

# Organic Chemistry

## CHEM 145

2 Credit hrs

*Chemistry Department*

*College of Science*

*King Saud University*

By

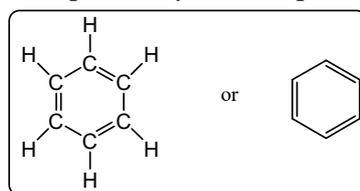
**Prof. Mohamed El-Newehy**

### Benzene & Aromatic Compounds

➡ Today a compound is said to be aromatic if it is *benzene-like in its properties*.

### Structure of Benzene: Resonance Description

➡ Benzene,  $C_6H_6$ , is a planar, cyclic compound.



➡ If the structure we have shown were correct.

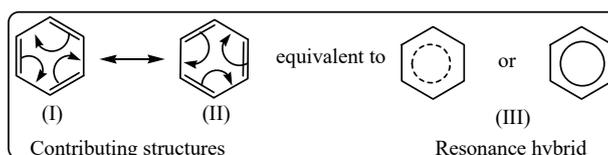
➡ We would expect benzene to be “1,3,5 cyclohexatriene”

➡ We would expect the molecule to have the shape of an irregular hexagon with

➡ three C—C bond lengths of 1.54 Å

➡ three C=C bonds of 1.34 Å

- ➔ X-ray diffraction experiments reveals that *all* carbon-carbon bonds in benzene are of **equal length, 1.39 Å**.
- ➔ Expect benzene to undergo addition reactions  
**the typical reaction of benzene is substitution, rather than addition.**
- ➔ The true structure of benzene can be explained by the **concept of resonance**.

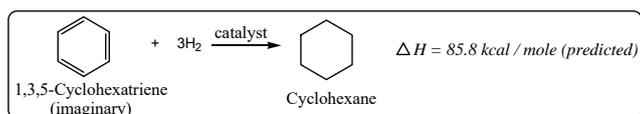
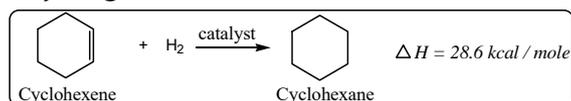


### Structure of Benzene: Molecular Orbital Description

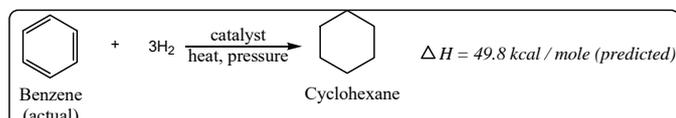
- ➔ We expect benzene to be
  - A planar molecule having the shape of a regular hexagon, with bond angles of  $120^\circ$ .
  - All the carbon-carbon bond distances to be intermediate (1.39 Å) between the usual C-C single bond (1.54 Å) and the typical C=C double bond (1.34 Å).

### Stability of Benzene: Resonance Energy

- ➔ The heat of hydrogenation



- ➔ Actually, when benzene is hydrogenated to cyclohexane, **only 49.8 kcal/mole of energy is liberated.**



- ➔ Recall that we defined aromatic compounds as *those with benzene-like properties*.
- ➔ Like benzene, aromatic compounds tend to undergo substitution rather than addition.

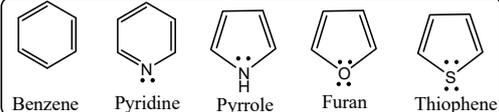
### Aromatic Character (Aromaticity): The $(4n + 2)$ Rule

➔ **Aromatic character (Aromaticity)** is associated with several structural requirements.

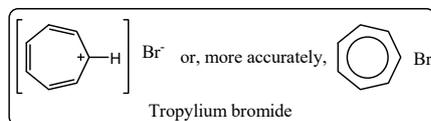
- ① **Aromatic compounds** are *cyclic structures that contain what looks like a continuous system of alternating double and single bonds.*
- ② **Aromatic compounds** must be planar.
- ③ **Aromaticity** is possible only if  
*i.e. obey Hückel's rule*  
*the number of  $\pi$  electrons in the compound =  $(4n + 2)$*

Where ( $n = 1, 2, 3,$  and so on).

### Aromatic Character (Aromaticity): The $(4n + 2)$ Rule

$n$	$4n + 2$	Structure and name of aromatic compound
1	6	 Benzene    Pyridine    Pyrrole    Furan    Thiophene

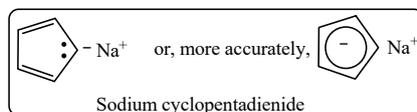
#### Examples



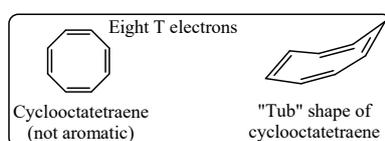
➔ **Tropylium ion** is a seven-membered ring that contains three double bonds.

