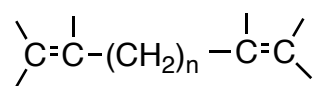


Dienes and Aromatic Compounds

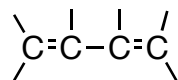
- **Molecular orbitals**

- **Reactivity**

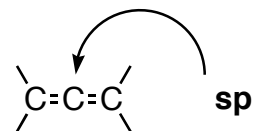
Dienes (McM 14.2)



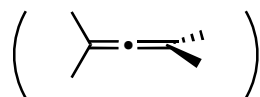
n: 1,2,3... non conjugated diene
n=1: Skipped diene
n>1: Isolated diene



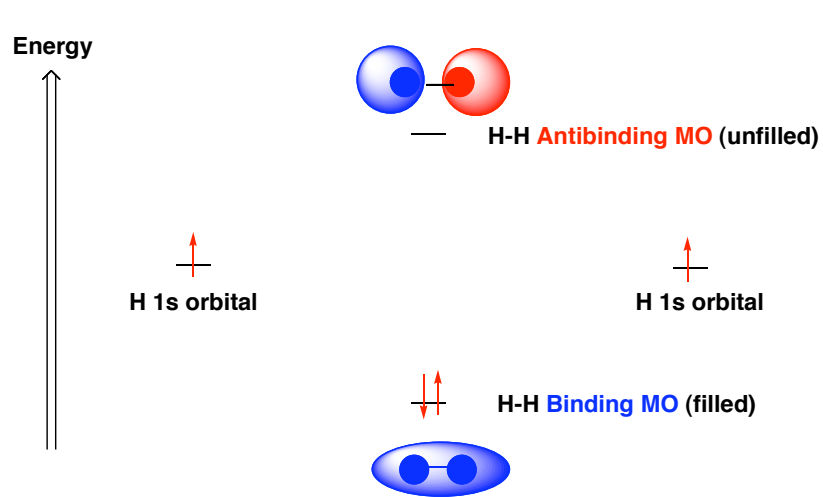
conjugated diene



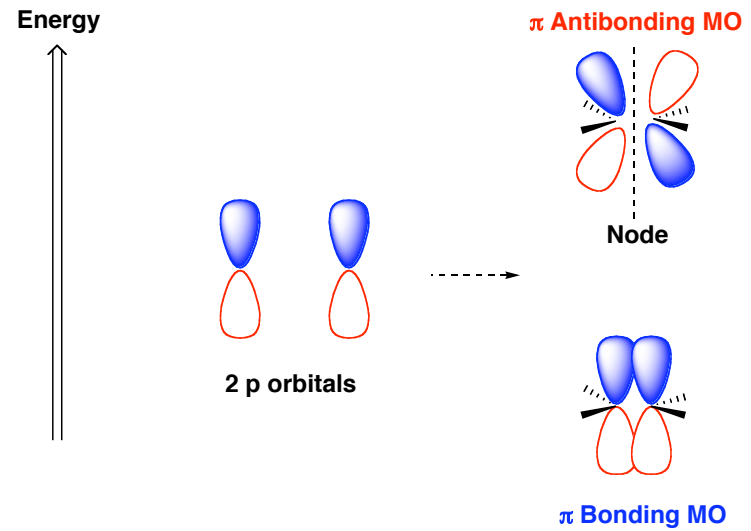
cumulated diene (allene)



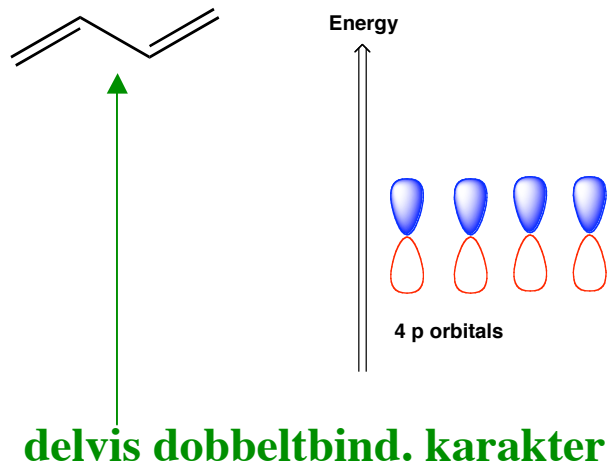
Molecular orbitals of H₂ (cf fig 1.20) - σ -bond



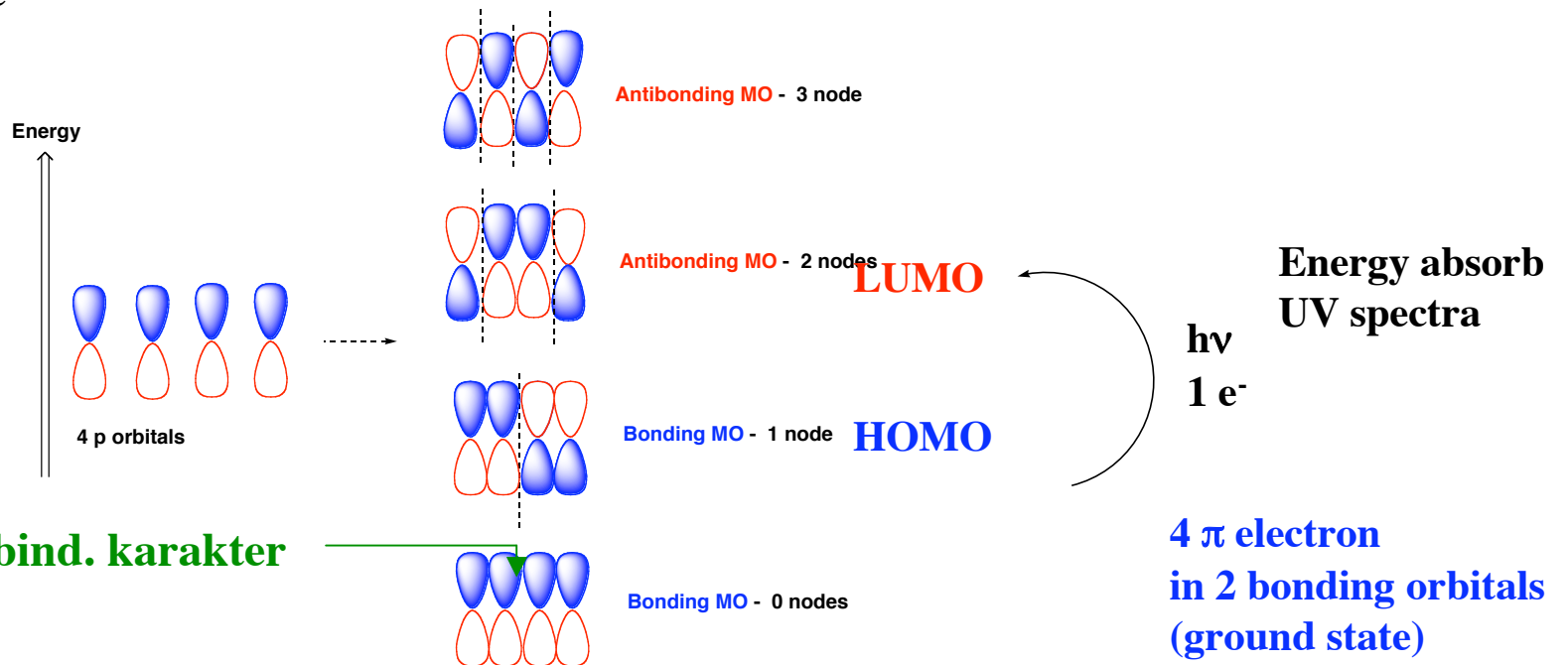
Molecular orbitals of π -bond (cf fig. 1.21)



