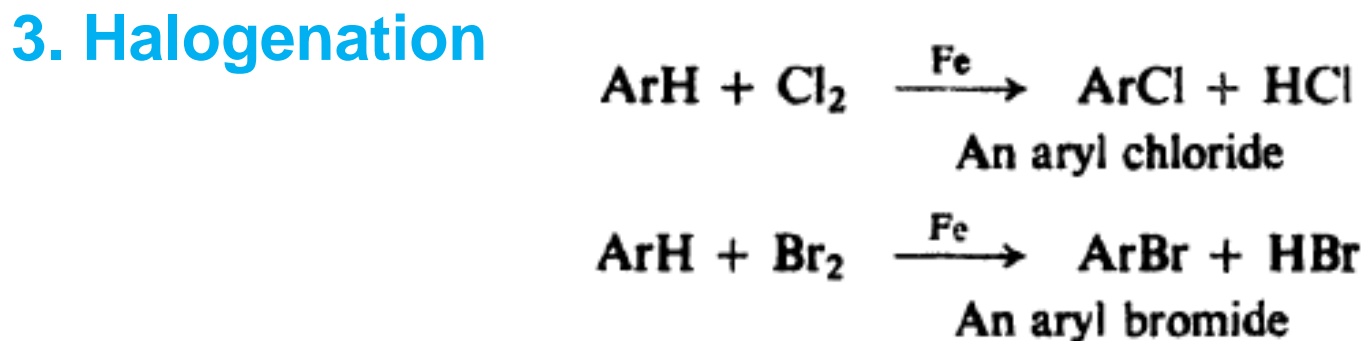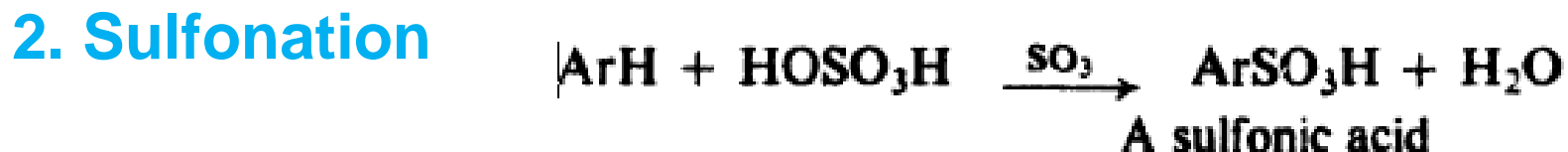# ELECTROPHILIC AROMATIC SUBSTITUTION

➢ Above and below the plane of the benzene ring there is a cloud of π electrons. Because of resonance

➢ It is not surprising that *in its typical reactions the benzene ring serves as* **a source of electrons**, that is, as a **base**. The compounds with which it reacts are deficient in electrons, that is, are *electrophilic reagents* or *acids*. Just as the typical reactions of the alkenes are electrophilic addition reactions, so the typical reactions of the benzene ring are **electrophilic substitution reactions**

➢ These reactions are characteristic not only of benzene itself, but of the benzene ring wherever it is found and, indeed, of many aromatic rings, benzenoid and non-benzenoid

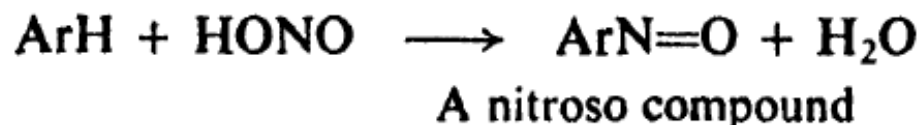# *Electrophilic Aromatic Substitution Reactions*