The ring has a total of **six  $\pi$  electrons**,

**It is therefore aromatic.**



- ➔ **Cyclopentadienide anion** is a five-membered ring  
 The ring has a sextet  $\pi$  electrons,  
 two double bonds and a pair of nonbonded electrons.  
 It is therefore aromatic

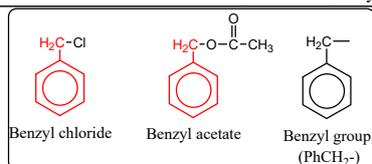
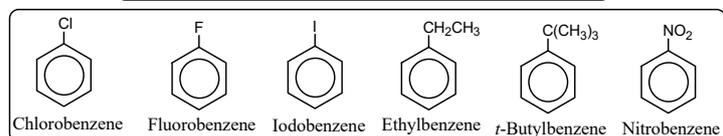
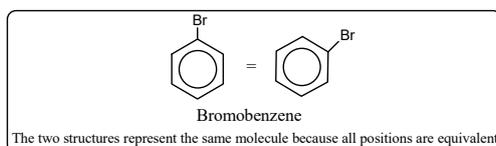


- ➔ **Cyclooctatetraene**,  
 $(4n + 2) = 8 \pi$  electrons  
 no integral value of  $n$   
 Cyclooctatetraene is not aromatic.

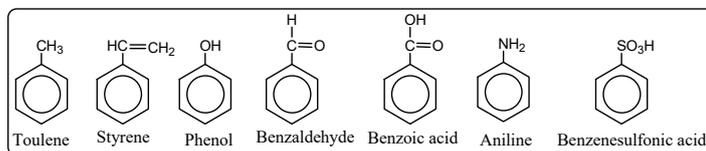
## Nomenclature of Aromatic Compounds

### Monosubstituted Benzenes

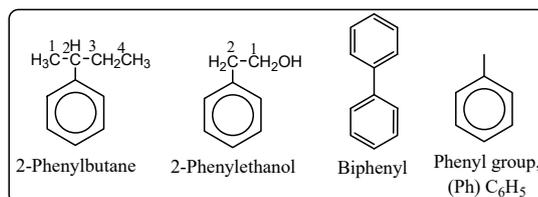
- ➔ Because all six positions in benzene are equivalent,  
 there is no need to specify by a number the position of a substituent for monosubstituted benzenes.



➡ Some monosubstituted benzenes are considered **parent compounds**;



➡ Sometimes it is more convenient to **name the benzene ring as a substituent**, as in the following structures.



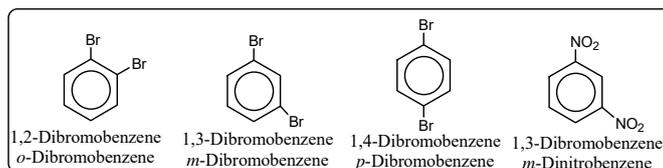
### Disubstituted Benzenes

➡ All disubstituted benzenes, no matter what the substituents, can give rise to three possible isomers.

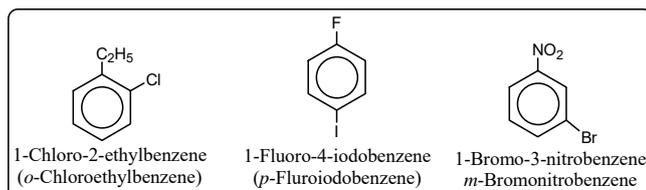
The relative positions of the substituents are designated by