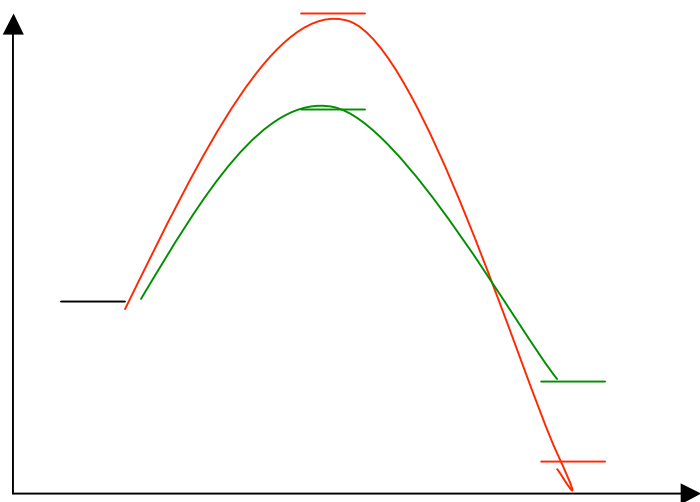
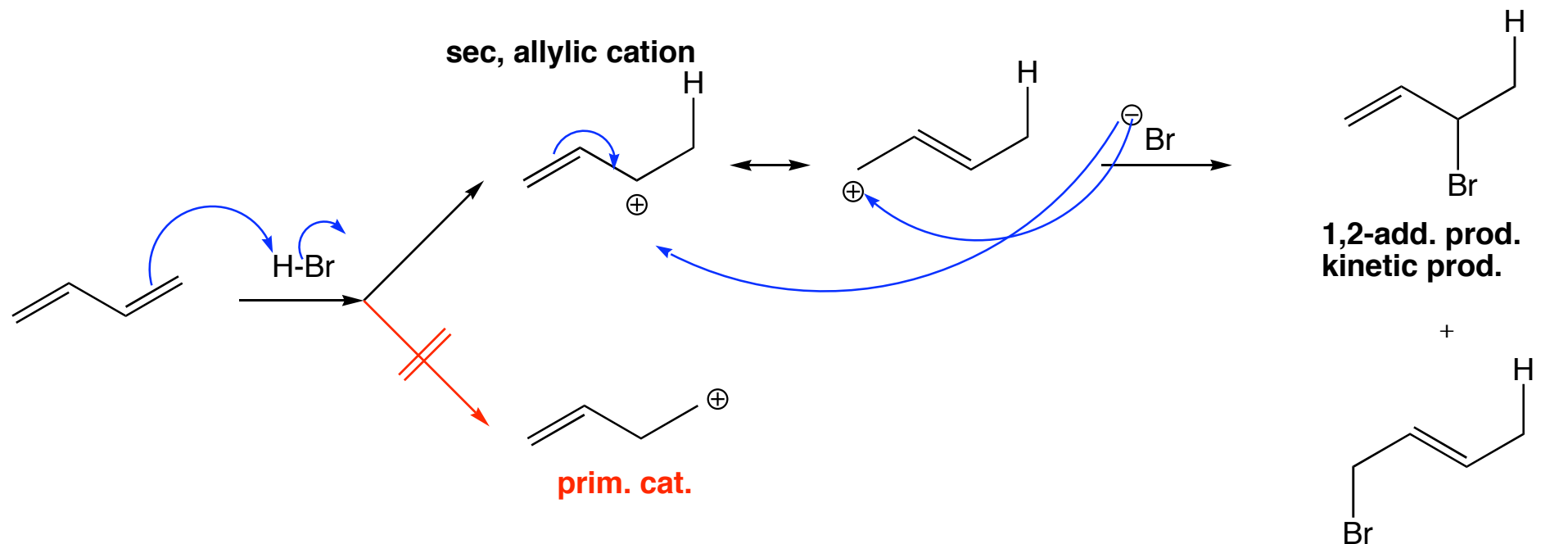
MO 1,3-butadiene cf fig 14.2



π Molecular orbitals



Electrophilic addition to conjugated dienes



Thermodyn prod: High activation barrier, most stable prod.

Vigorous cond. (high temp), reversible

Kinetic prod: Low activation barrier, less stable prod.

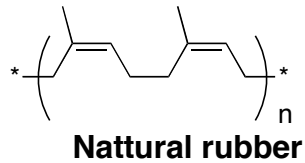
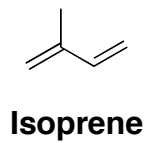
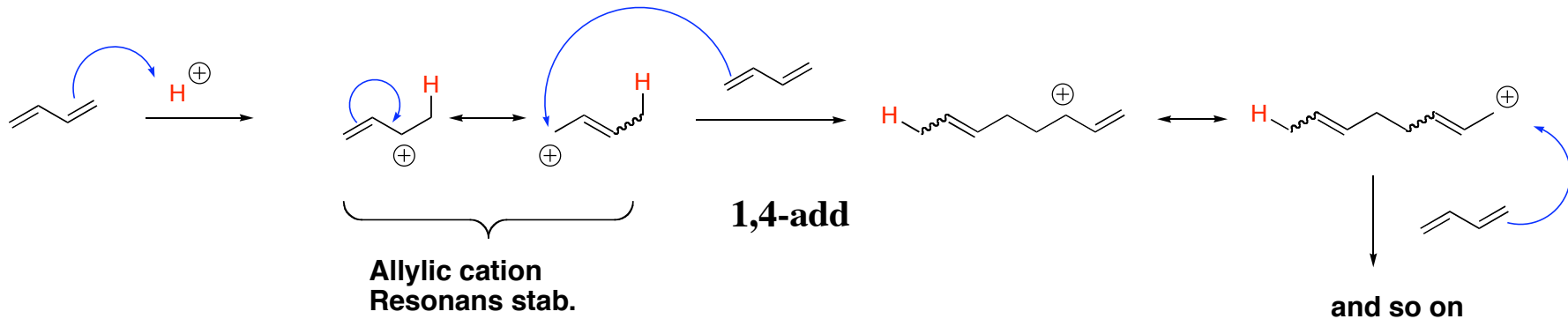
Mild cond, (low temp,) irreversible

