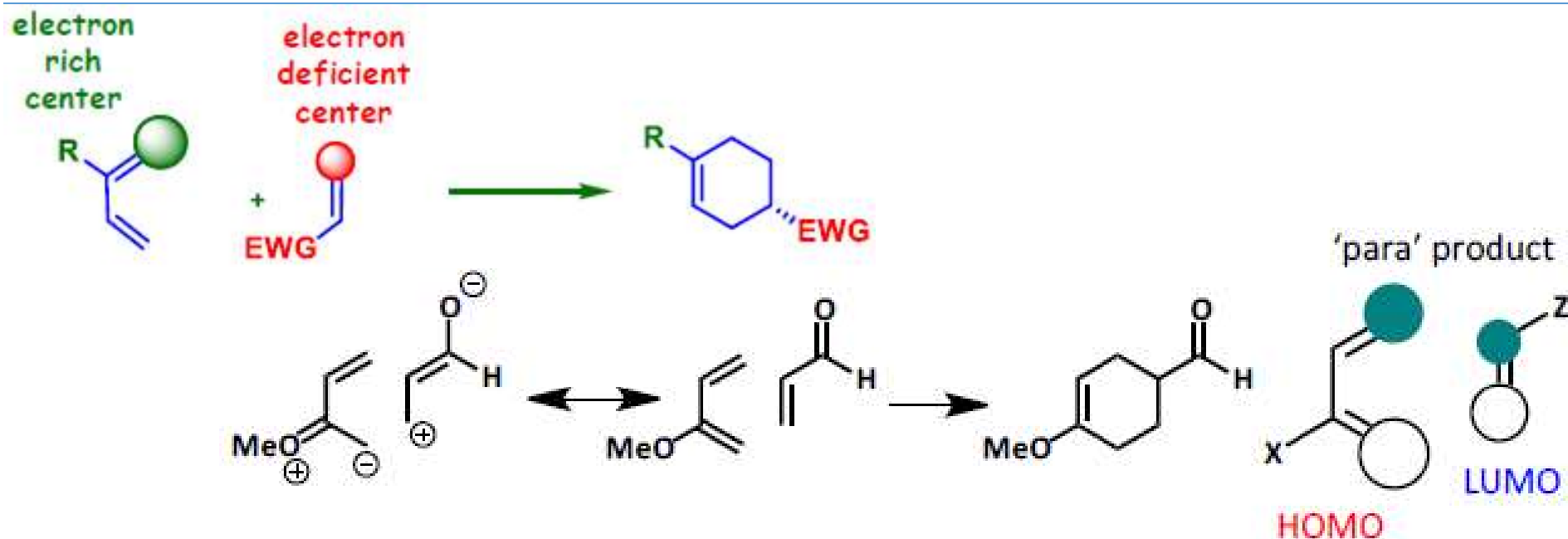
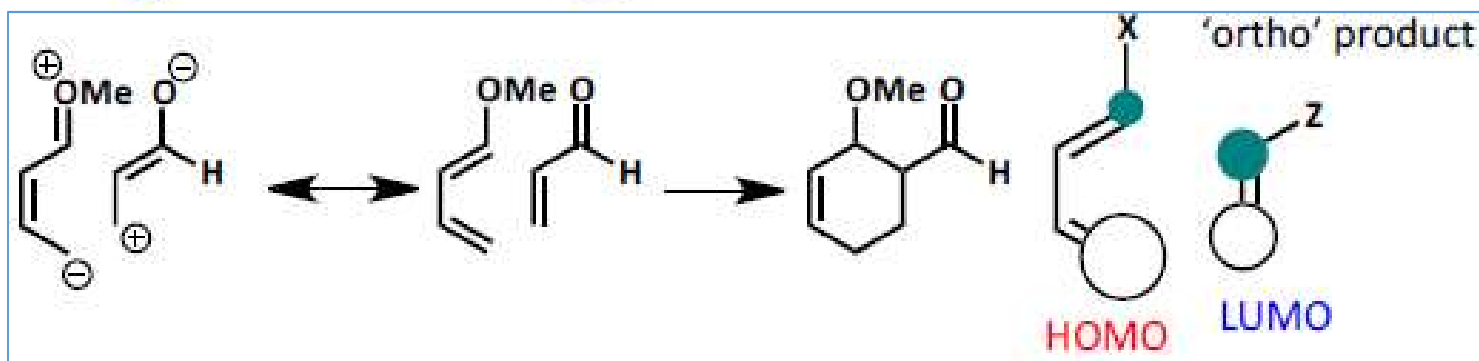
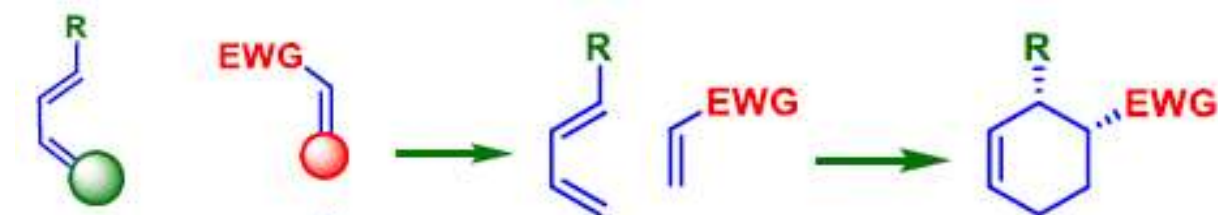
- The diene must be in the ***s-cis* conformation** to react.
- *s-trans* conformation would lead to formation of a highly unstable *trans* bond in a 6-membered ring.
- Cyclic dienes which must be in the *s-cis* conformation are highly reactive, e. g. cyclopentadiene is so reactive that it spontaneously undergoes Diels-Alder reaction with itself at room temperature.
- This dimer can be “cracked” (**undergo retro-Diels-Alder reaction**) by heating and the cyclopentadiene product is isolated by distillation.
- Both sigma bonds are on same face of the diene: **syn stereochemistry**. The Diels-Alder reaction is **stereospecific**.