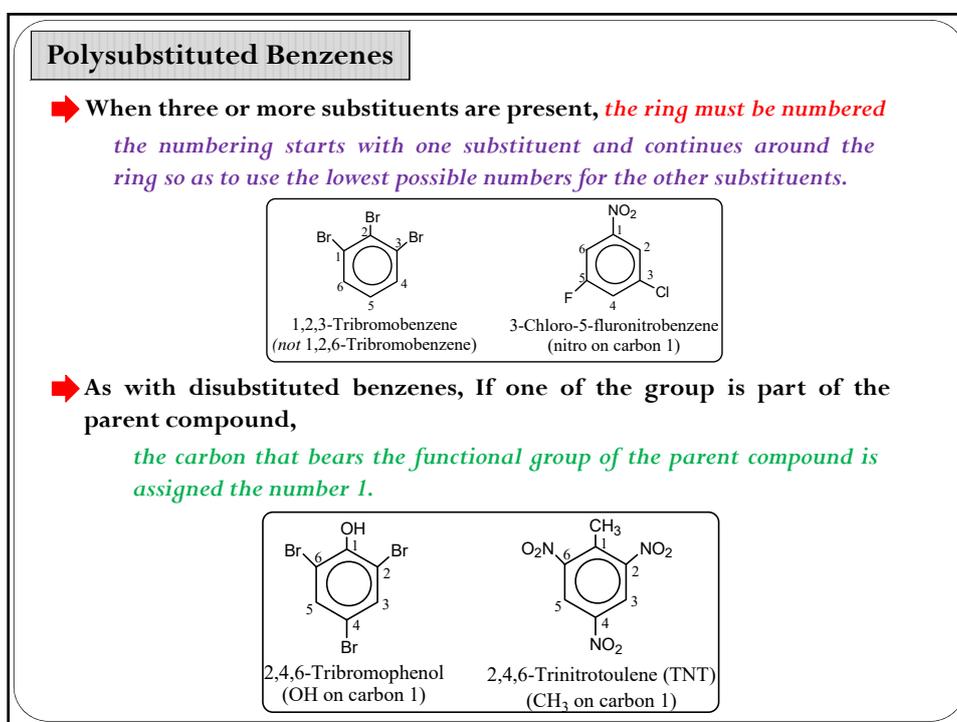
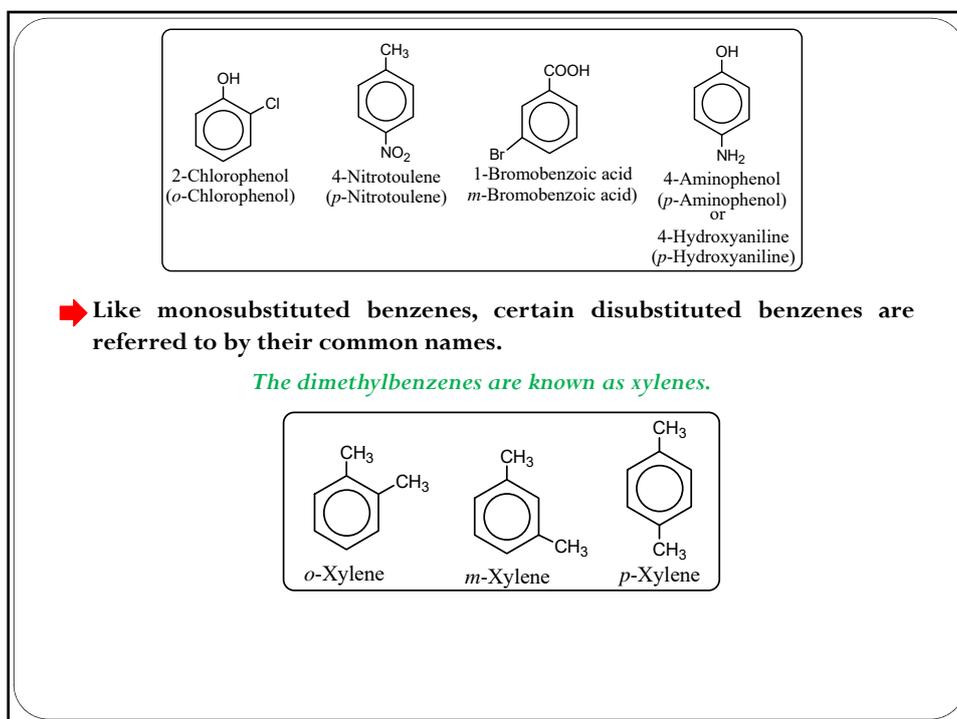
**numbers**

**more commonly, by the prefixes ortho (o-), meta (m-), or para (p-).**



➡ When the substituents are different, they are listed in alphabetical order.



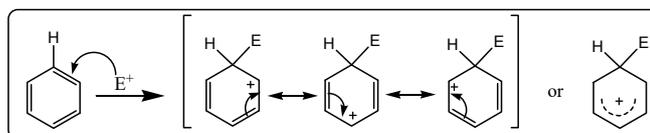


## Electrophilic Aromatic Substitution

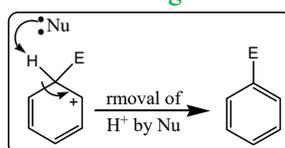
### General Mechanism

- ➔ The aromatic ring, with its delocalized  $\pi$  electrons is an electron-rich system.
- ➔ Attack on the ring takes place by means of an electron-deficient species (Electrophile) ( $E^+$ ).