Polymerization of dienes

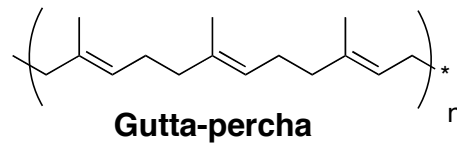
Natural and synthetic rubber

- Radical polymerization
- Cationic polymerization

Acid cat polymerization of 1,3-butadiene



Hevea brasiliensis,
tropical Americas.
Cautchuc

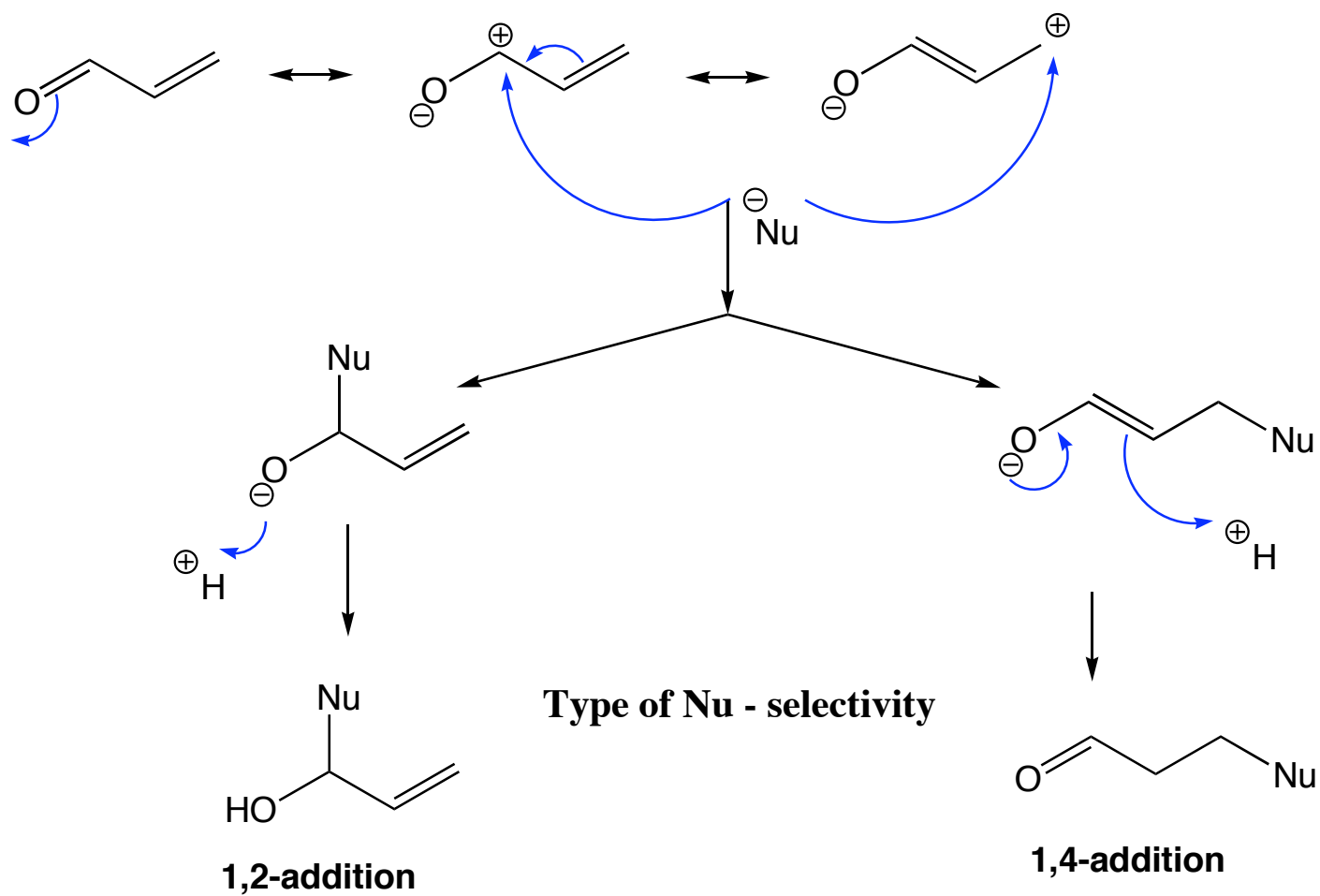


resin from the Isonandra Gutta tree (South east Asia)



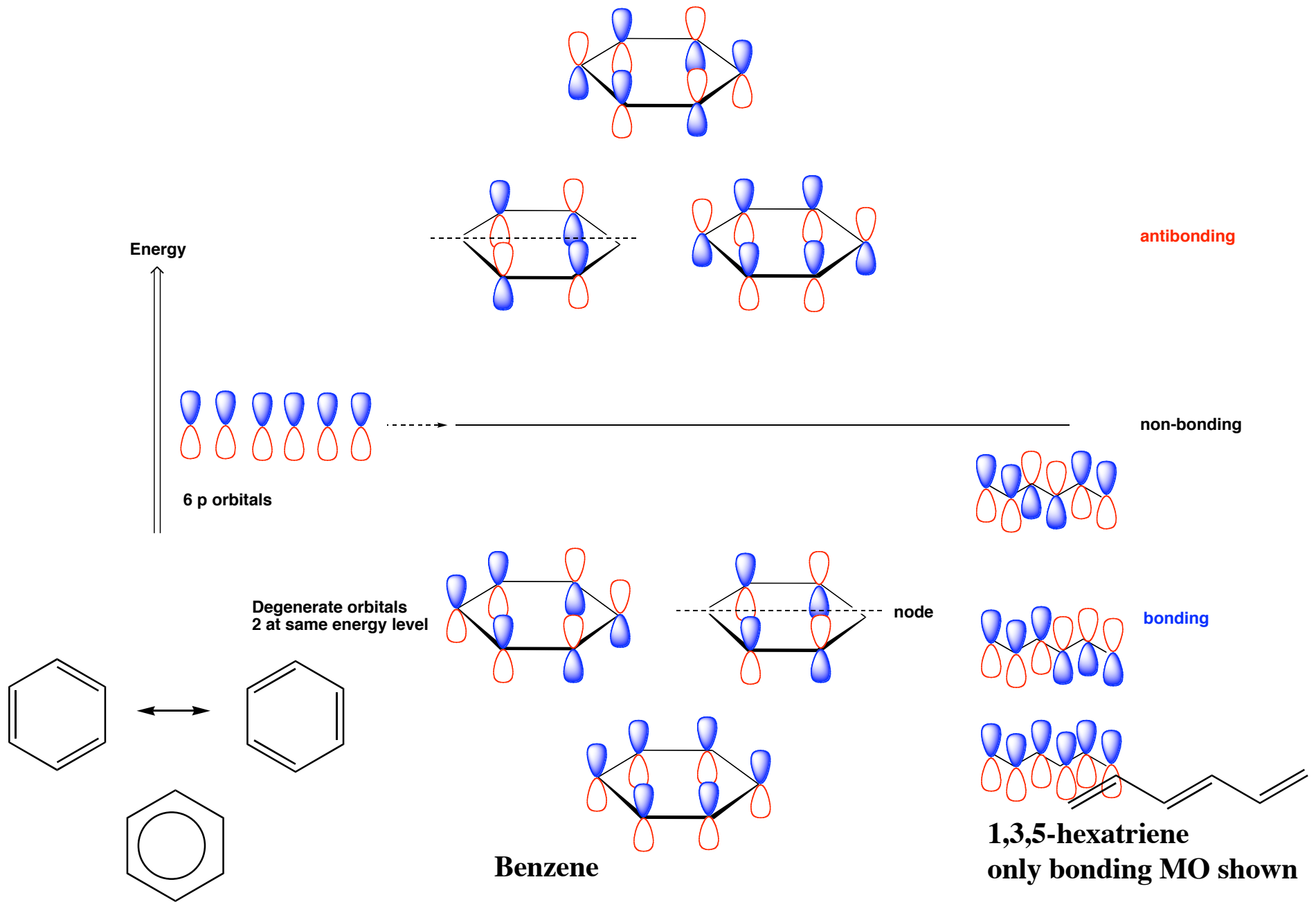
Less elastic than nat. rubber
Isolation under-water cables
Little use today

Nucleophilic 1,2- or 1.4 add.



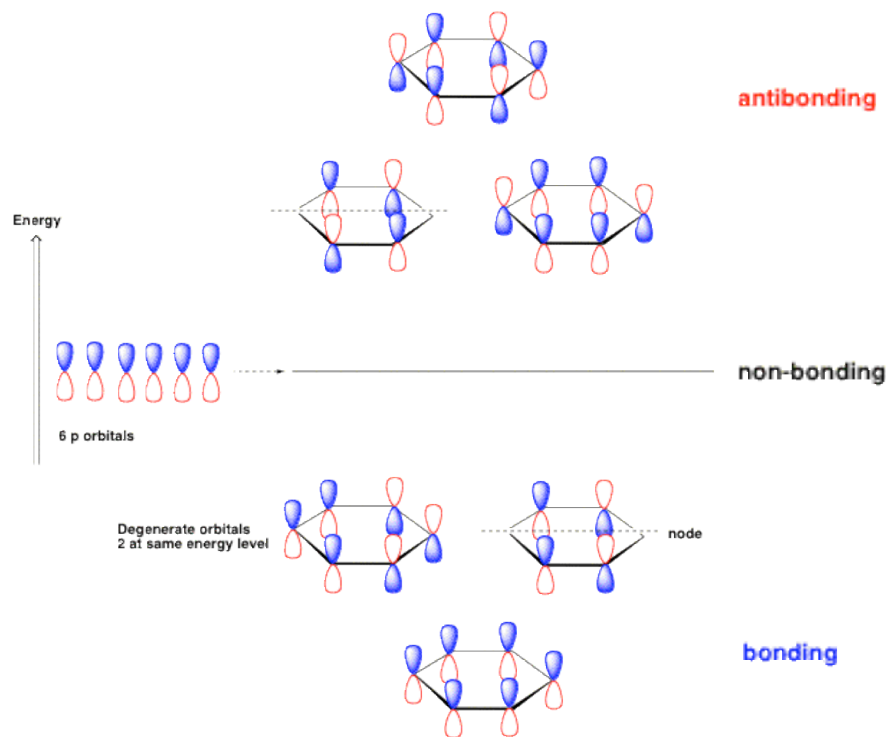
Dienes and cycloadd. (Diels Alder) - Chapt. 30

MO orbitals benzene - aromaticity (McM 15.4 - 15.5)