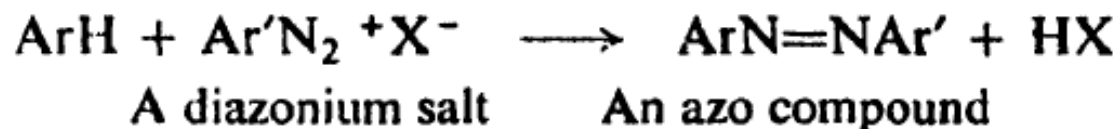Ar = *aryl*, any aromatic group with attachment directly to ring carbon

1. Nitration.

$$ArH + HONO_2 \xrightarrow{H_2SO_4} ArNO_2 + H_2O$$

A nitro compound

2. Sulfonation

$$ArH + HOSO_3H \xrightarrow{SO_3} ArSO_3H + H_2O$$

A sulfonic acid

3. Halogenation

$$ArH + Cl_2 \xrightarrow{Fe} ArCl + HCl$$

An aryl chloride

$$ArH + Br_2 \xrightarrow{Fe} ArBr + HBr$$

An aryl bromide

4. Friedel-Crafts alkylation

$$ArH + RCl \xrightarrow{AlCl_3} ArR + HCl$$

An alkylbenzene

5. Nitrosation

$$ArH + HONO \longrightarrow ArN{=}O + H_2O$$

A nitroso compound

Only for highly reactive ArH

6. Diazo coupling

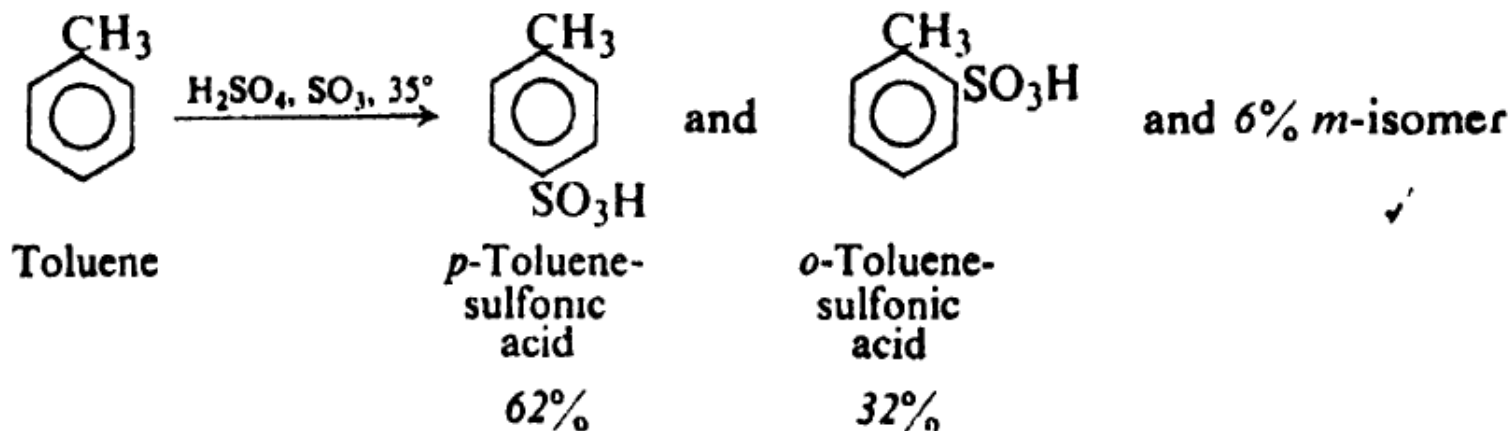$$ArH + Ar'N_2{}^+X^- \longrightarrow ArN{=}NAr' + HX$$

A diazonium salt   An azo compound

Only for highly reactive ArH

Effect of substituent groups

➢ Like benzene, toluene undergoes electrophilic aromatic substitution: sulfonation

➢ There are three possible monosulfonation products, this reaction actually yields appreciable amounts of only two of them: the *o-* and *p*-isomers

Toluene →(H₂SO₄, SO₃, 35°) p-Toluenesulfonic acid 62% and o-Toluenesulfonic acid 32% and 6% *m*-isomer

