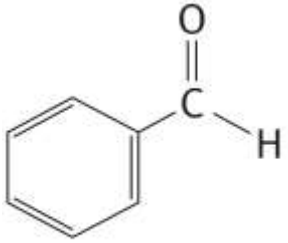
Chapter 4

Aromatic Compounds

Bitter almonds are source of benzaldehyde



benzaldehyde

4.1 Some Facts About Benzene :

Benzene **(C_6H_6)** is the parent hydrocarbon of the **especially stable** **aromatic compounds**.

C_6H_6 : highly unsaturated.

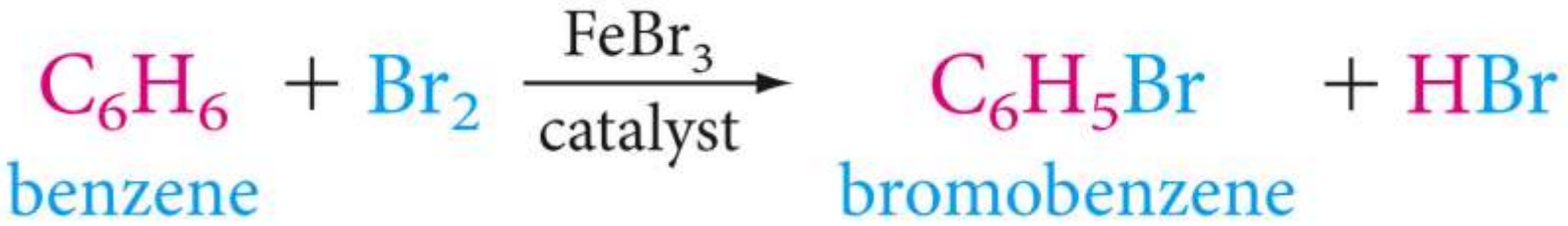
But

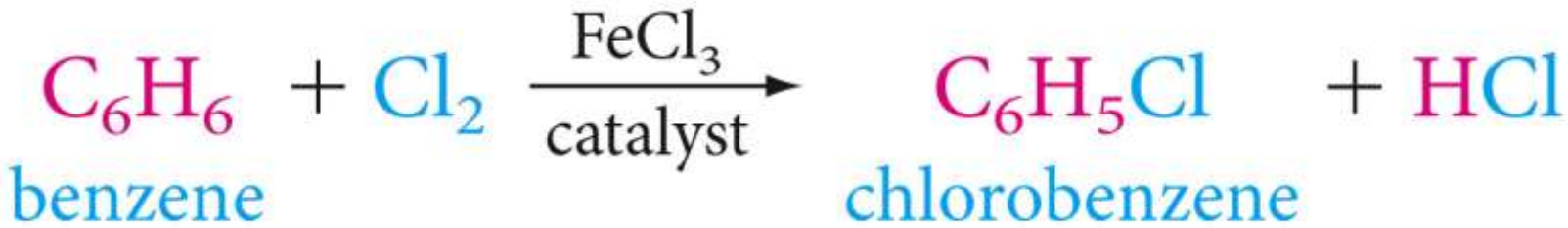
1- It does not behave as unsaturated
2- It reacts by substitution not by addition
3- It does not decolorize Br_2.
4- It is not oxidized by $KMnO_4$.

Reactions with Halogens (Br_2 and Cl_2):

1- require Lewis acid catalyst

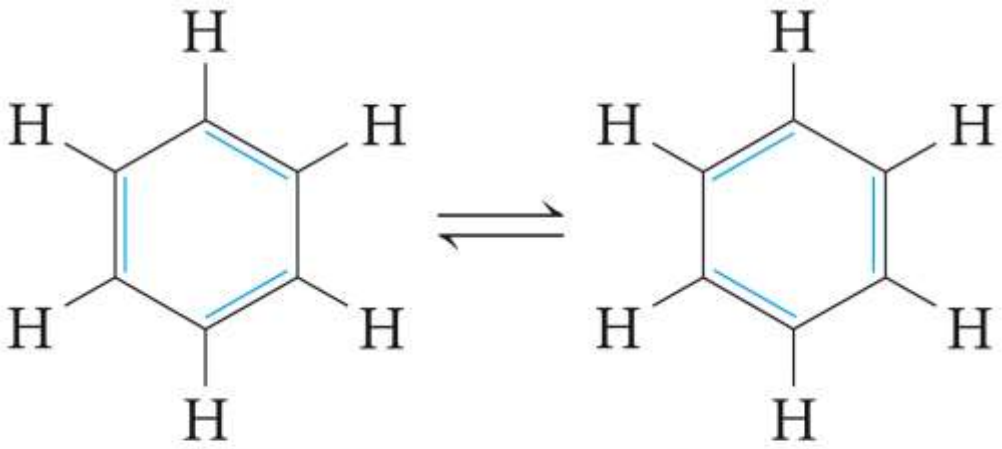
2- occur by substitution, not by addition





4.2 The Kekulé Structure for Benzene

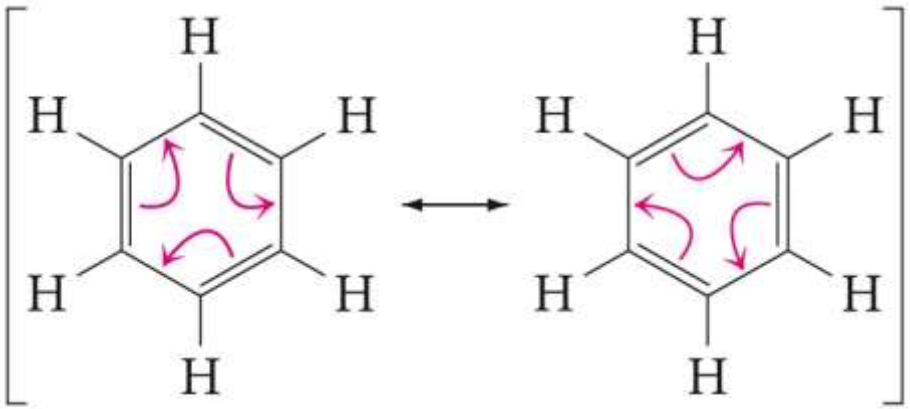
In 1865, Kekulé proposed a reasonable structure for benzene



the Kekulé structures for benzene

These structures *differ only* in the arrangement of π-electrons.
So they are two **Resonance structures**

4.3 The Resonance Structure of Benzene



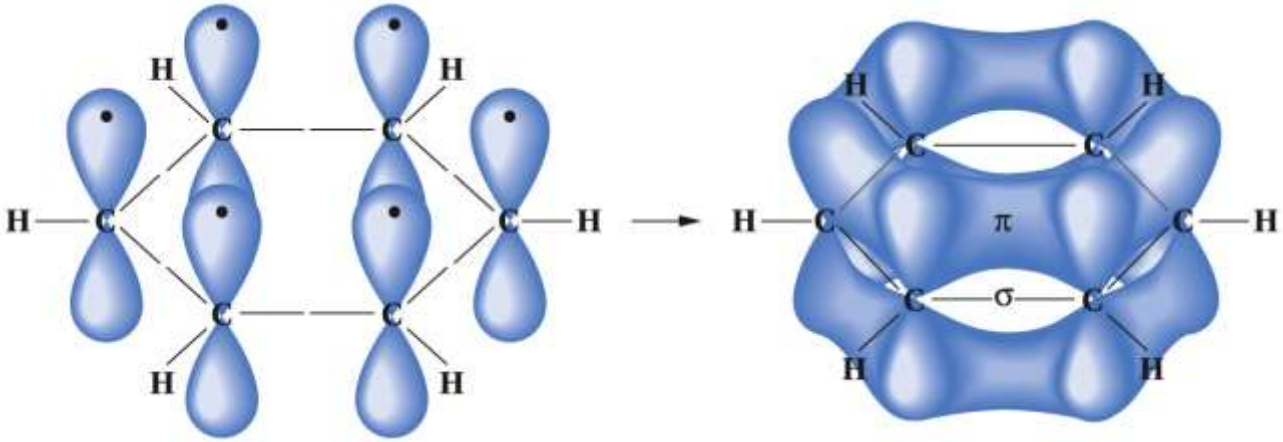
Benzene is a resonance hybrid of these two contributing structures.

Support for resonance structure:

1- Benzene has planar geometry allowing *p-p* orbital overlap

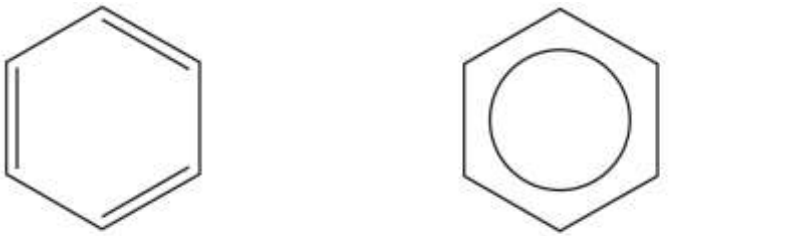
2- All C-C bond lengths are equal (1.39 Å) intermediate between C-C (1.54 Å) and C=C (1.34 Å)

4.4 The Orbital Model for Benzene :



p- orbitals on all carbon atoms overlap to form **π**-bonds creating a cloud of electrons above and below the plane of the ring.