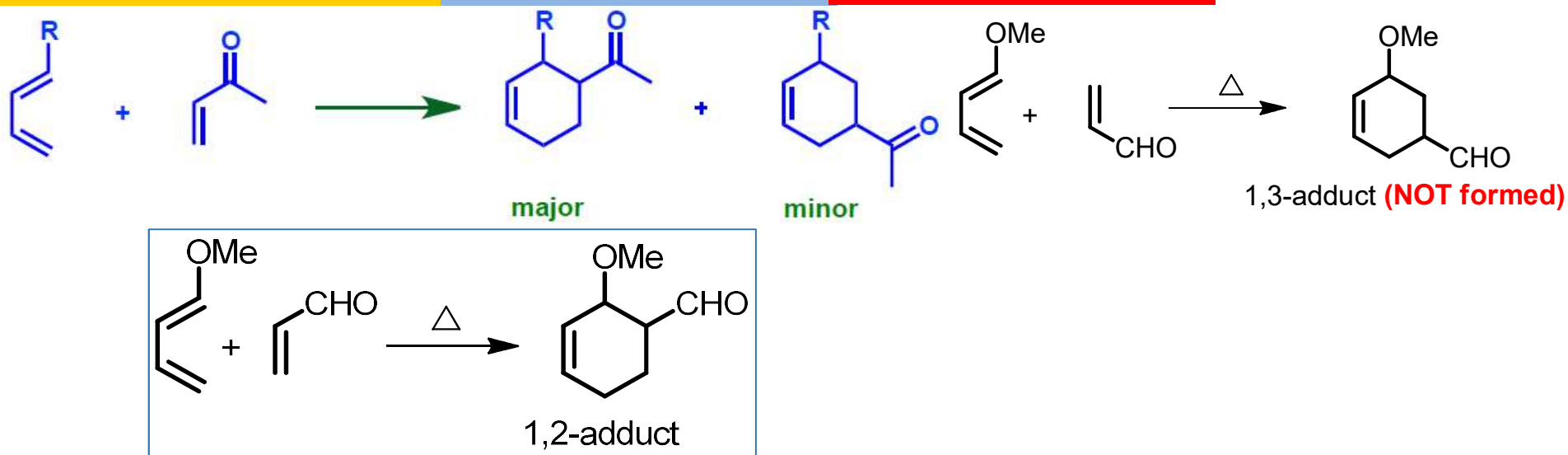
# Stereo-specificity of Diels-Alder Reaction



# [4+2] cycloaddition: Regioselectivity



# [4+2] cycloaddition: Regioselectivity



❑ **Regioselective Reaction:** Dienes with electron-donating groups and dienophiles with electron-withdrawing groups react well together.