➢ A group that makes the ring more reactive than benzene is called **an activating group**. A group that makes the ring less reactive than benzene is called a **deactivating group**

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➢ A group that causes attack to occur chiefly at positions ortho and para to it is called an ortho, para director. A group that causes attack to occur chiefly at positions *meta* to it is called a meta director
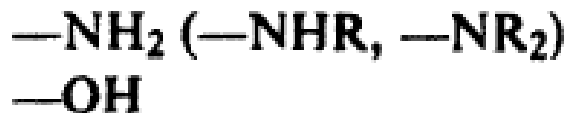
Classification of substituent groups

➢ All groups fall into one of two classes: activating and *ortho .para* directing, or deactivating and *meta*-directing. The halogens are in a class by themselves, being deactivating but *ortho.para*-directing.
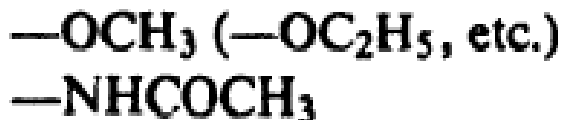
EFFECT OF GROUPS ON ELECTROPHILIC AROMATIC SUBSTITUTION

Activating: *Ortho,para* **Directors**

   Strongly activating
      $-NH_2$ ($-NHR$, $-NR_2$)
      $-OH$

   Moderately activating
      $-OCH_3$ ($-OC_2H_5$, etc.)
      $-NHCOCH_3$

   Weakly activating
      $-C_6H_5$
      $-CH_3$ ($-C_2H_5$, etc.)

Deactivating: *Meta* **Directors**

      $-NO_2$
      $-N(CH_3)_3^+$
      $-CN$
      $-COOH$ ($-COOR$)
      $-SO_3H$
      $-CHO$, $-COR$
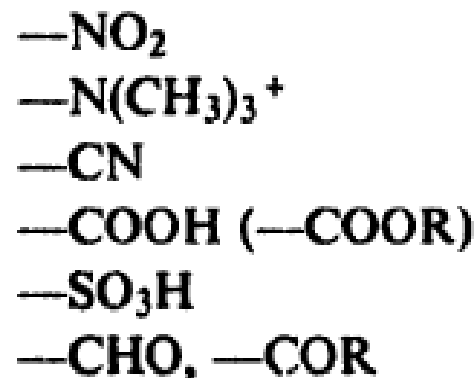
Deactivating: *Ortho,para* **Directors**

 $-F$, $-Cl$, $-Br$, $-I$

Orientation in disubstituted benzenes

➢ **The two substituents may be located so that the directive influence of one *reinforces* that of the other; for example, in I, II, and III the orientation clearly must be that indicated by the arrows.**
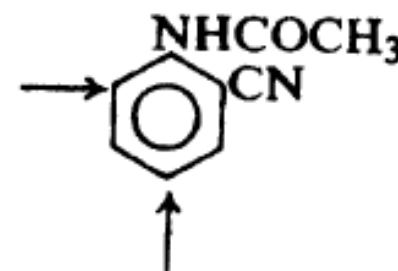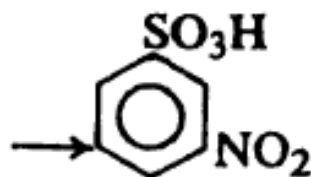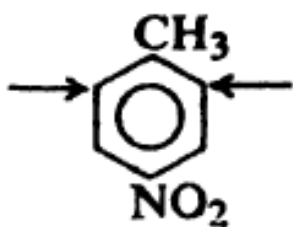

➢ When the directive effect of one group *opposes* that of the other, it may be difficult to predict the major product; in such cases complicated mixtures of several products are often obtained.