*Step 1. The electrophile  $E^+$  approaches the cloud of the aromatic ring and forms a bond to carbon, creating a +ve charge in the ring.*

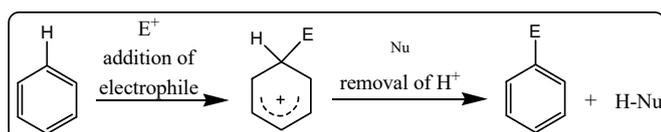


*Step 2. The removal of the proton by the nucleophile Nu, which leads to the restoration of the aromatic ring*



- ➔ The net overall result is the substitution of the group  $E^+$  for a proton  $H^+$ .

i.e. **electrophilic aromatic substitution.**



### The Role of Catalysts

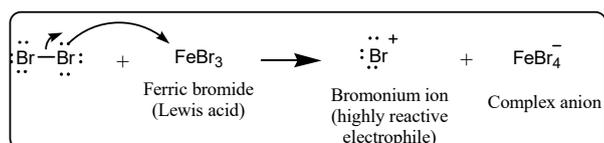
- ➔ The catalysts are **Lewis acids** or a **protonic acid**.

The purpose of these catalysts is to generate **powerful electrophiles**.

### Bromination of benzene

It requires the presence of a **Lewis acid catalyst, ferric bromide**.

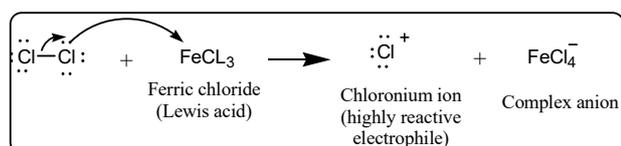
**Ferric bromide** will help to generate a **highly reactive electrophile, the bromonium ion ( $Br^+$ )**.



### Chlorination of benzene

It requires the presence of a **Lewis acid catalyst, ferric chloride**.

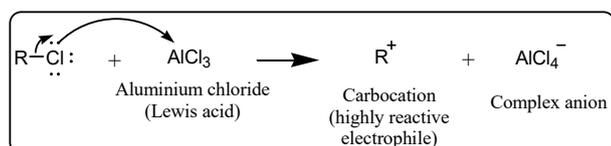
**Ferric chloride** will help to generate a **highly reactive electrophile, the chloronium ion ( $\text{Cl}^+$ )**.



### Alkylation of benzene

It requires the presence of a **Lewis acid catalyst, Aluminium chloride**.

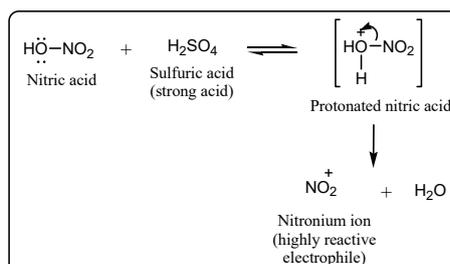
**Ferric chloride** will help to generate a **highly reactive electrophile, the carbocation ( $\text{R}^+$ )**.



### Nitration of benzene

It requires the presence of a **protonated acid, Sulfuric acid**.

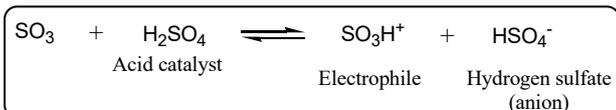
The attacking electrophile in nitration is the **nitronium ion ( $\text{NO}_2^+$ )**.



### Sulfonation of benzene

It carried out in fuming sulfuric acid, which is a solution of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$ .

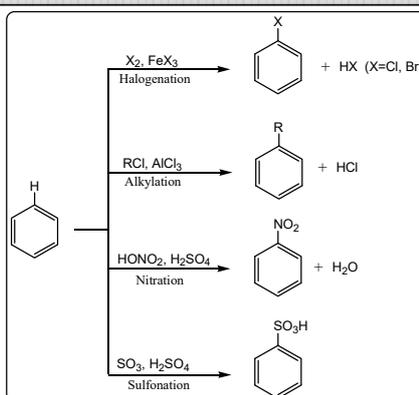
The attacking electrophile in sulfonation is the  **$\text{SO}_3\text{H}^+$** .