Criteria for Aromaticity (Hückel)

- (Monocyclic) ring
- Planar
- No of π -electrons in conjugation $4n+2$ ($n: 0, 1, 2, \dots$)



Benzene:

The 3 bonding MOs are filled

Filled shell of MOs

(cf. filled shell of atomic orbitals noble gasses)

Less than 6 π -electrons:

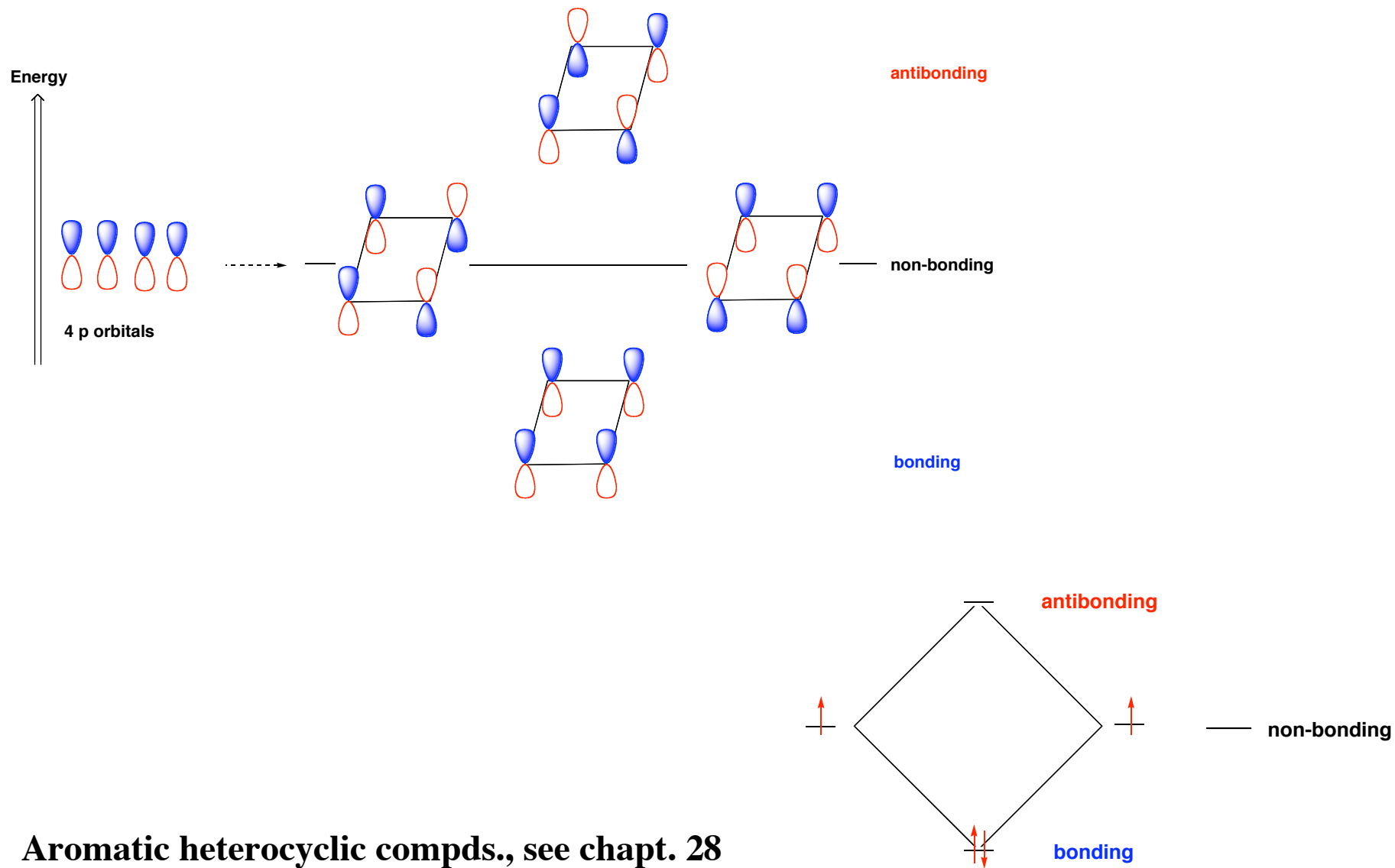
Half-filled orbital(s) - radical character

More than 6:

Electron in antibonding orbitals

Unstable, high-energy species

Ex. of an anti-aromatic compound - Cyclobutadiene

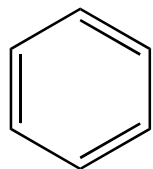


Aromatic heterocyclic compds., see chapt. 28

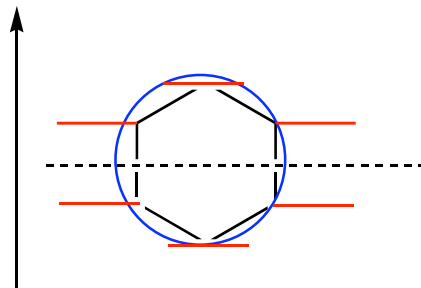
Frost circles / Frost devices (not in McM)

How to find rel. energies of MO for planar, cyclic, fully conjug. compds. (aromatic compds?)
No math. involved

Benzene



Energy



3 antibonding MO (2 degenerate)

3 bonding MO (2 degenerate)

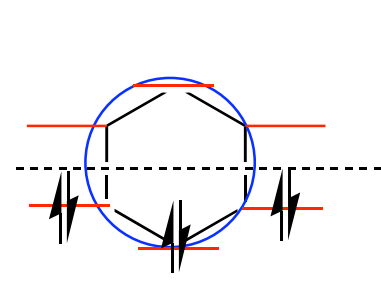
Hexagon inside circle
Vertex (corner) down

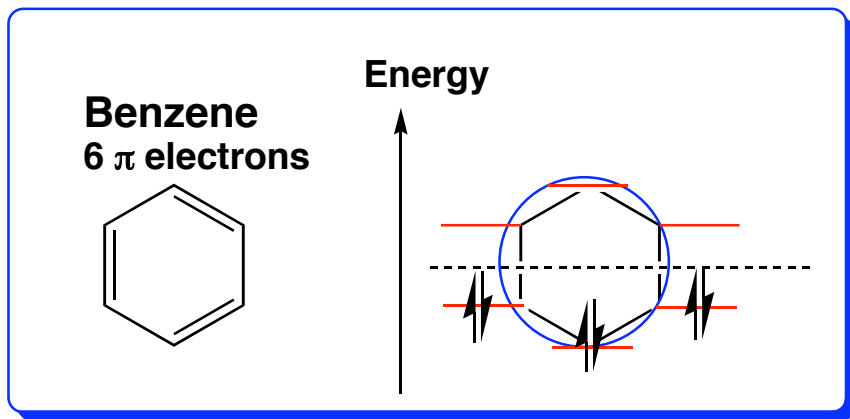
Molecular orbitals

----- Level of a non-bonding MO

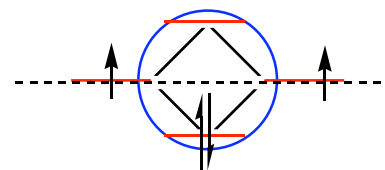
6 π -electrons in 3 bonding MO

Energy



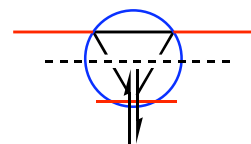
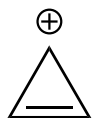


Cyclobutadiene
4 π electrons



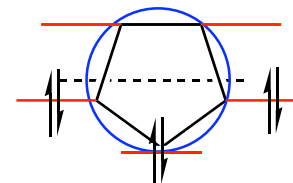
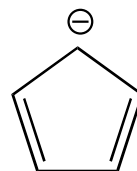
Diradical

Cyclopropenium cation
2 π -electrons



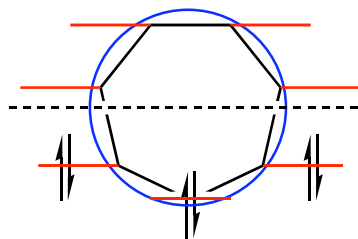
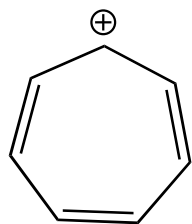
All π electrons in the bonding MO