➢ (a) **Strongly activating groups generally win out over deactivating or weakly activating groups**. The differences in directive power in the sequence

$$-NH_2, \; -OH \; > \; -OCH_3, \; -NHCOCH_3 \; > \; -C_6H_5, \; -CH_3 \; > \; meta \; \text{directors}$$

Sole product

Chief product

Chief product
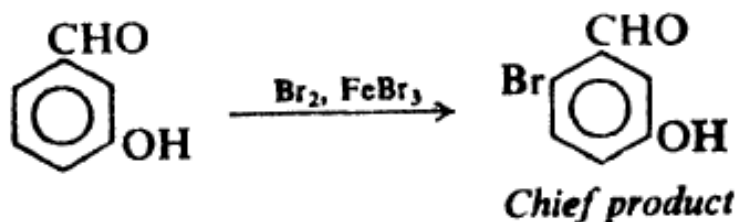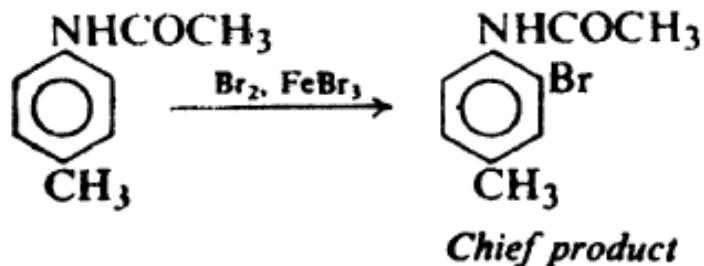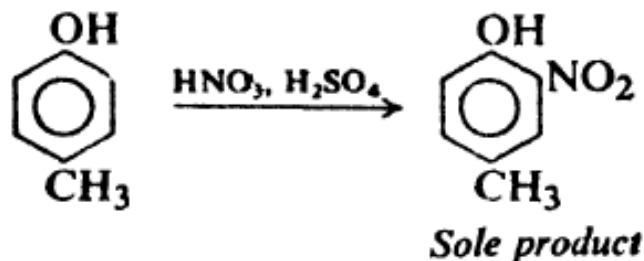
➢ There must be, however, a fairly large difference in the effects of the two groups for clear-cut results; otherwise one gets results like these:

CH₃ ───HNO₃, H₂SO₄──→ CH₃NO₂ and CH₃NO₂
Cl   Cl   Cl
                        58%   42%
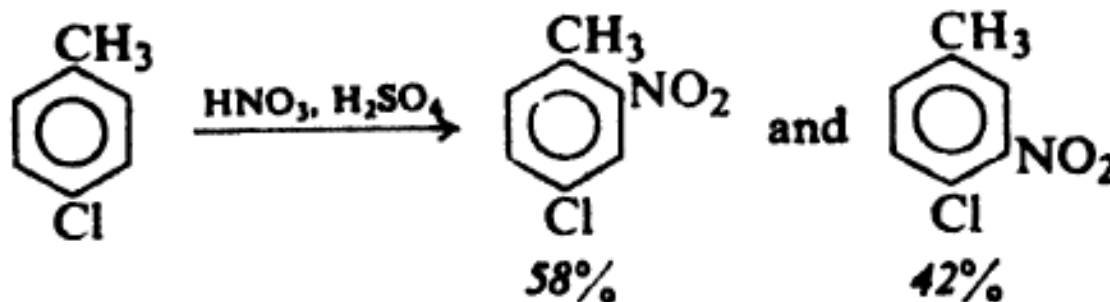
(b) **There is often little substitution between two groups that are meta to each other**.
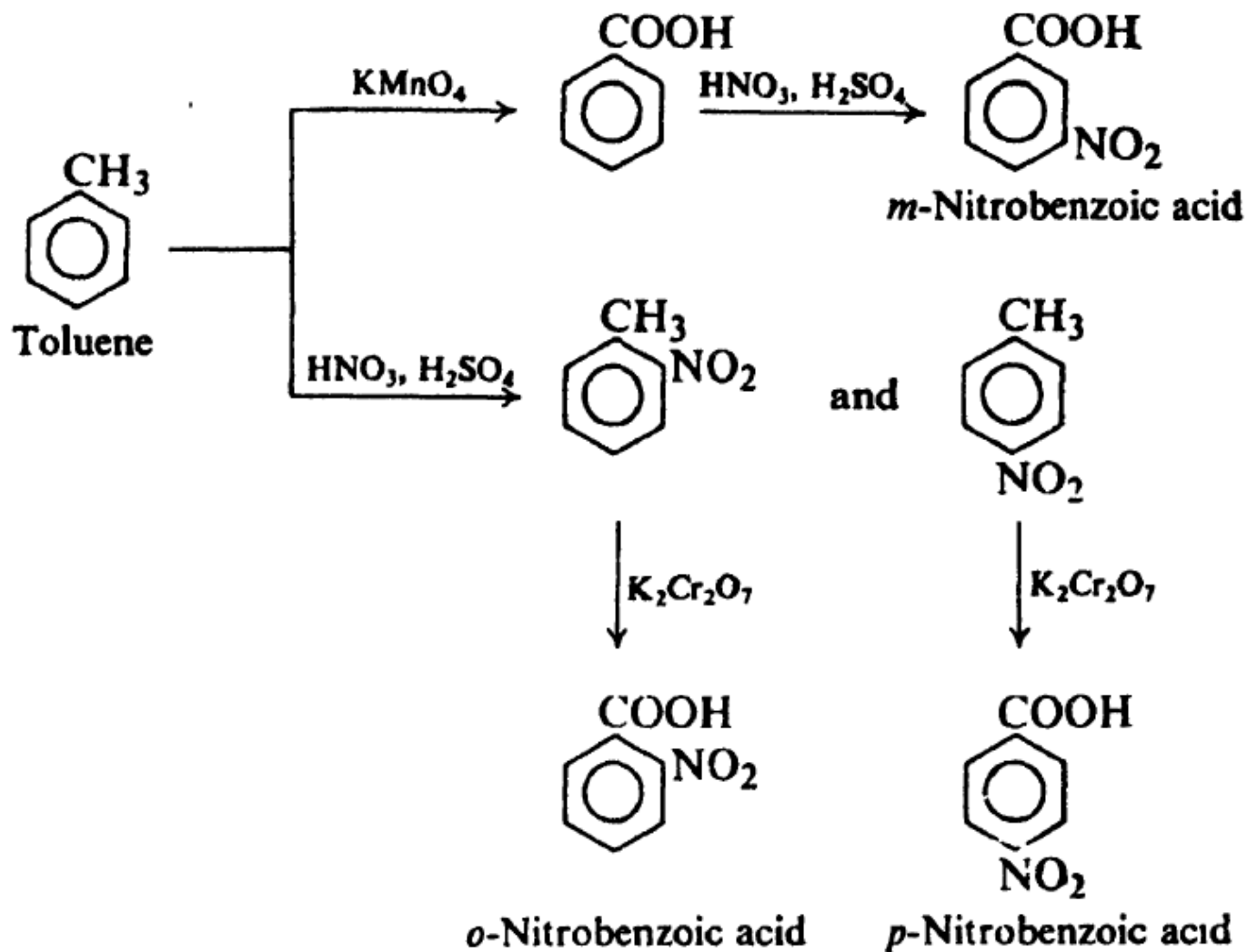
37% Cl 1% Br 62%

59% CH₃ 9% Cl 32%
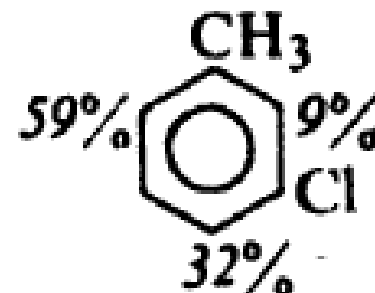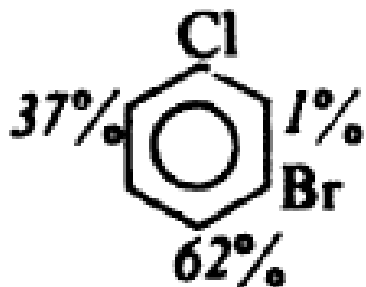
Orientation and synthesis

➤ A laboratory synthesis is generally aimed at obtaining a single, pure compound.