4.5 Symbols for Benzene:

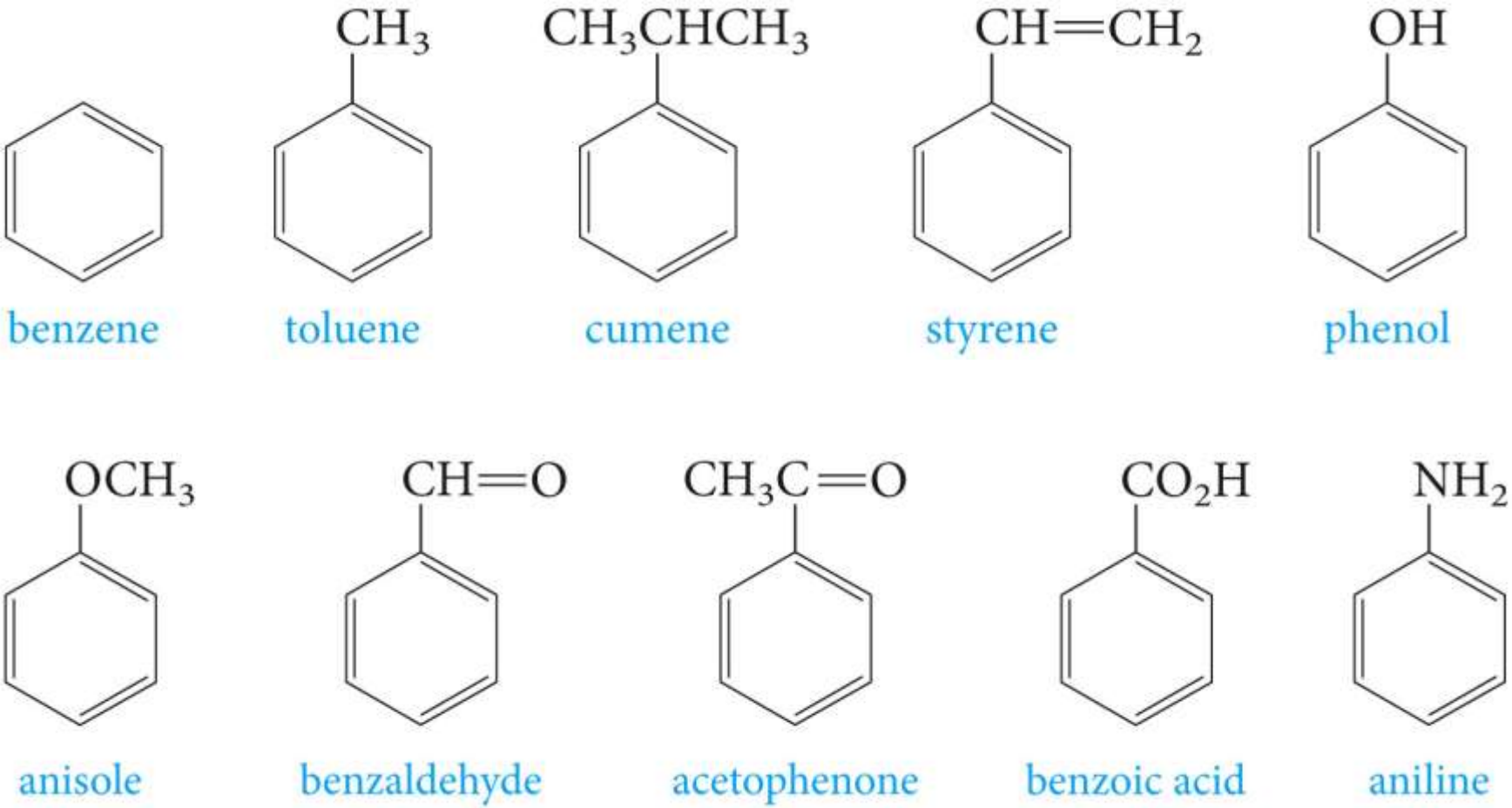


Kekulé

delocalized pi cloud

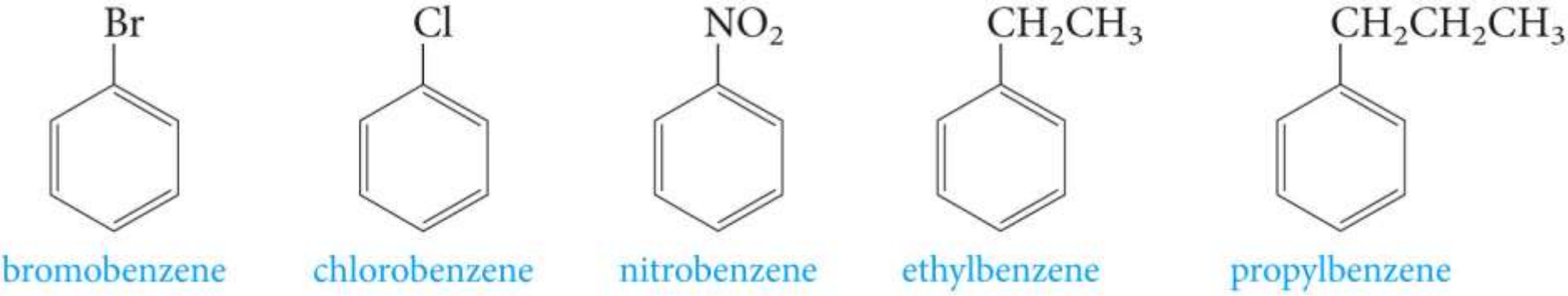
4.6 Nomenclature of Aromatic Compounds :

Some common names of *mono*-substituted benzene:



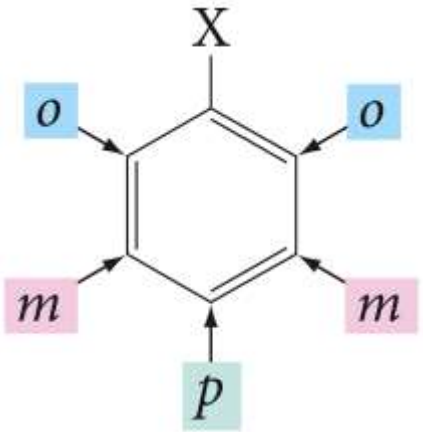
IUPAC names :

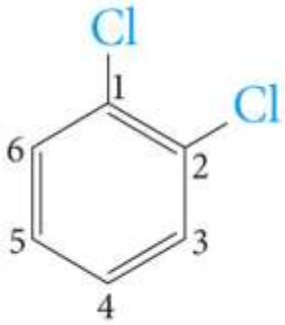
1- *mono*-substituted benzene : **No numbers**



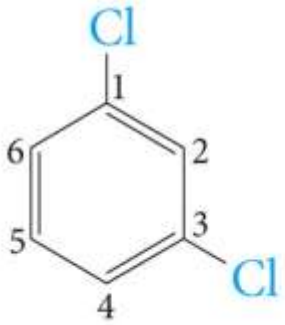
2- di-substituted benzene :

use **numbers** or **prefixe**s: (*ortho*-, *meta*-, *para*-). [*o-, m-, p-*]

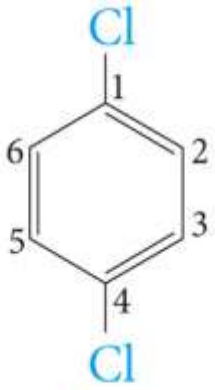




ortho-dichloro-benzene



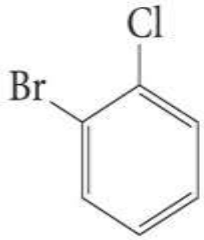
meta-dichloro-benzene



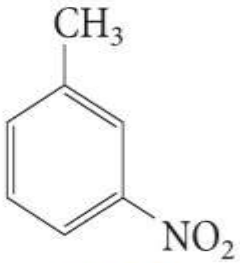
para-dichloro-benzene

para-xylene**

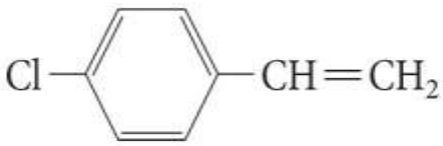
para-chlorobenzene-sulfonic acid



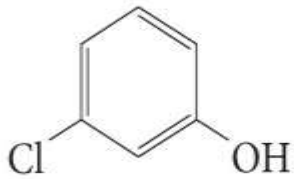
o-bromochlorobenzene (note alphabetical order)



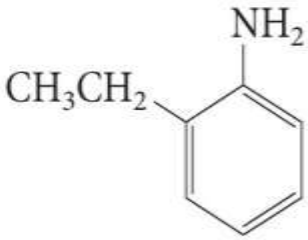
m-nitrotoluene



p-chlorostyrene

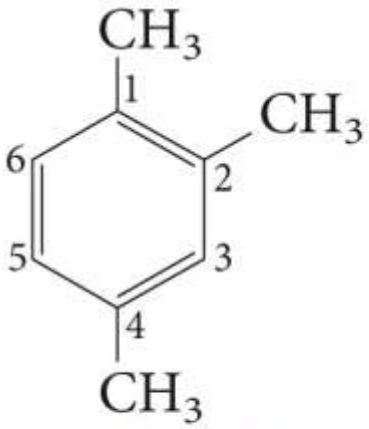


m-chlorophenol

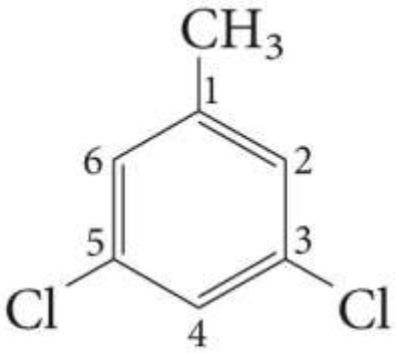


o-ethylaniline

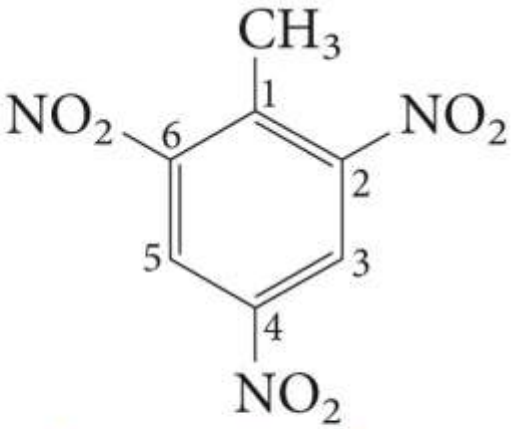
More than two substituents : **only numbers** used.



1,2,4-tri-methylbenzene



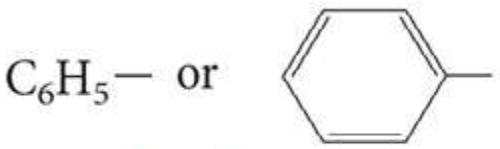
3,5-dichlorotoluene



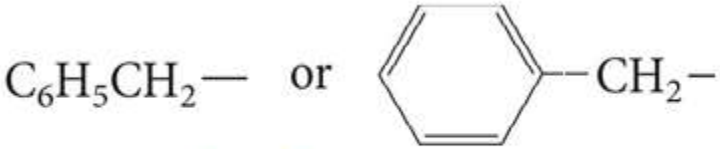
2,4,6-trinitrotoluene (TNT)

Arenes : aromatic hydrocarbons as a class

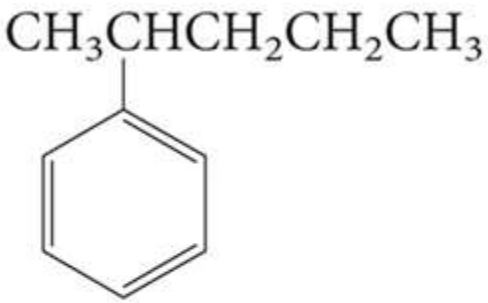
Aryl group (Ar) : any aromatic substituent



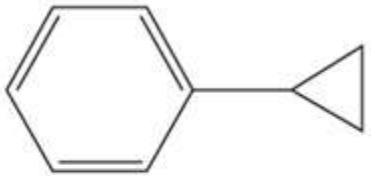
phenyl group



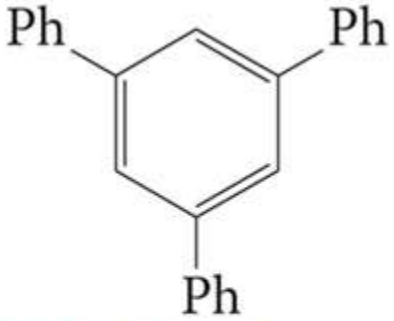
benzyl group



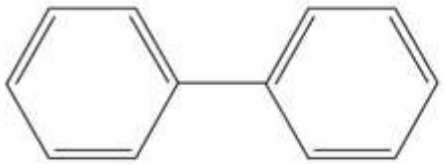
2-phenylpentane
(or 2-pentylbenzene)