Cyclopentadienyl anion
6 π -electrons



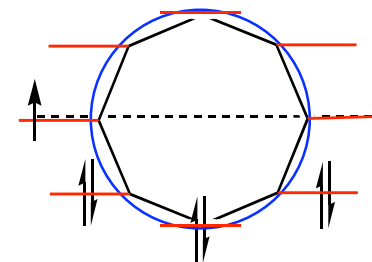
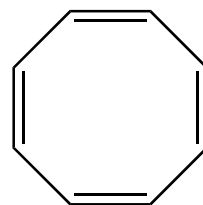
All π electrons in the bonding MO

Tropylium cation
6 π -electrons



All π electrons in the bonding MO

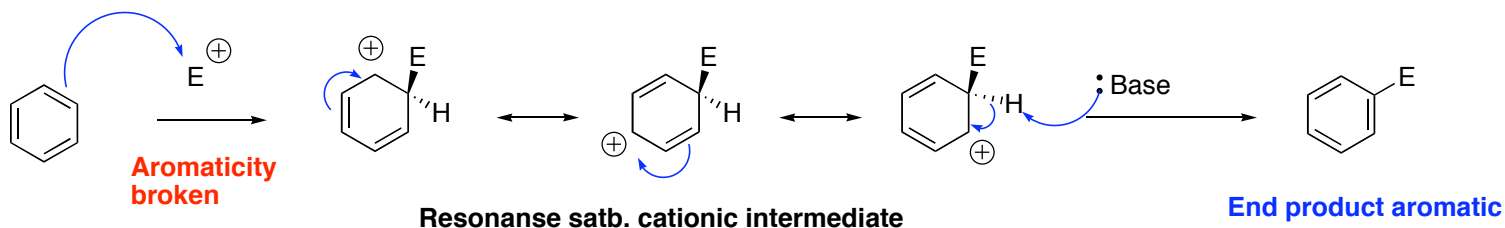
Cyclooctatetraene
8 π -electrons



Diradical

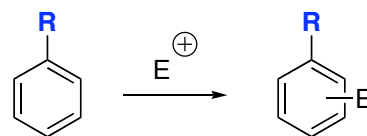
Electrophilic Aromatic Substitution and Substituent Effects

(McM. 16.5 - 16.6)



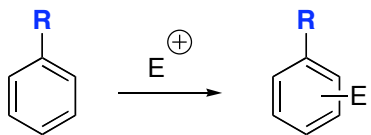
1. step \approx 1. step in E-fil add. to alkene

- Halogenation (bromination)
- Nitration
- Sulfonation
- Alkylation (Friedel Craft)
- Acylation (Friedel Craft)□



R influence:

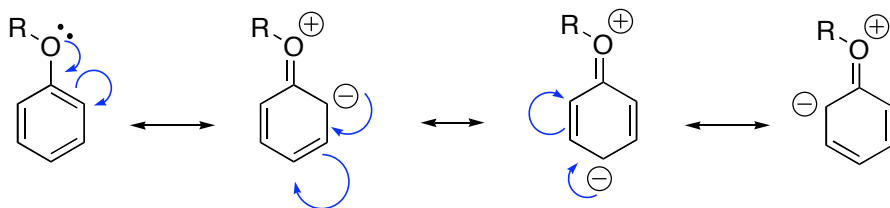
- Reactivity
- Regiochemistry



R: Electron donating

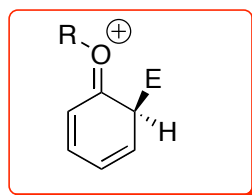
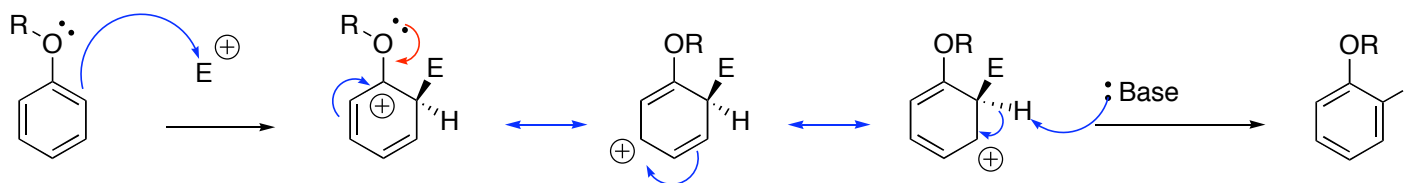
By resonance

ex. $\text{R}\ddot{\text{O}}^-$, $\text{H}\ddot{\text{O}}^-$, $^-\text{O}^-$, $\text{R}_2\ddot{\text{N}}^-$, $\text{RHN}\ddot{}$, $\text{H}_2\ddot{\text{N}}^-$, $\text{RCOH}\ddot{\text{N}}^-$

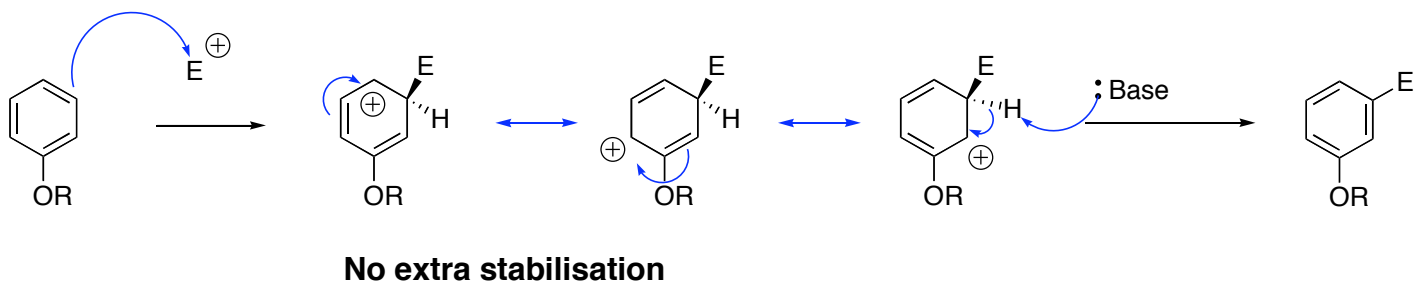
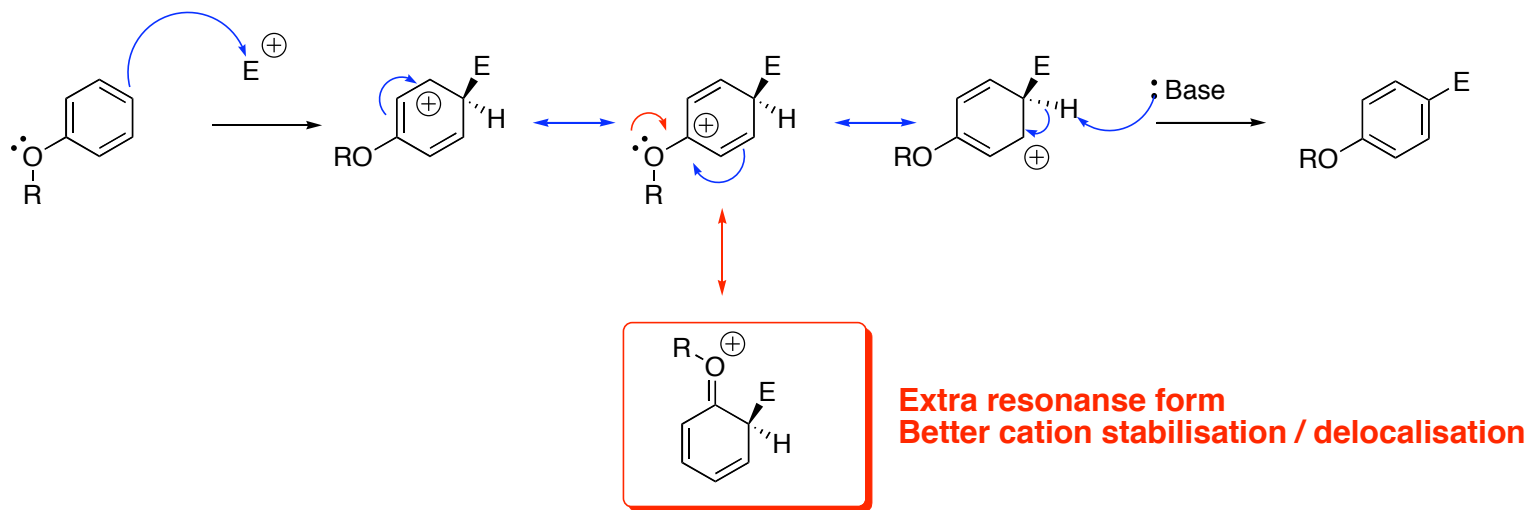


**o- and p-pos.
Electron rich / nucleophilic**

**The ring is activated for E-fil ar subst
More reactive than benzene**

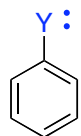


**Extra resonance form
Better cation stabilisation / delocalisation**

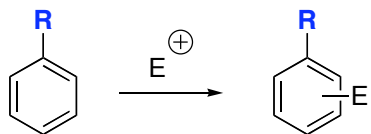


Reaction in *o* or *p* pos.