➤ **A goal of aromatic synthesis is control of orientation**: the preparation, at will and from the same substrate, of a pure *ortho*, a pure *meta*, or a pure *para* isomer.

➤ First of all, *we must consider the order in which we introduce these various substituents into the ring*. In the preparation of the bromonitrobenzenes, for example:
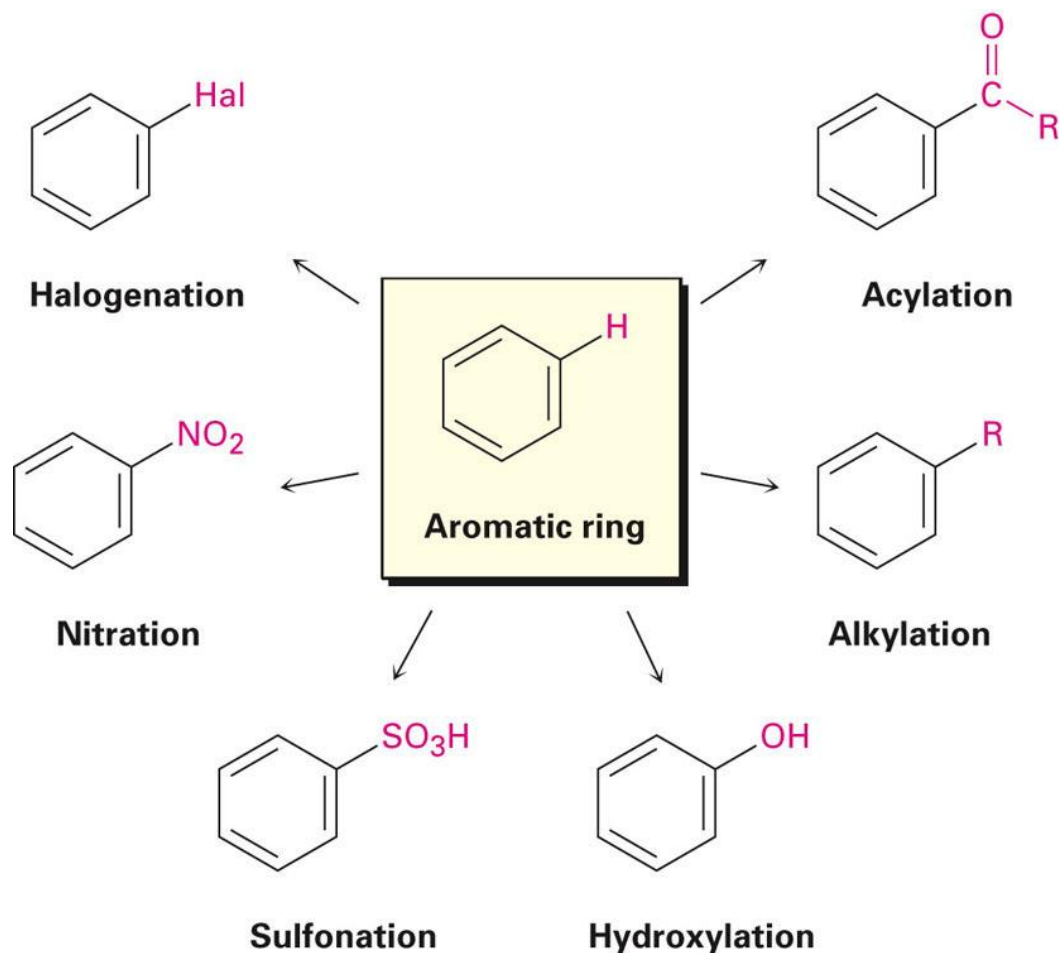