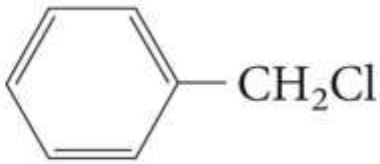
phenylcyclopropane
(or cyclopropylbenzene)



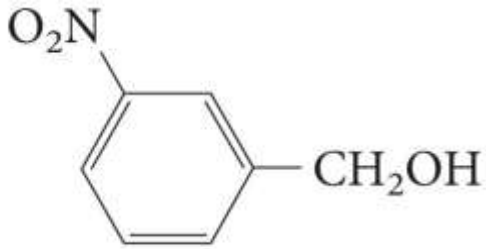
1,3,5-triphenylbenzene



biphenyl



benzyl chloride



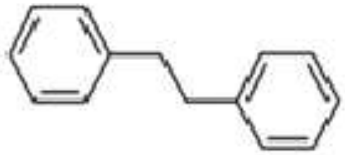
m-nitrobenzyl alcohol

PROBLEM 4.9 Draw the structure of

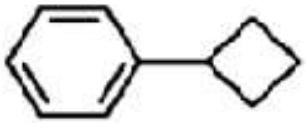
a. dibenzyl
b. cyclobutylbenzene
c. benzyl iodide
d. *p*-phenylstyrene

Answer :

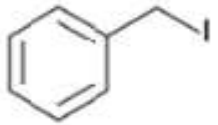
a)



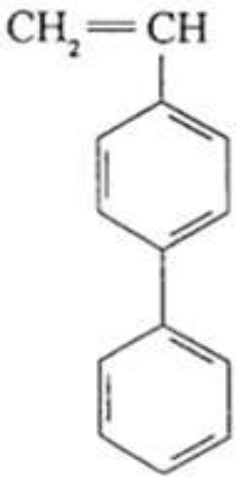
b)



c)

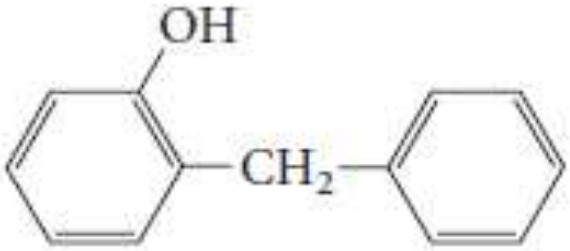


d)



PROBLEM 4.10 Name the following structures:

a. 

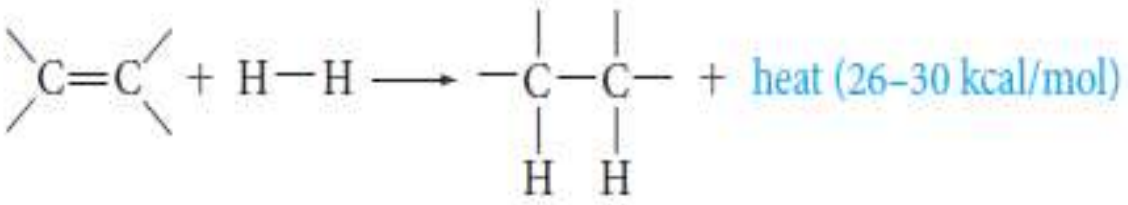
b. 

Answer :

a. phenylcyclohexane or cyclohexylbenzene
b. *o*-benzylphenol

4.7 Resonance Energy of Benzene :

ΔH (**Hydrogenation**) of π-bond in alkene **≈ (- 28)** kcal/mol



(**exothermic**)

> For **1,3**-cyclohexa**diene** (2 C=C) : **ΔH = 2** X 28.6 = **57.2** kcal/mol.

> **Expected** for **1,3,5**-cyclohexa**triene** : **ΔH = 3** X 28.6 ≈ **86** kcal/mol.

(**Note:** **1,3,5**-cyclohexatriene with **localized π-bonds** does not exist)

> **ΔH** (Hydrogenation) of benzene = **50** kcal/mol

(36 kCal **less** than expected)

➢ **Explanation:**

Benzene is stabilised by 36 kcal/mol because of resonance.

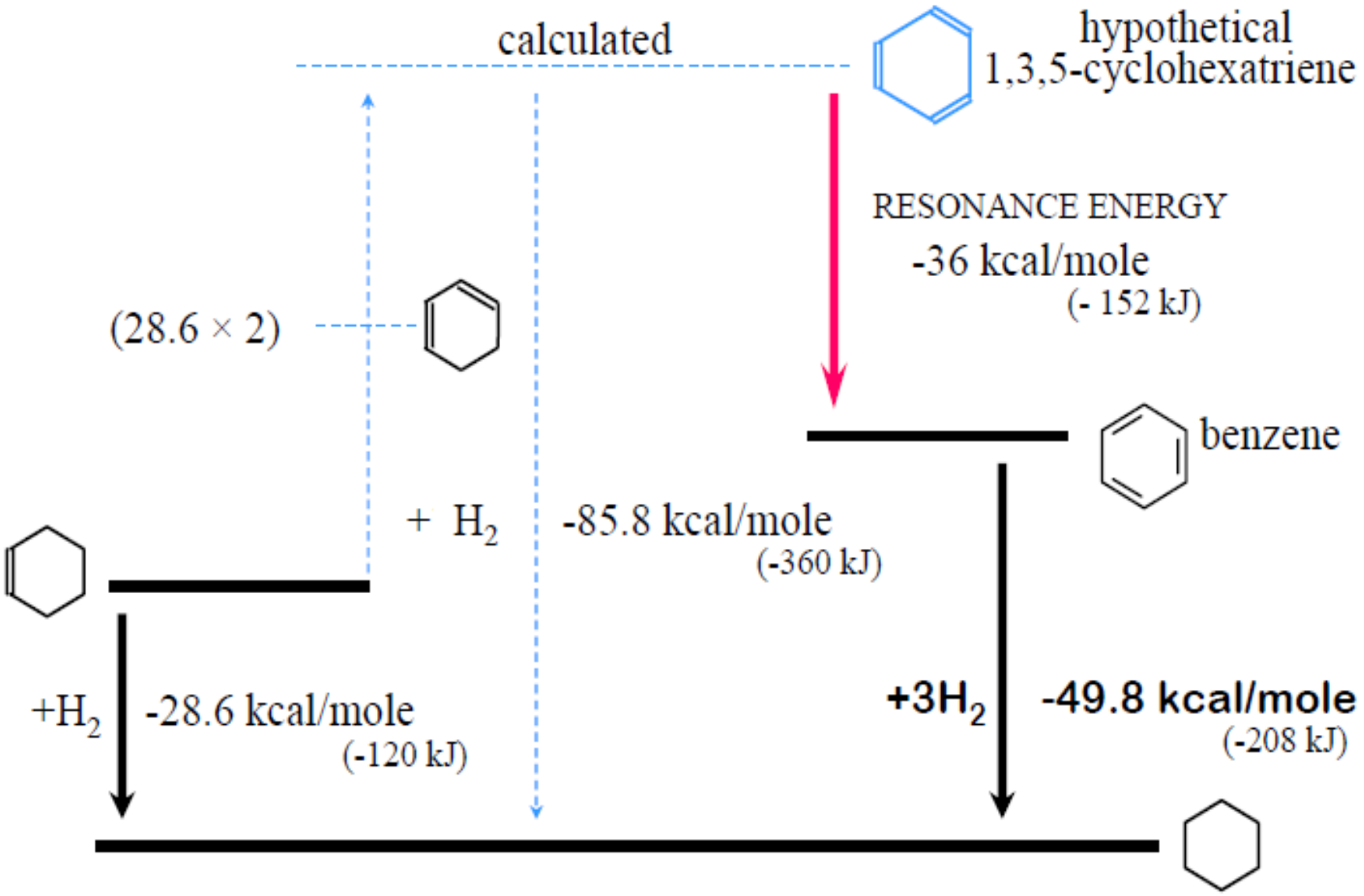
(Resonance Energy **(stabilization by resonance)** in benzene = 36 kcal/mol)

Conclusions :

1- Actual benzene molecule (with delocalized C=C bonds) more stable than contributing resonance structures (with localized C=C bonds) by **36 kcal/mol** (86 - 50 = 36).

2- Resonance energy is the difference between energy of real molecule and calculated energy of the most stable resonance structure.

3- Benzene and all aromatic compounds react in a way to **preserve aromaticity** and retain stabilization.

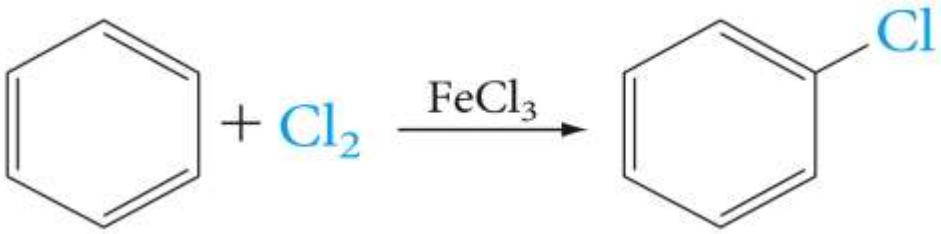

calculated
hypothetical
1,3,5-cyclohexatriene
RESONANCE ENERGY
-36 kcal/mole
(- 152 kJ)
(28.6 × 2)
benzene
+ H2
-85.8 kcal/mole
(-360 kJ)
+H2
-28.6 kcal/mole
(-120 kJ)
+3H2
-49.8 kcal/mole
(-208 kJ)

4.8 Electrophilic Aromatic Substitution :

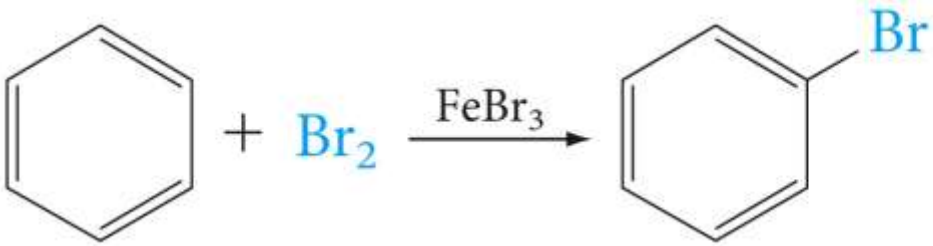
Benzene reacts in a way to preserve aromaticity and retain its resonance energy (stabilization)

Reactions : Benzene is electron-rich, it reacts with Electophiles to give aromatic products by substitution of H (**Electrophilic Aromatic Substitution**)

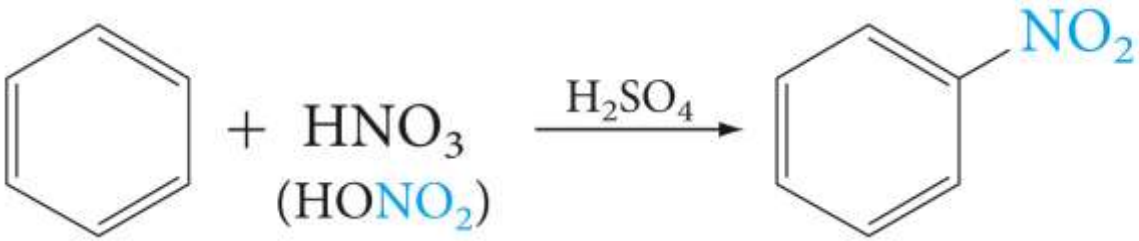
.