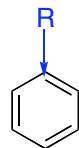
..



Activating, *o/p* directing



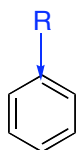
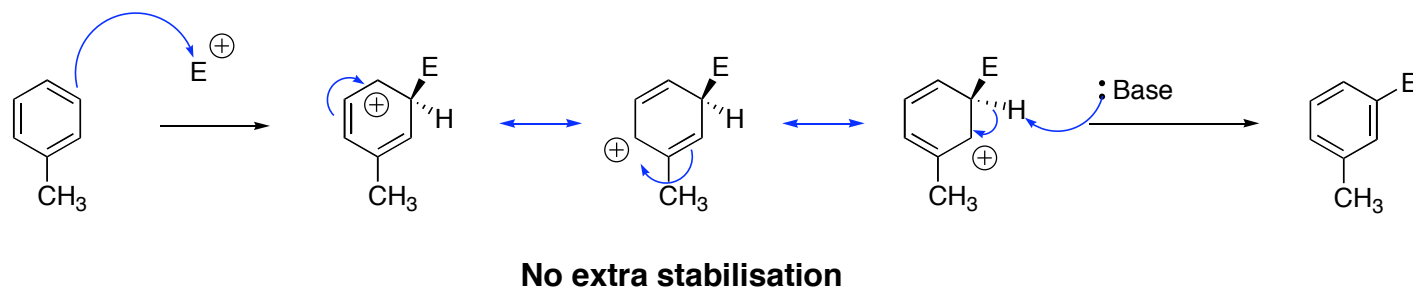
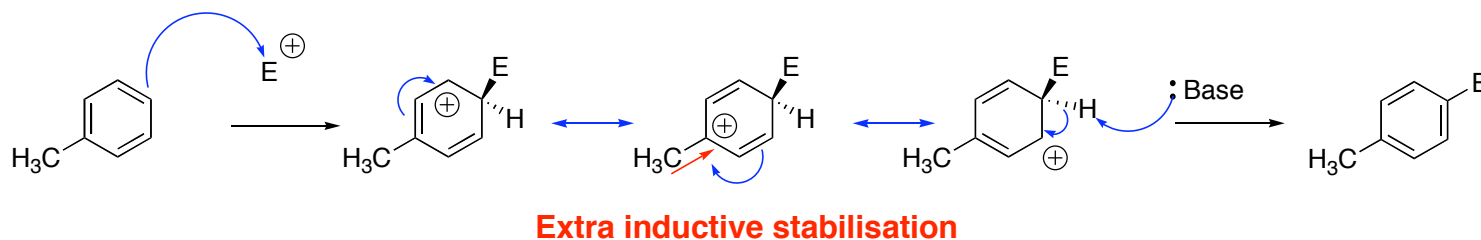
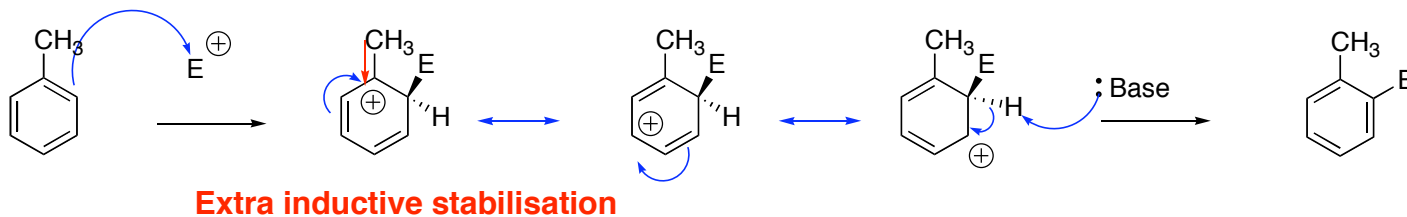
R: Electron donating



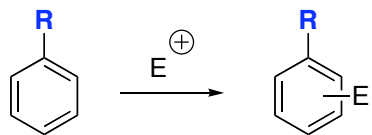
**The ring is activated for E-fil ar subst
More reactive than benzene**

By inductive effect

ex. alkyls



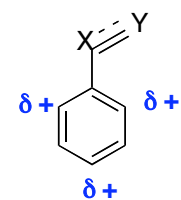
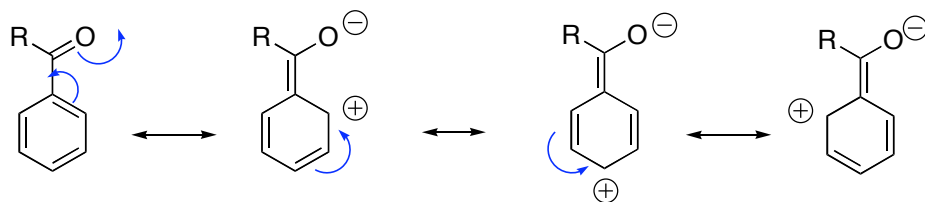
Activating, o/p directing



R: Electron withdrawing

By resonance effect:

-CN, -COR, COH, CO₂H, CO₂R, -NO₂, -SO₂R etc

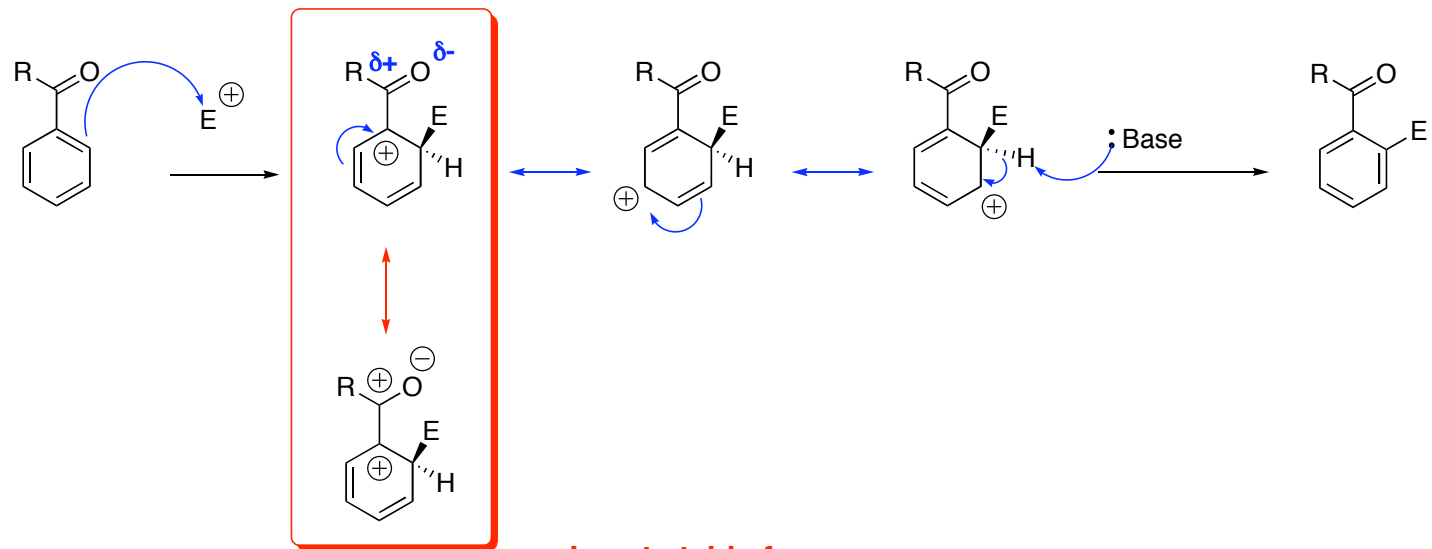


***o*- and *p*-pos.
Electron poor / less nucleophilic**

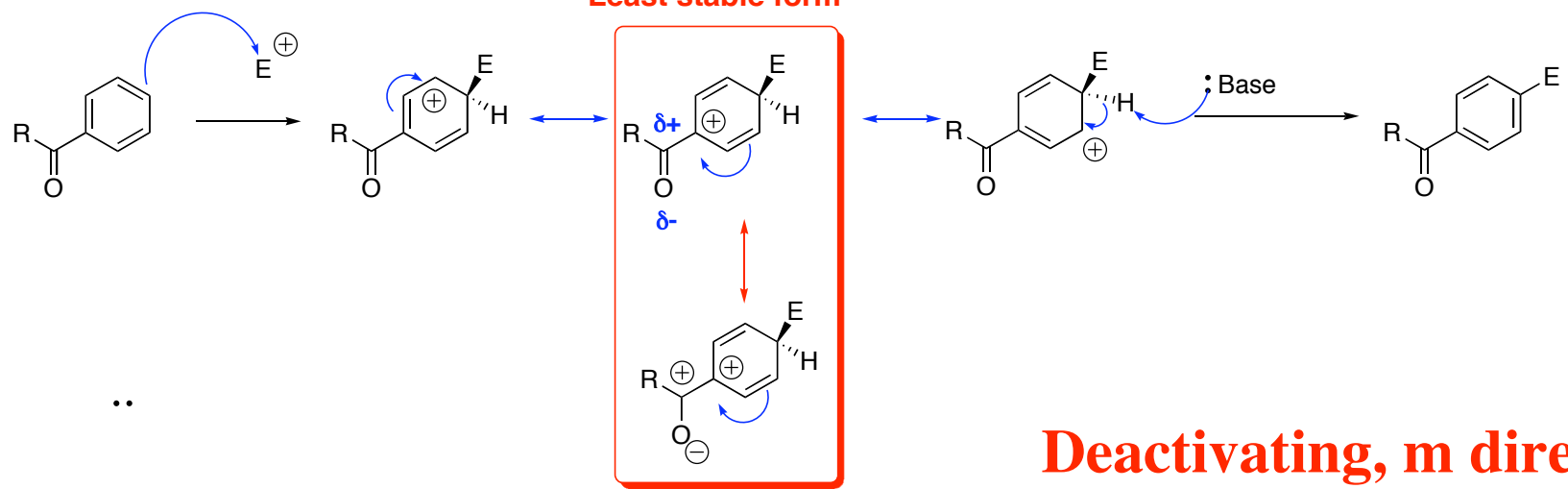
Especially electron poor in *o*/*p* pos

**The ring is deactivated for E-fil ar subst
Less reactive than benzene**

Least stable form

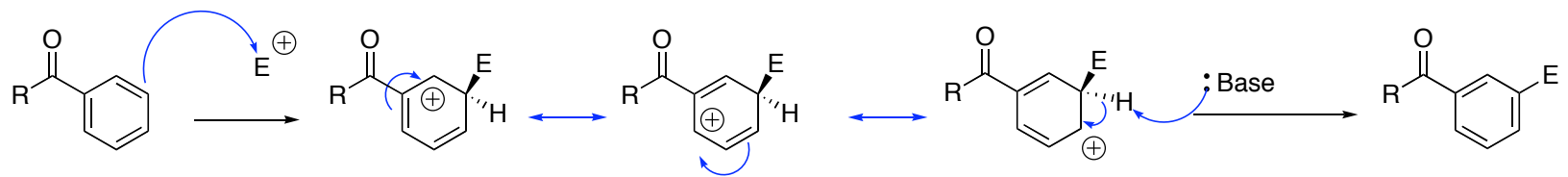


Least stable form

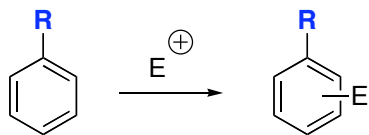


..

Deactivating, m directing

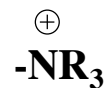


R: Electron withdrawing



By inductive effect:

Alternative A:

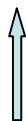


Deactivating, m directing

Alternative B:

-Halogens

Deactivating, but o/p directing!!

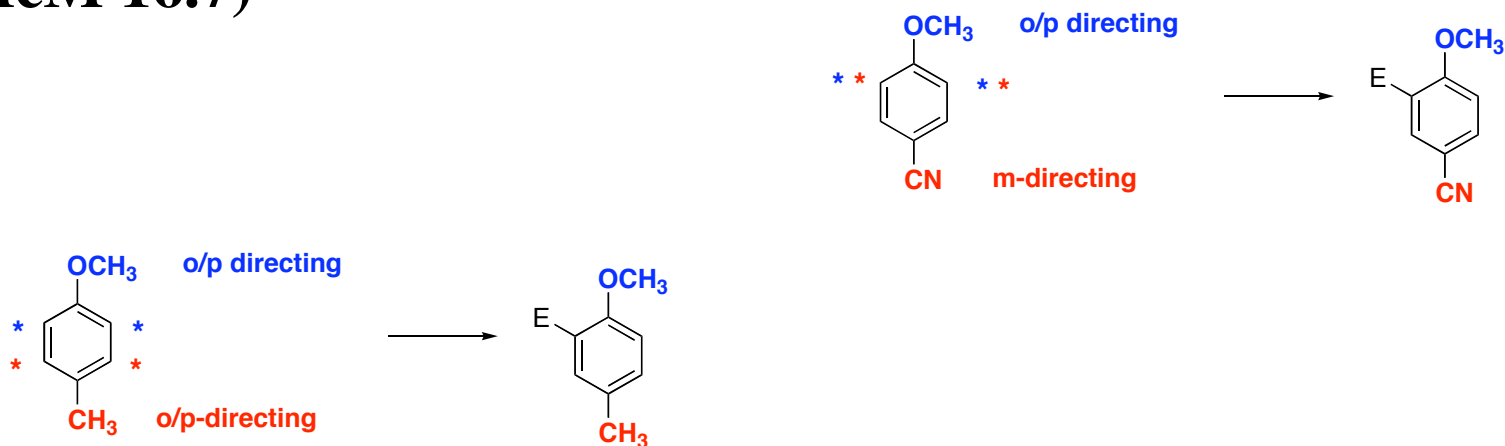


**Inductively strong
withdrawing effect**

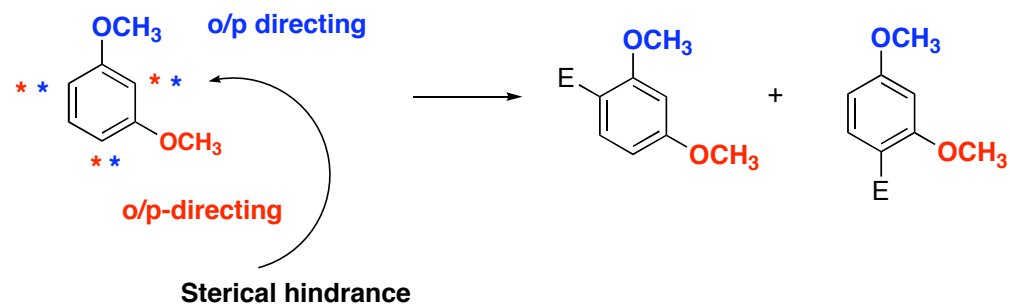


**Electron donor by resonance
(lone pairs) weak effect**

Regiochemistry in E-fil aromatic subst of disubst. benzene derivs. (McM 16.7)