► **The electrophiles in common aromatic substitution reactions.**

Electrophile	Name of reaction
$\text{Cl}^+$ or $\text{Br}^+$	Halogenation
$\text{R}^+$	Alkylation
$\text{NO}_2^+$	Nitration
$\text{SO}_3\text{H}^+$	Sulfonation

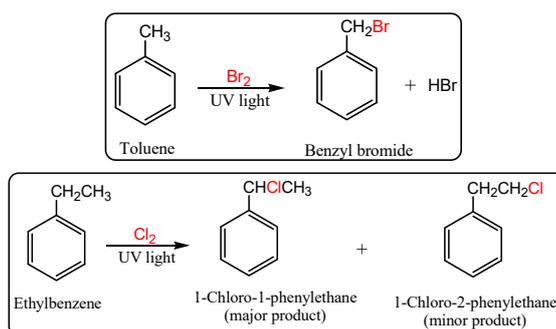
**Specific Electrophilic Aromatic Substitution Reactions**

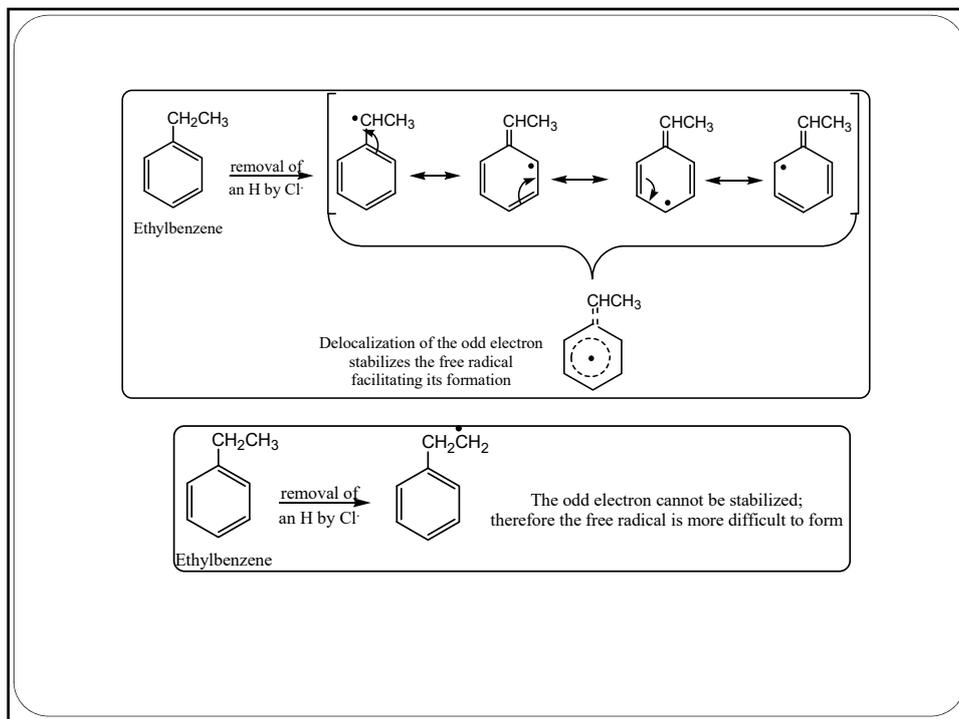


**Side-Chain Reactions of Aromatic Compounds**

**A. Halogenation of an Alkyl Side Chain**

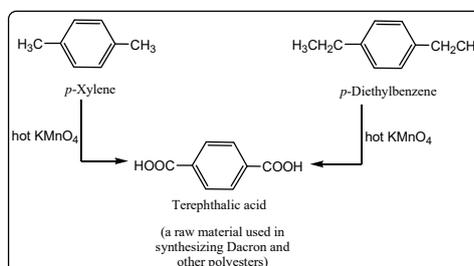
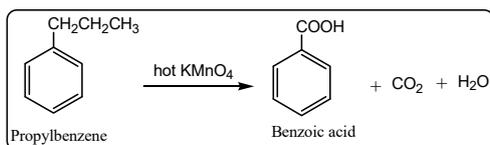
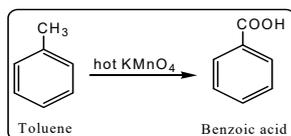
- **Free radical substitution on alkane.**  
**No substitution in the aromatic ring.**