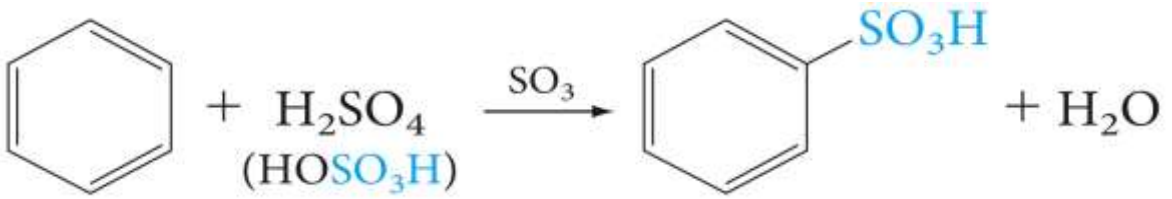
Chlorination



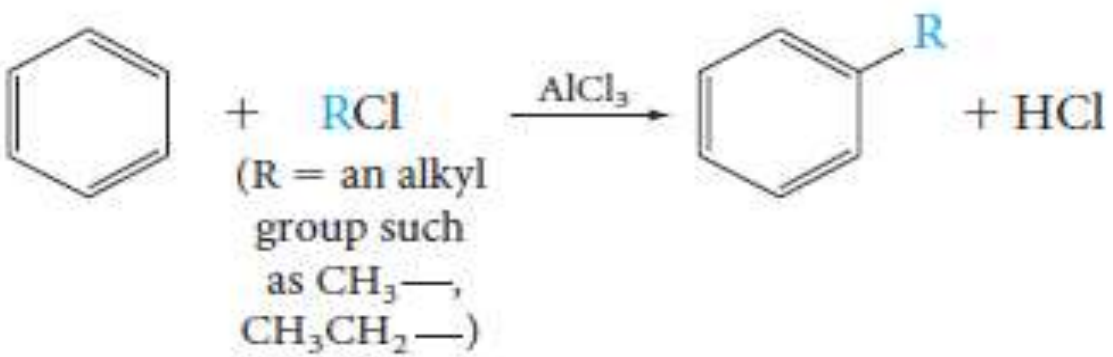
Bromination



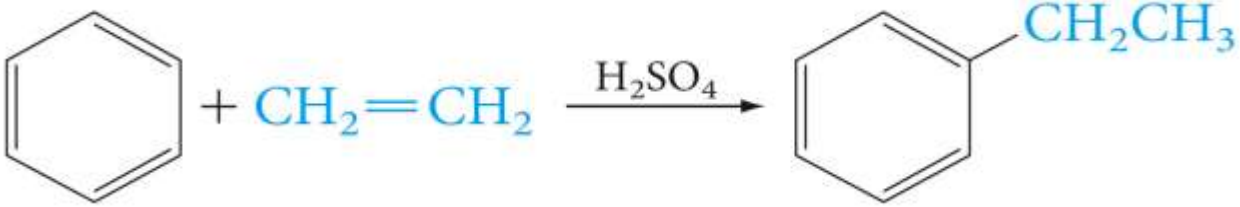
Nitration



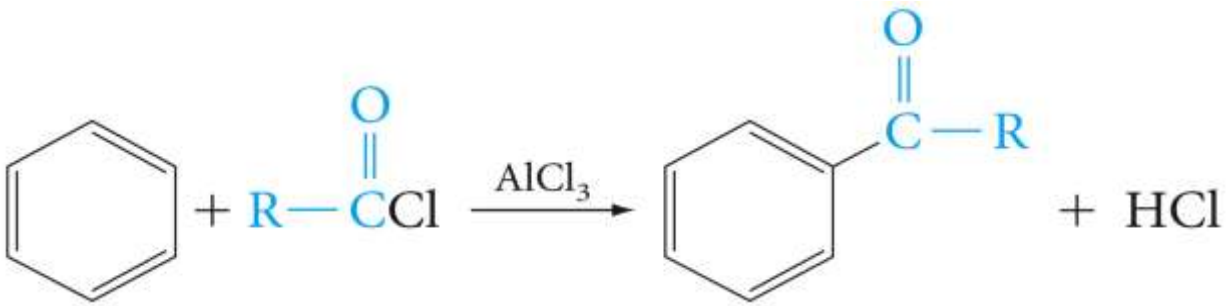
sulfonation



Friedel-Craft's alkylation



alkylation

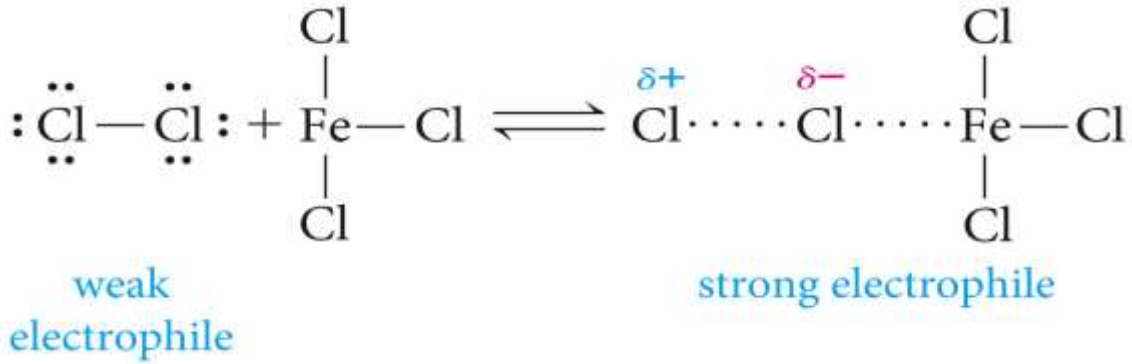


acylation

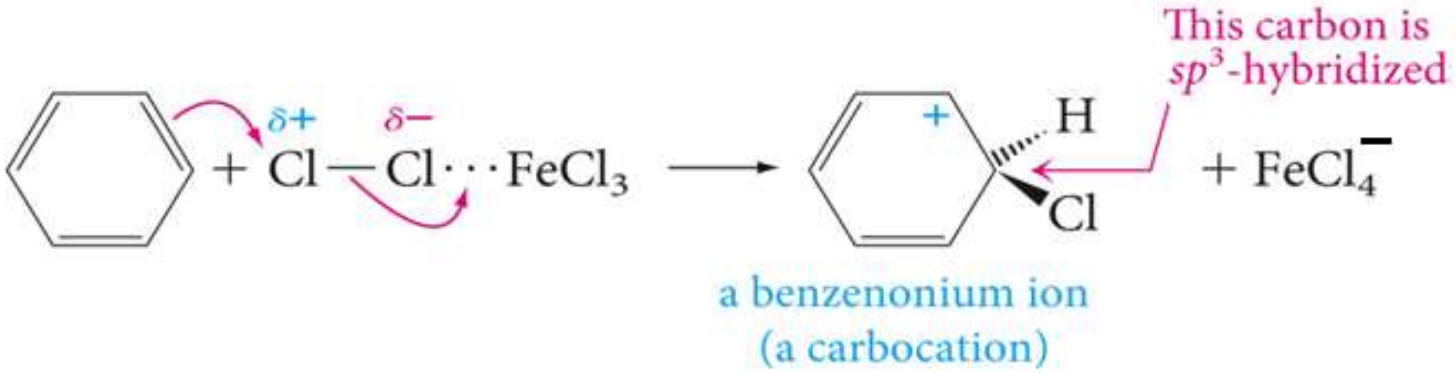
4.9 Mechanisms of Electrophilic Aromatic Substitution :

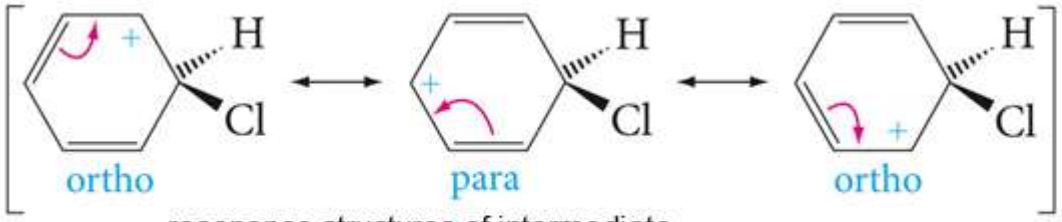
Halogenation:

1- FeCl3 catalyst (Lewis acid) generates the electrophile : **$Cl^{+\delta}$**

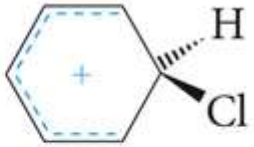


2- Benzene donates electrons to the electrophile forming a carbocation intermediate, thus losing aromaticity.



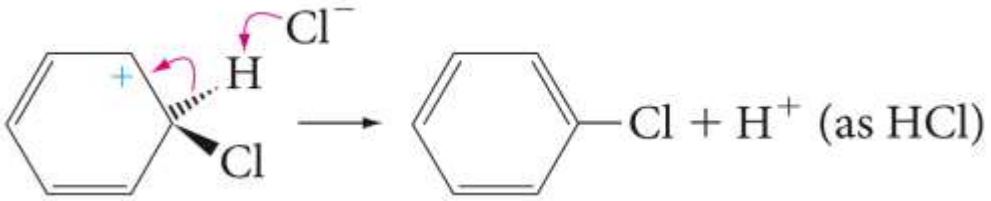


resonance structures of intermediate
+ charge appears at ortho and para positions