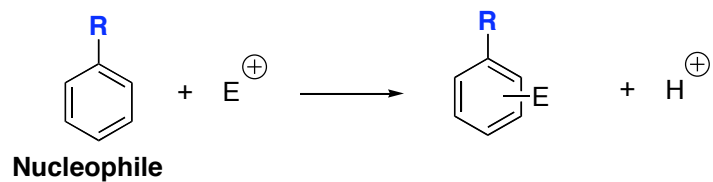
Resonance effects more powerful than inductive effects



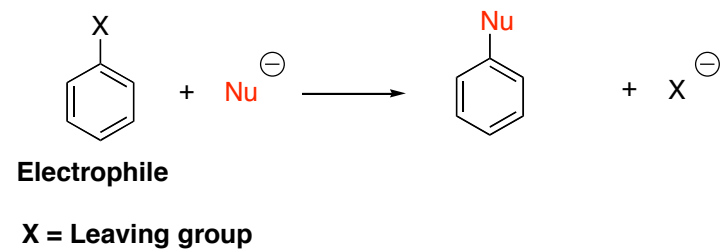
Synth of trisubst. benzene deriv. - Planning of a good reaction sequence (McM 16.12)

Nucleophilic Aromatic Substitution (McM 16.8 - 16.9)

E-fil Ar subst



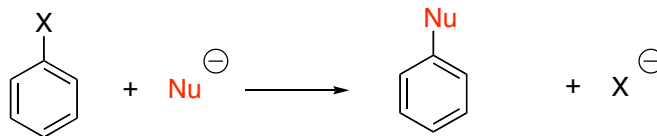
Nu-fil Ar subst



More common on π -deficient heterocycles, see chapt 28

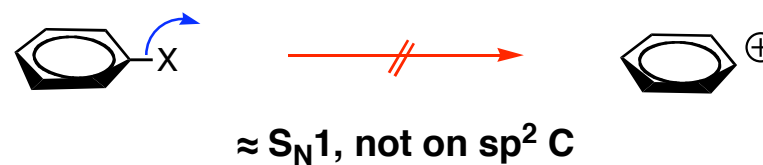
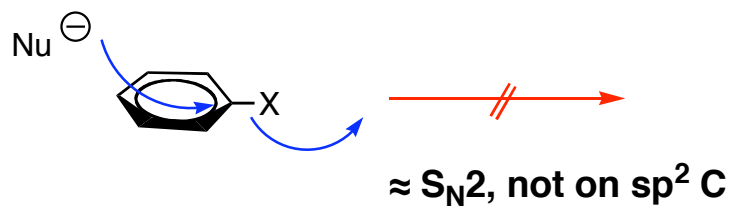
Not like S_N2 (or S_N1)

Nu-phil Ar subst



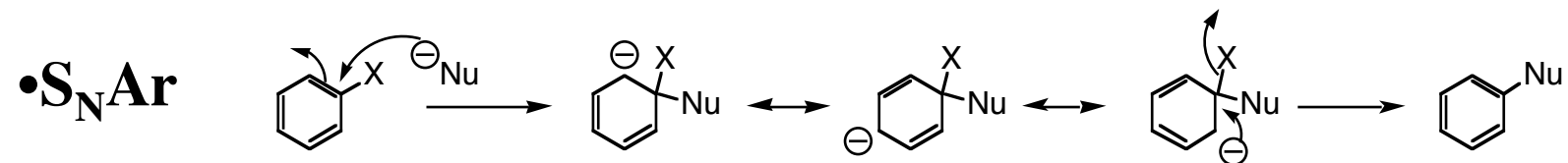
Electrophile

X = Leaving group



(but NB! diazotation, chapt. 24.8)

Mechanisms:



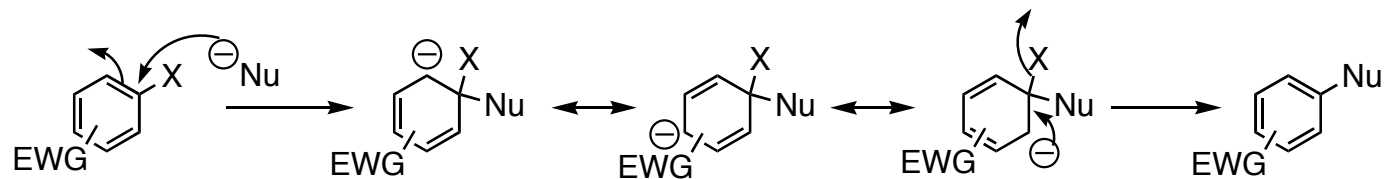
• S_N1: Via diazonium salts (McM 24.8)

• **Benzyne**

• (SRN1: Involves radicals)

• (VNS: Vicarious nucl. Subst.)

•S_NAr



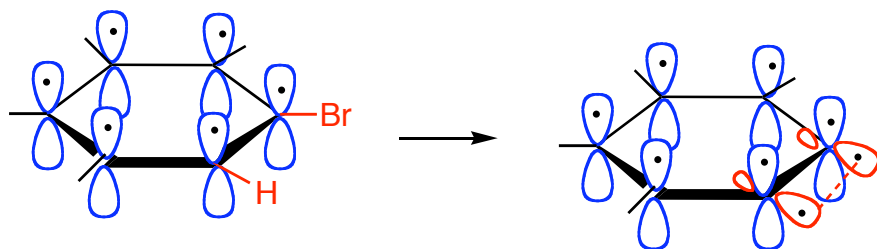
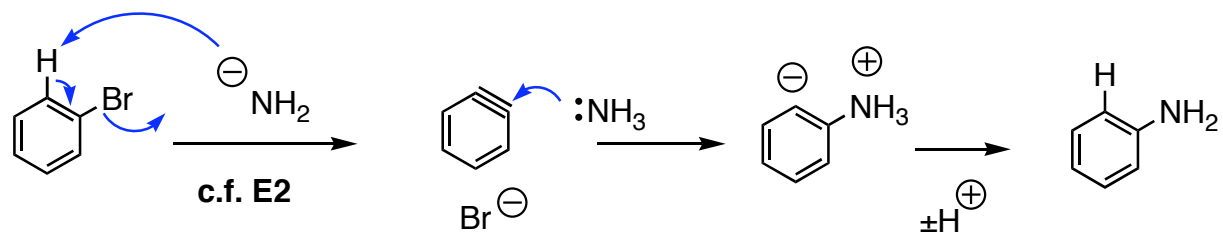
Only on electron deficient arenes (EWG o/p to X, Anion stabilizing effect)

(Aromatic heterocycles, McM 28.6)

1st step rate limiting (Aromaticity broken)

X=F>Cl>Br>I

•Benzyne

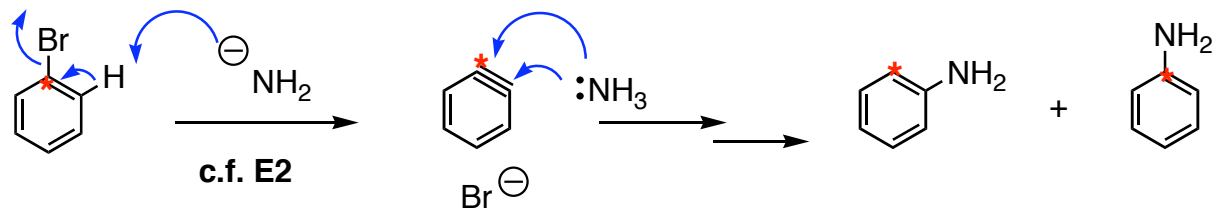


“Triple bond” between sp^2 C

p-p overlap

sp^2 - sp^2 overlap - weak bond

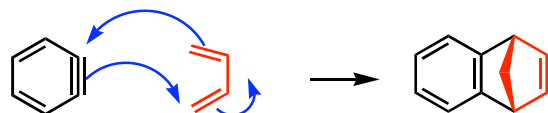
Benzyne unstable / reactive intermed.



Reactivity of benzyne:

* ^{14}C

- Adds nucleophiles
- Dienophile in Diels Alder react.



Reactivity of aromatic side chains

- **Ox. of alkyl side chains**
- **Halogenation benzylic position (c.f. Lab ex. 1)**

- **No ox. cleavage of “double bonds” in benzene**
- **Reduction of benzene (hydrogenation) difficult**