### B. Oxidation of an Alkyl Side Chain

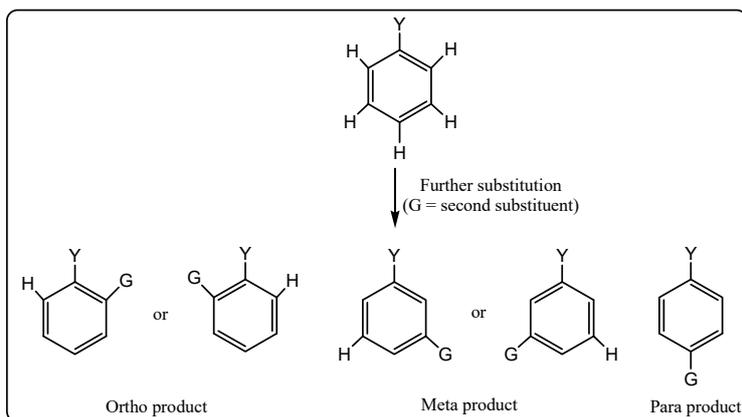
- Conversion into a carboxyl group, **-COOH**, by treatment with **hot potassium permanganate**.
- Regardless the **length of the alkyl chain**, the product is always the same, **Benzoic acid**.



### Disubstituted Benzenes: Orientation

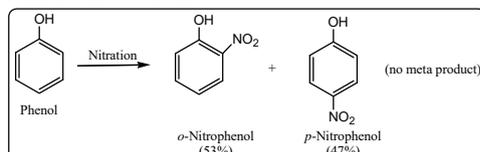
- Introduction of a second group, **G**, into a monosubstituted benzene,  $C_6H_5-Y$ .

*Three possible isomeric compounds can theoretically be formed.*

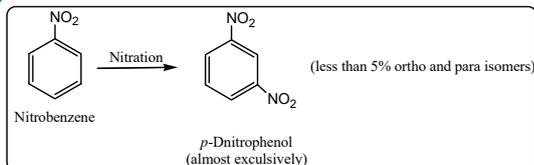


- The actual distribution depends on **the nature of the first substituent, Y**.

- For example; Nitration of Phenol



- For example; Nitration of Nitrobenzene



- Orientation Effects of Substituents **Y** in Electrophilic Aromatic Substitution.

Ortho, para directors	Meta directors
-OH, -OR	-NO <sub>2</sub>
-NH <sub>2</sub> , -NHR, -NR <sub>2</sub>	-SO <sub>3</sub> H
-C <sub>6</sub> H <sub>5</sub>	-COOH, -COOR
-CH <sub>3</sub> , -R (Alkyl)	-CHO, -COR
-F, -Cl, -Br, -I	-CN

### Disubstitution: Reactivity

➤ **The orientation Effect**

The presence of a substituent also affects the rate of electrophilic substitution reactions.

- Substituents that **release electrons** to the ring will **activate the ring** toward electrophilic substitution.
- Substituents that **withdraw electrons** from the ring will **deactivate the ring** toward electrophilic substitution.

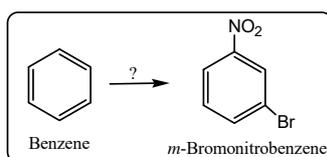
Substituent	Effect on reactivity
<b>Ortho, para directors</b>	
-OH, -OR, -NH <sub>2</sub> , -NHR, -NR <sub>2</sub>	Strongly activating
-C <sub>6</sub> H <sub>5</sub> , -CH <sub>3</sub> , -R (Alkyl)	Moderately activating
-F, -Cl, -Br, -I	Deactivating
<b>Meta directors</b>	
-NO <sub>2</sub> , -SO <sub>3</sub> H, -COOH, -COOR	Strongly deactivating
, -CHO, -COR, -CN	

### Planning an Aromatic Synthesis

- **Example;** Starting from benzene, synthesize *m*-bromonitrobenzene.

**Solution**

- 1) Draw the structure of the starting material and the structure of the product.

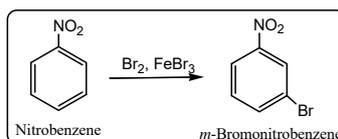


- 2) Decide what reaction leads to the product.

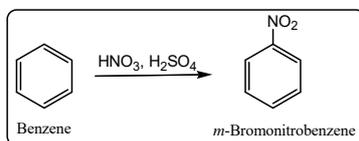
**-NO<sub>2</sub> group is a meta director.**

**-Br group is an ortho, para- directing group.**

**i.e. the last reaction is bromination of nitrobenzene**



3) The reactants leading to nitrobenzene are



4) Write the overall synthesis in the right order.