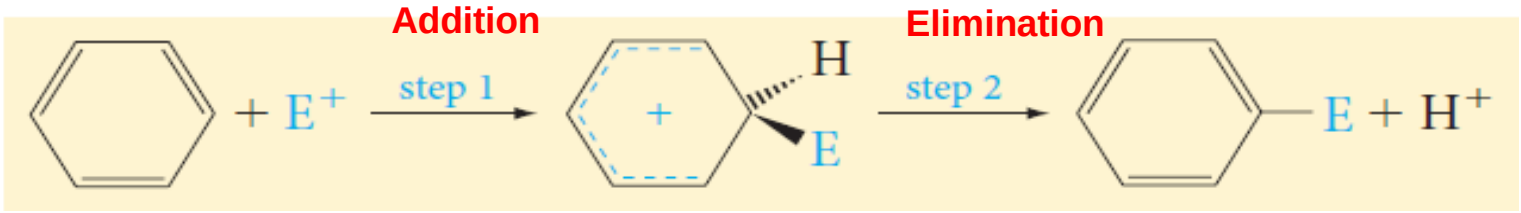


resonance hybrid
of the benzenonium ion

3- The nonaromatic intermediate regains aromaticity by loss of proton

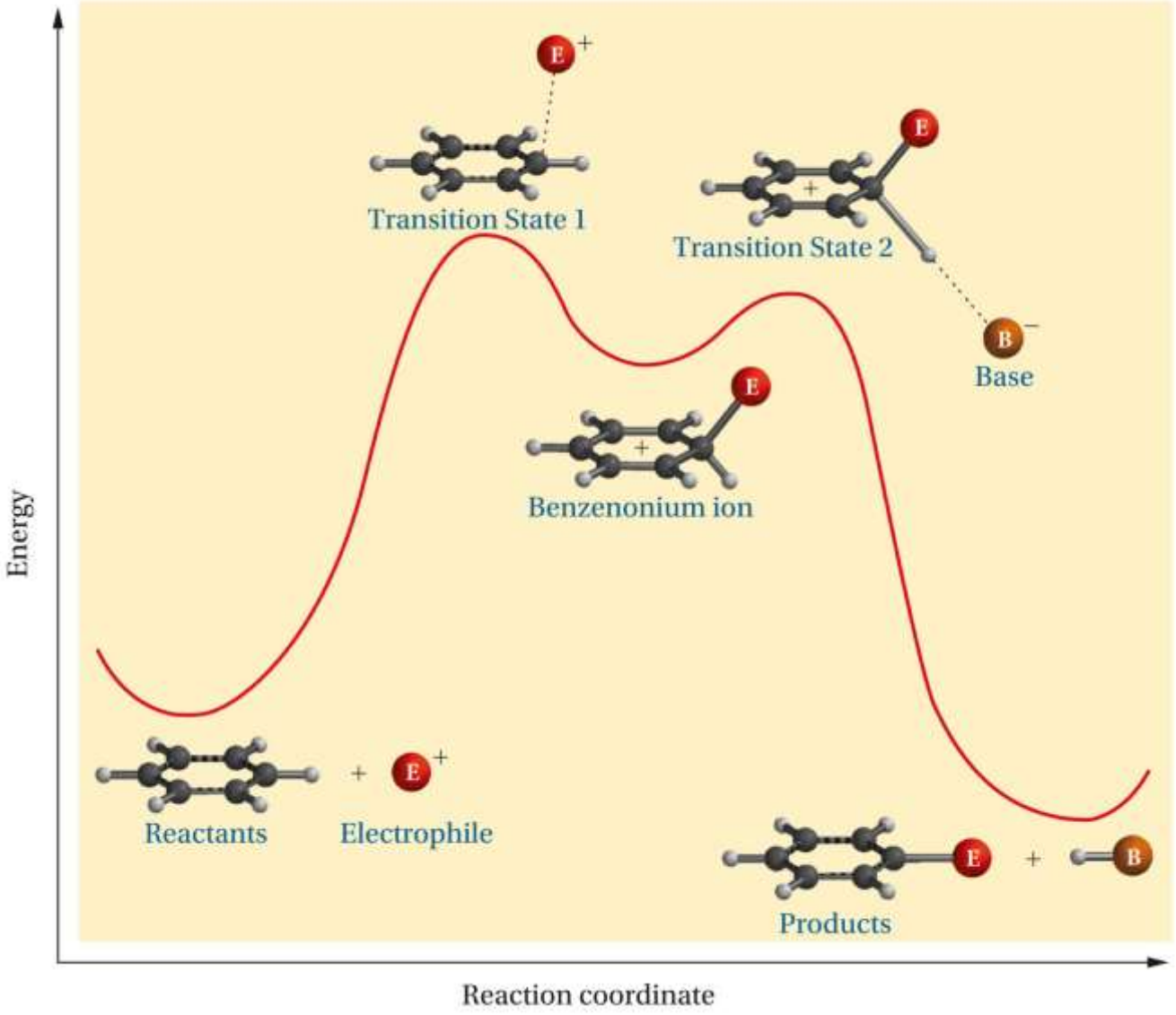


General Reaction Mechanism :



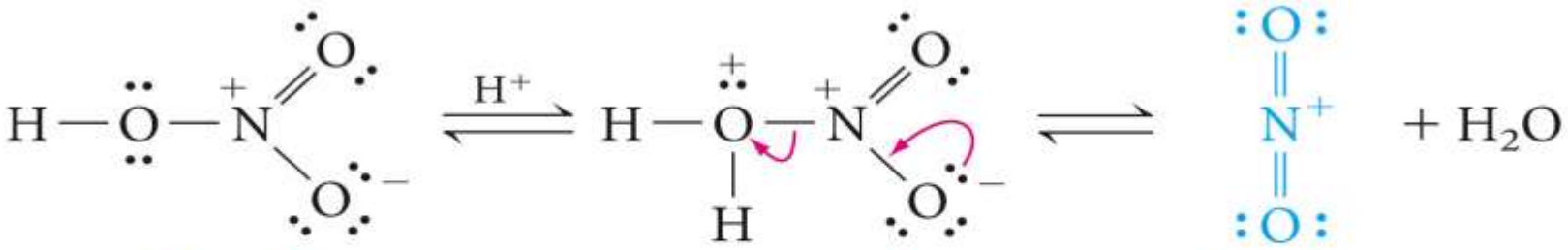
Benzenonium ion intermediate

Reaction energy diagram



Nitration :

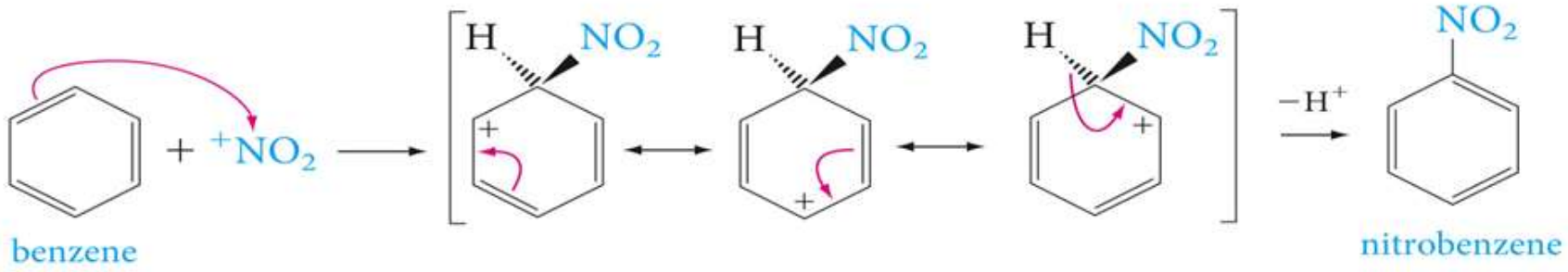
1- Generation of nitronium ion (electrophile) from HNO_3



nitric acid — protonated nitric acid — nitronium ion

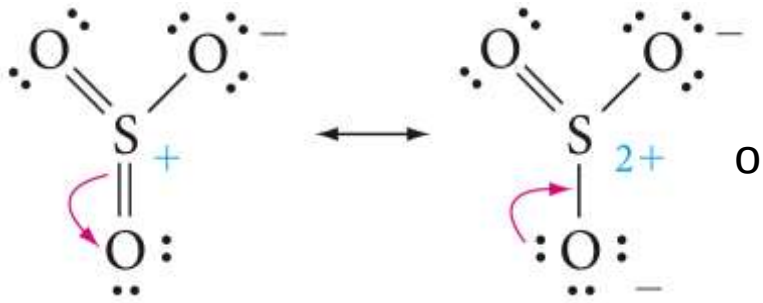
(Electrophile)

2- Addition of electrophile followed by elimination of proton

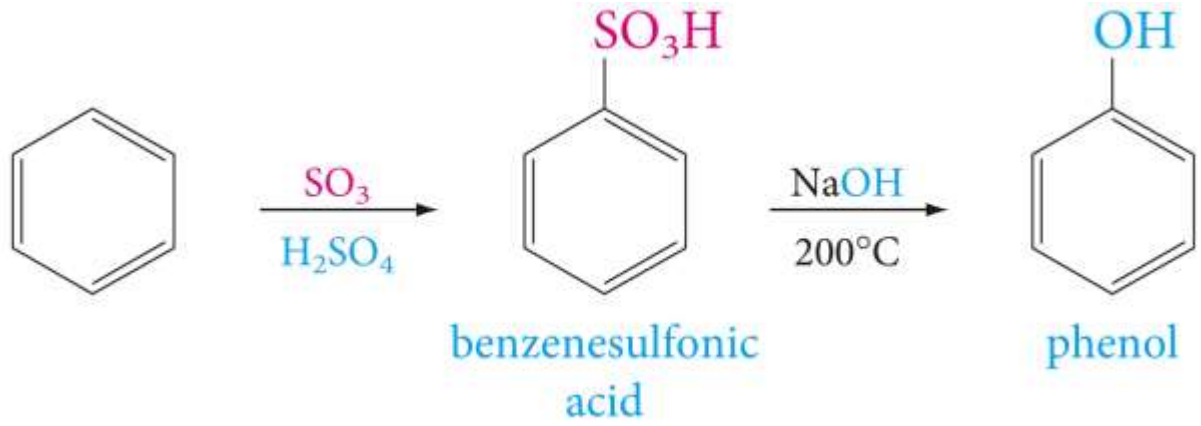


benzene — nitrobenzene

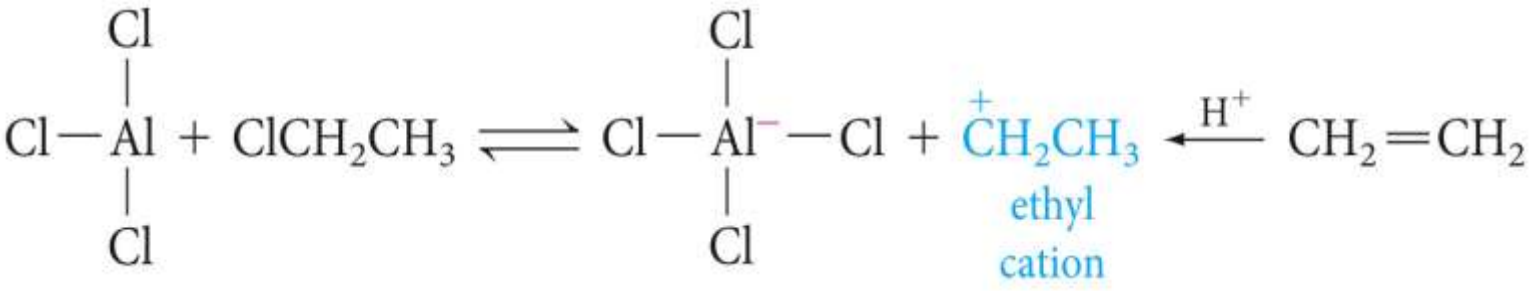
Sulfonation:



or **[SO3H]+** **(Electrophile)**

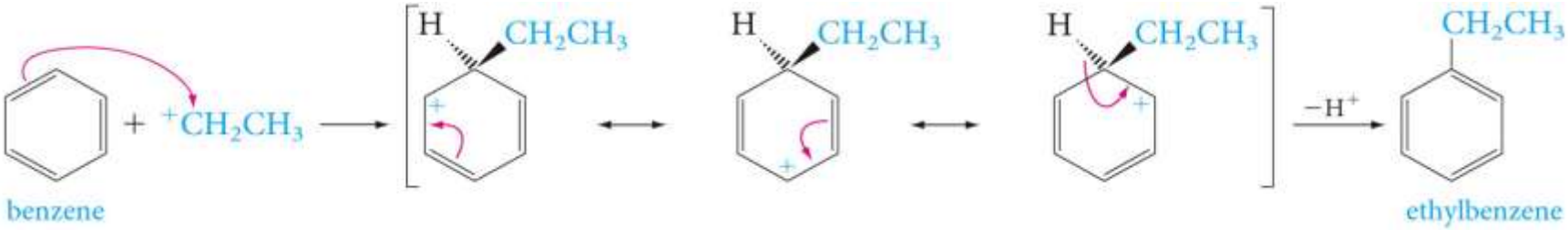


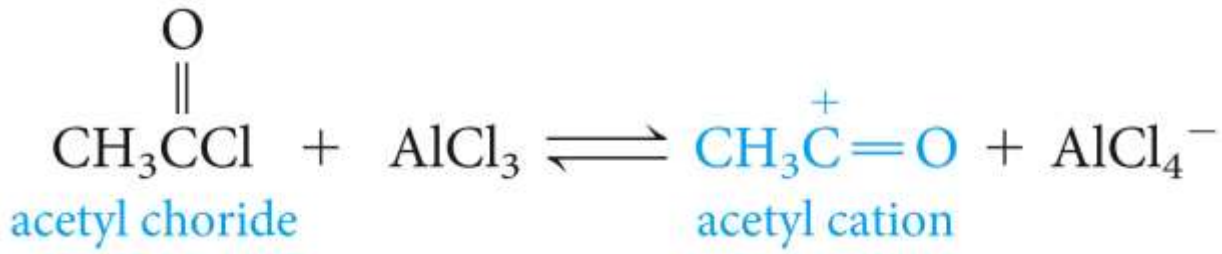
Friedel-Crafts alkylation and acylation :



(carbocation)

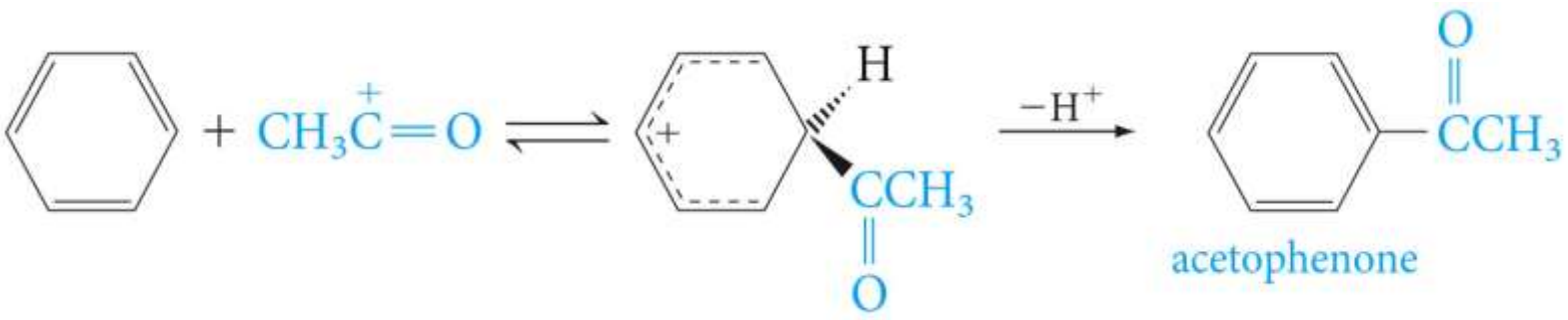
(Electrophile)





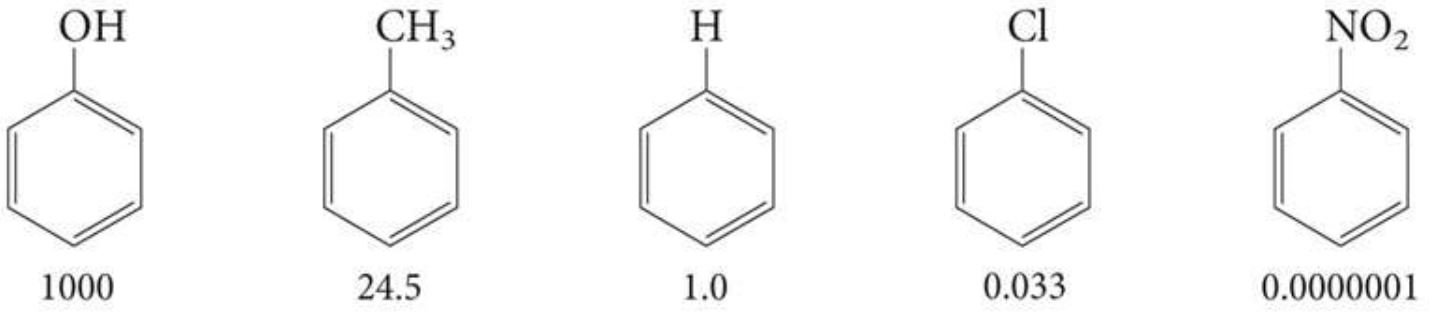
(acylium ion)

(Electrophile)



4.10 Ring-Activating and Ring-Deactivating Groups :

Relative rates of nitration



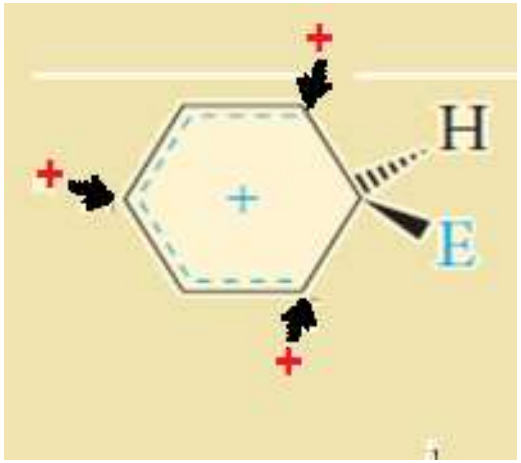
Faster **Slower**

1- e-donating (releasing) substituents increase electron density on the ring and speed up the reaction **(Activating)**

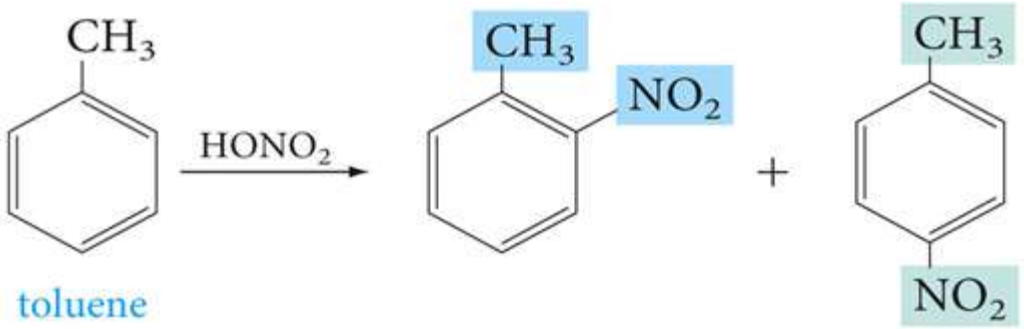
2- e-withdrawing substituents decrease electron density on the ring and slow down the reaction **(Deactivating)**

4.11 ortho, para- and meta-directing groups :

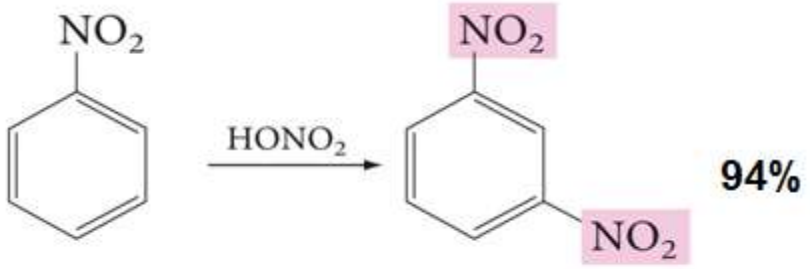
Groups present on the ring determine the position of new substituent



We need e-releasing groups at these positions
But e-withdrawing groups better at m-position

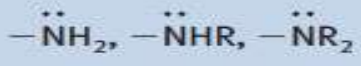
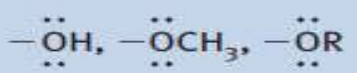
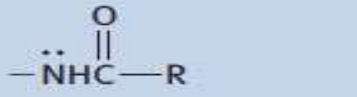
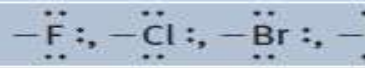
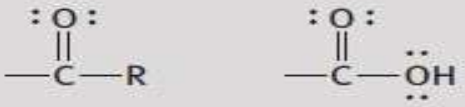
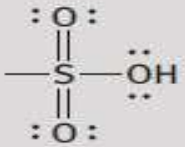
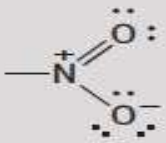


Alkyl groups are activating and o-, p-directing

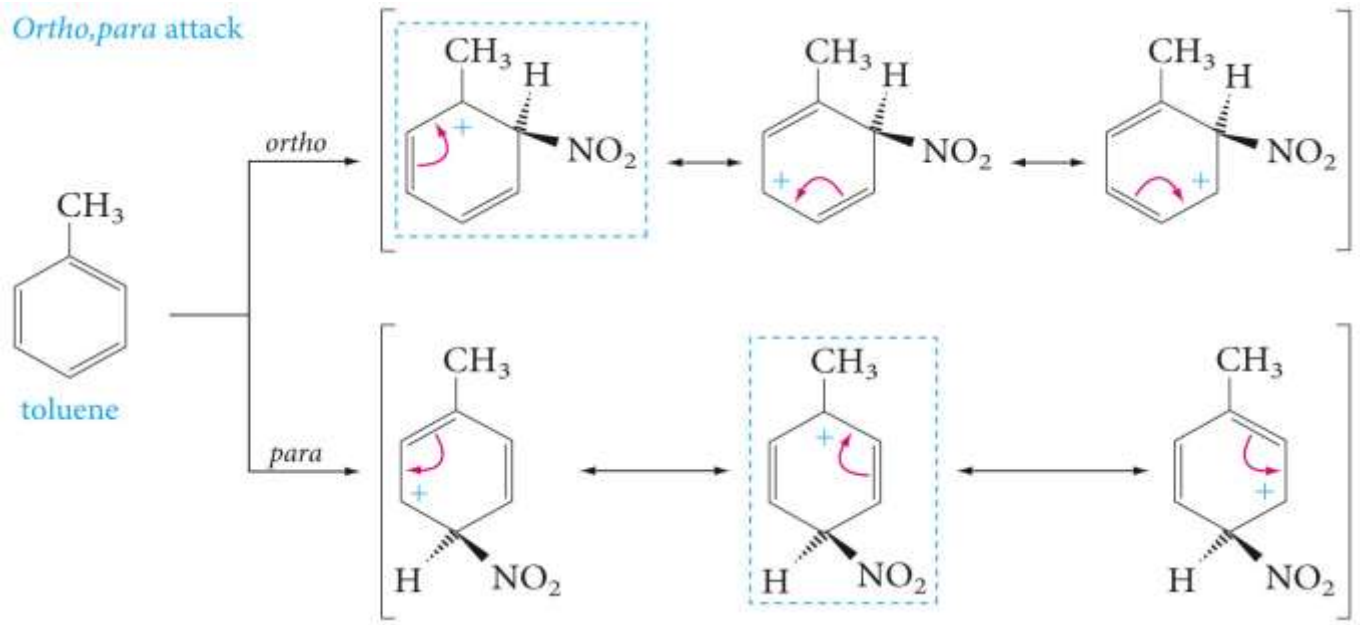


E-withdrawing groups are deactivating and m-directing

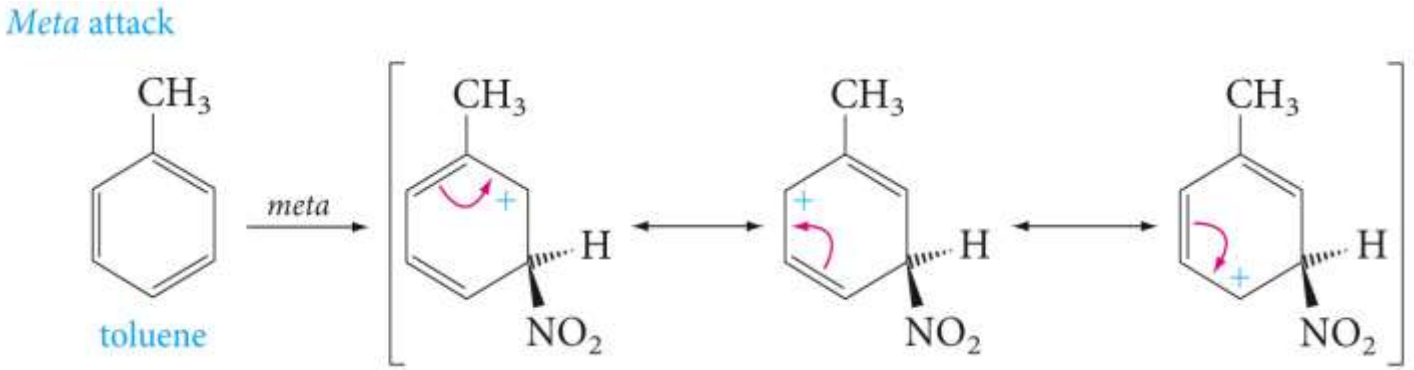
Table 4.1 Directing and Activating Effects of Common Functional Groups (Groups are Listed in Decreasing Order of Activation)

	Substituent group	Name of group	
Ortho,Para-Directing		amino	Activating
		hydroxy, alkoxy	
		acylamino	
		alkyl	
		halo	Deactivating
Meta-Directing		acyl, carboxy	
		carboxamido, carboalkoxy	
		sulfonic acid	
		cyano	
		nitro	

1- ortho, para-directing groups :



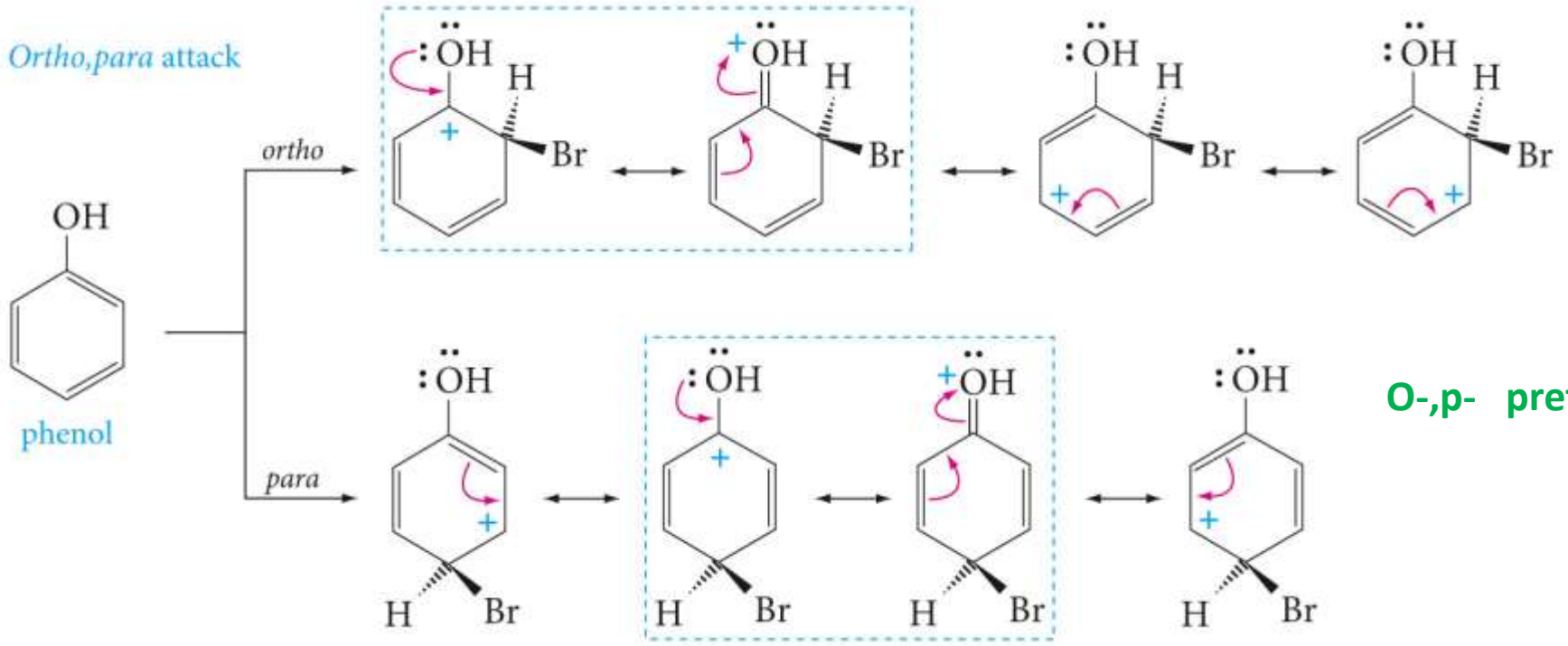
O-,p- preferred

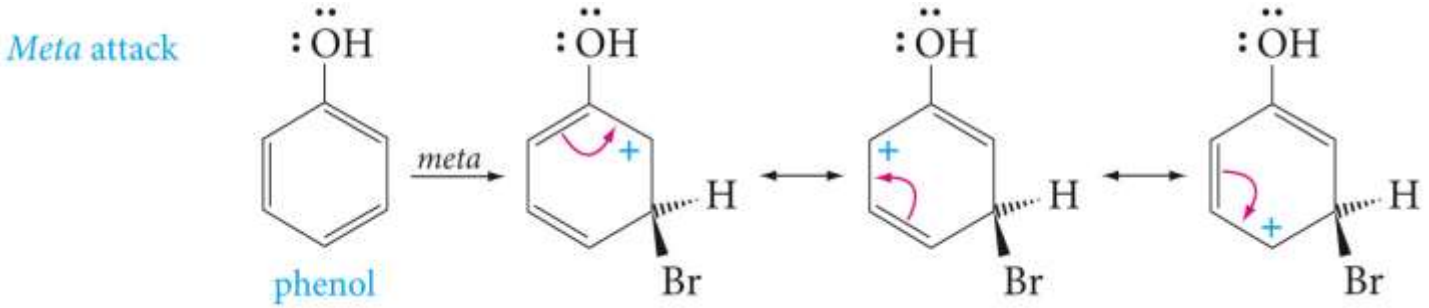


m- Not preferred.

groups with unshared electrons are strong activating and o-, p-directing:

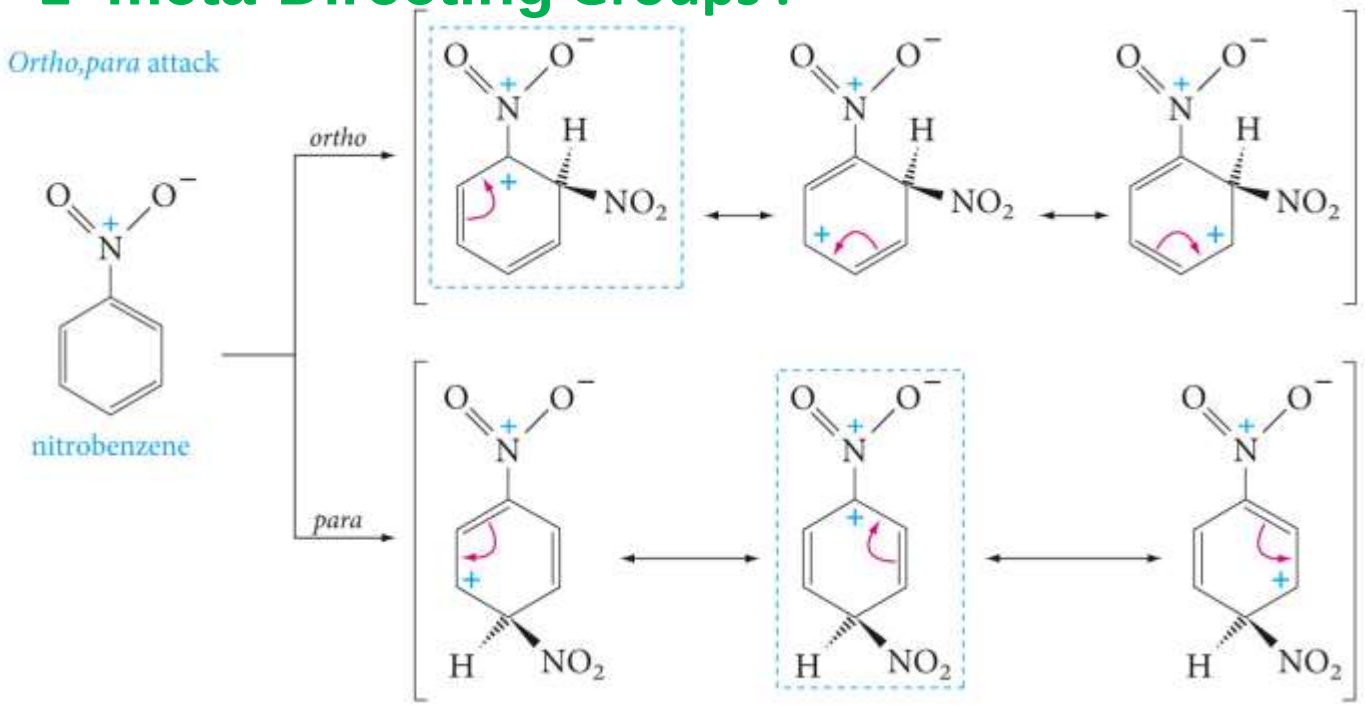
OH OCH3 OCOCH3 NH2 NHCH3 N(CH3)3 NHCOCH3





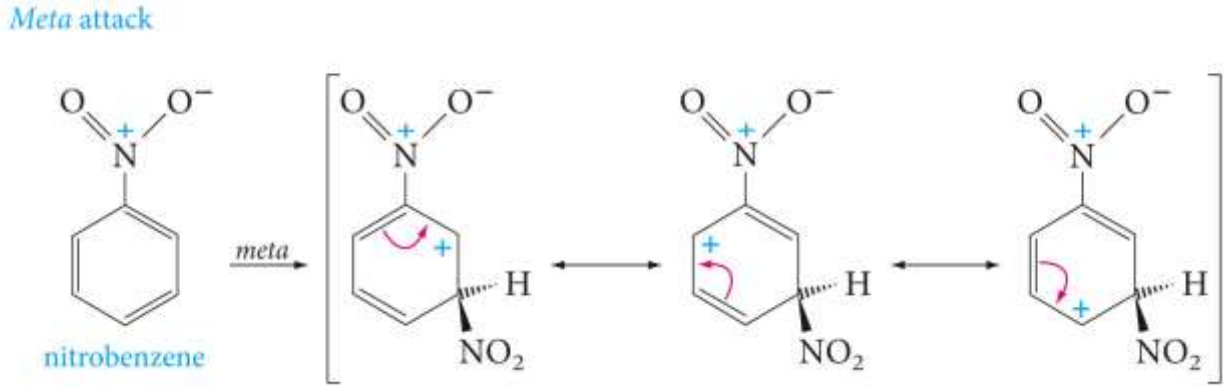
m- Not preferred.

2- meta-Directing Groups :



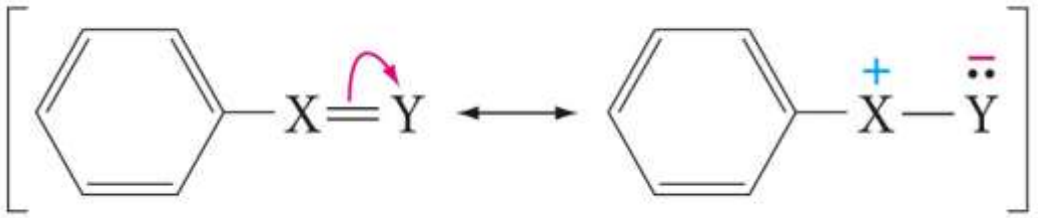
o,p-substitution
Not preferred

One resonance structure has two adjacent +ve charges (highly unstable)

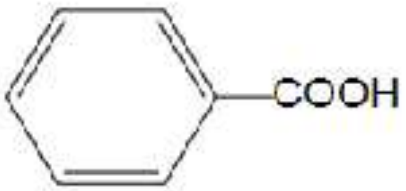


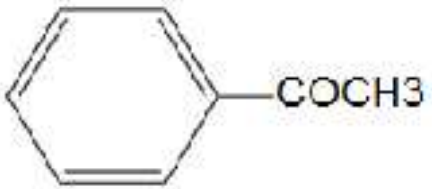
meta substitution preferred.

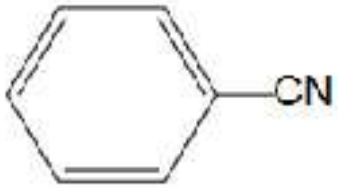
Groups in which the atom directly attached to the ring is positively charged or part of a multiple bond to electronegative element are *meta*-directing.

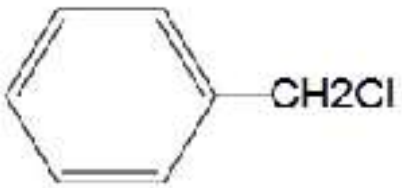


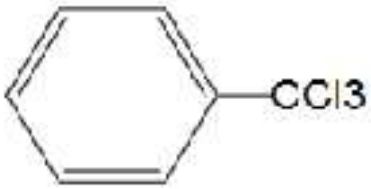
Y is an electron-withdrawing atom such as oxygen or nitrogen; atom X carries a positive charge in one of the resonance contributors.











Substituent Effect on Reactivity :

1) ortho,para-directing groups donate electrons to the ring.

They are activating.

2) meta-directing groups are e-withdrawing (have +ve or partial +ve charge)

They are deactivating .

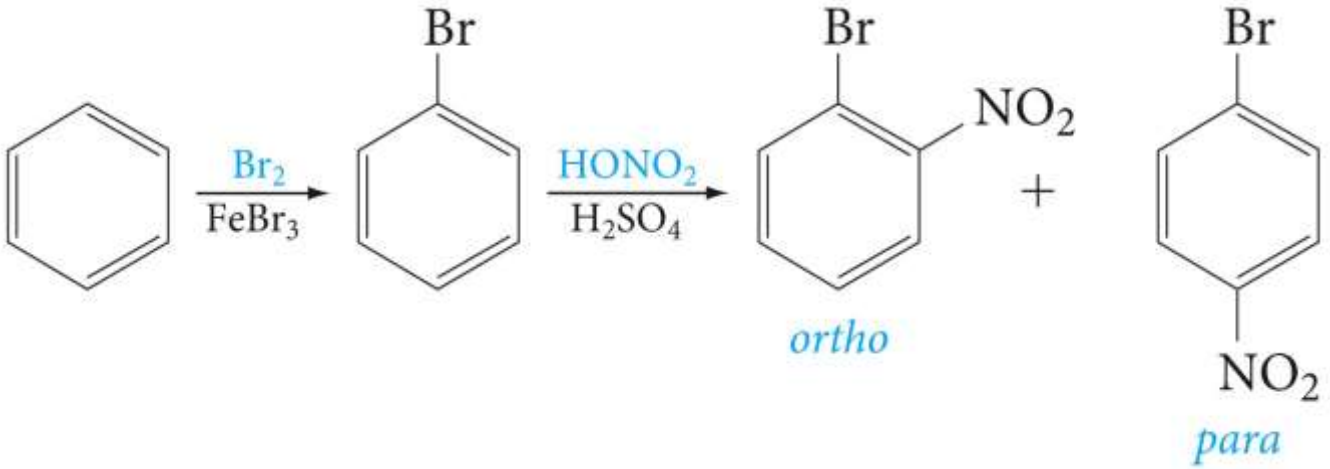
3) Exception : **Halogens** (F, Cl, Br, and I) have two opposing effects:

They are electron withdrawing and **deactivating**

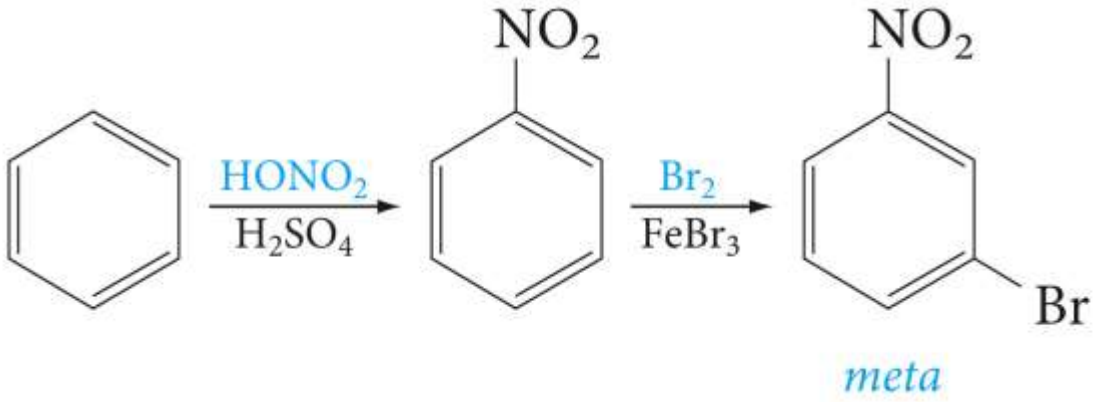
But they have unshared es, so they are **ortho,para-directing**.

4.12 Importance of Directing Effects in Synthesis :

a- How to prepare p-Bromonitrobenzene ?



b- How to prepare m-Bromonitrobenzene ?

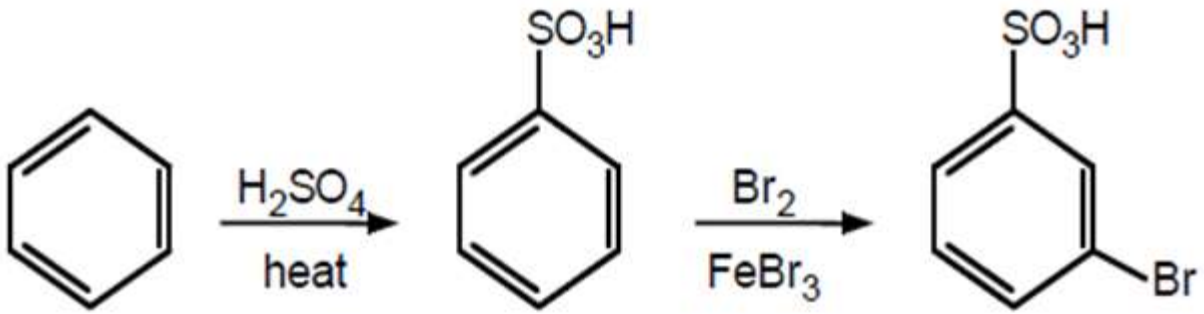


PROBLEM 4.16

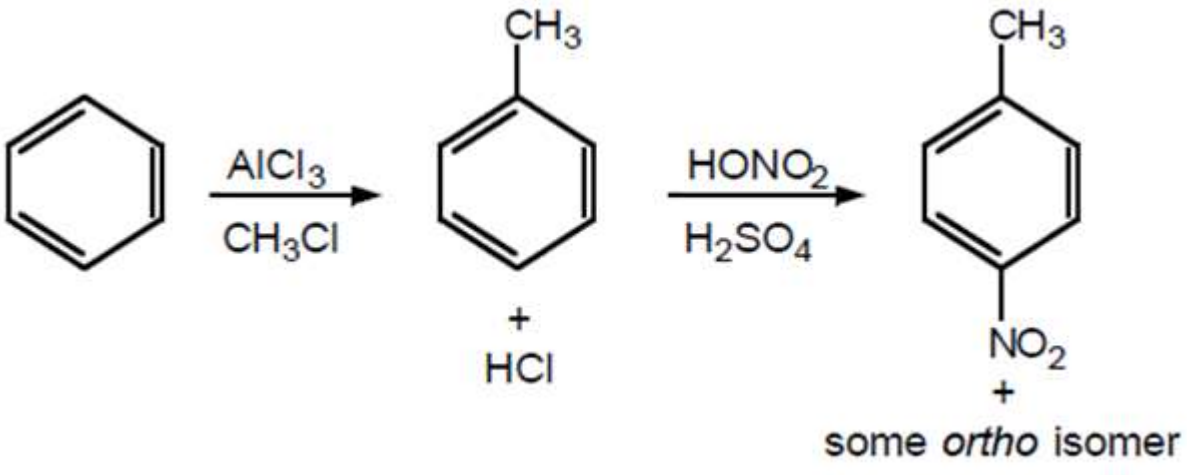
Devise a synthesis for the following, starting with benzene:

a- *m*-bromobenzenesulfonic acid **b-** *p*-nitrotoluene

a-



b-



Questions

Chapt 3 : 33 34 37 38 41 42 53 55 59

Chapt 4 : 21-24 30-32 37-40 43