m-Bromonitrobenzene

Bromonitrobenzene

ortho-
38%

para-
62%
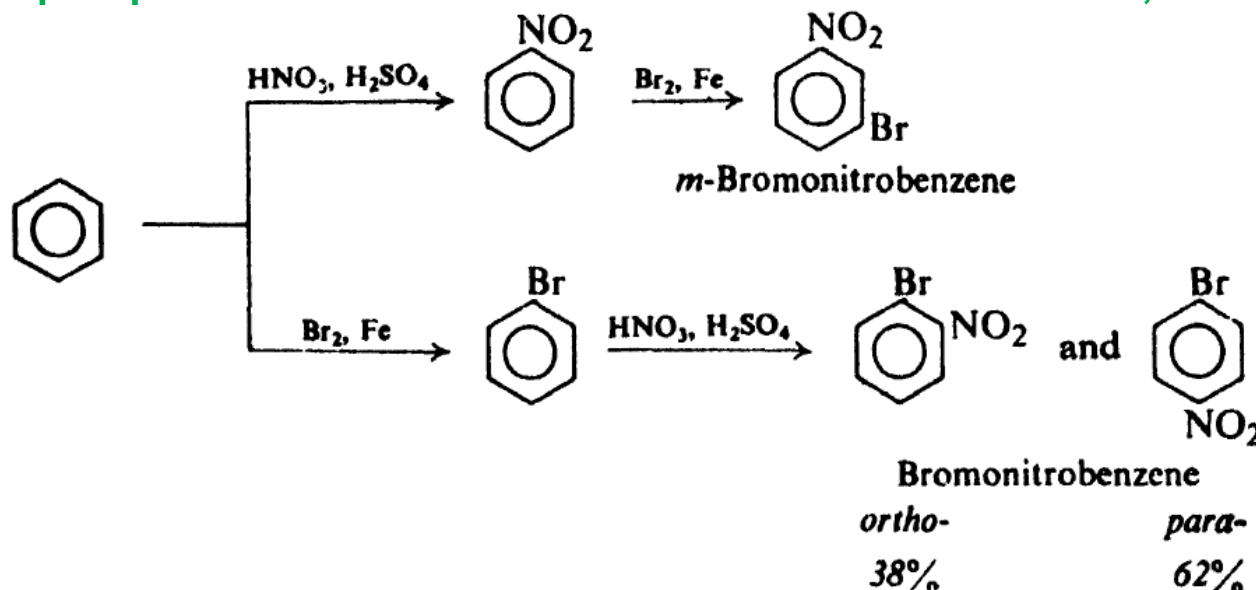
➢ If our synthesis involves conversion of one group into another, For example, oxidation of a methyl group yields a carboxyl group.


COOH

KMnO₄ → [benzene ring with COOH]

HNO₃, H₂SO₄ → [benzene ring with COOH and NO₂]

m-Nitrobenzoic acid

CH₃

[benzene ring]

Toluene

HNO₃, H₂SO₄ → [benzene ring with CH₃ and NO₂]   and   [benzene ring with CH₃ and NO₂]

K₂Cr₂O₇ ↓   K₂Cr₂O₇ ↓

COOH [benzene ring with NO₂]   COOH [benzene ring with NO₂]

o-Nitrobenzoic acid   *p*-Nitrobenzoic acid

Substitution Reactions of Benzene and Its Derivatives

➤ Benzene is aromatic: a cyclic conjugated compound with 6 π electrons

➤ Reactions of benzene lead to the retention of the aromatic core

Mechanism of nitration

➢ The combination of nitric acid and sulfuric acid produces NO_2^+ (nitronium ion)

➢ The reaction with benzene produces nitrobenzene

Nitric acid

Nitronium ion

Nitrobenzene
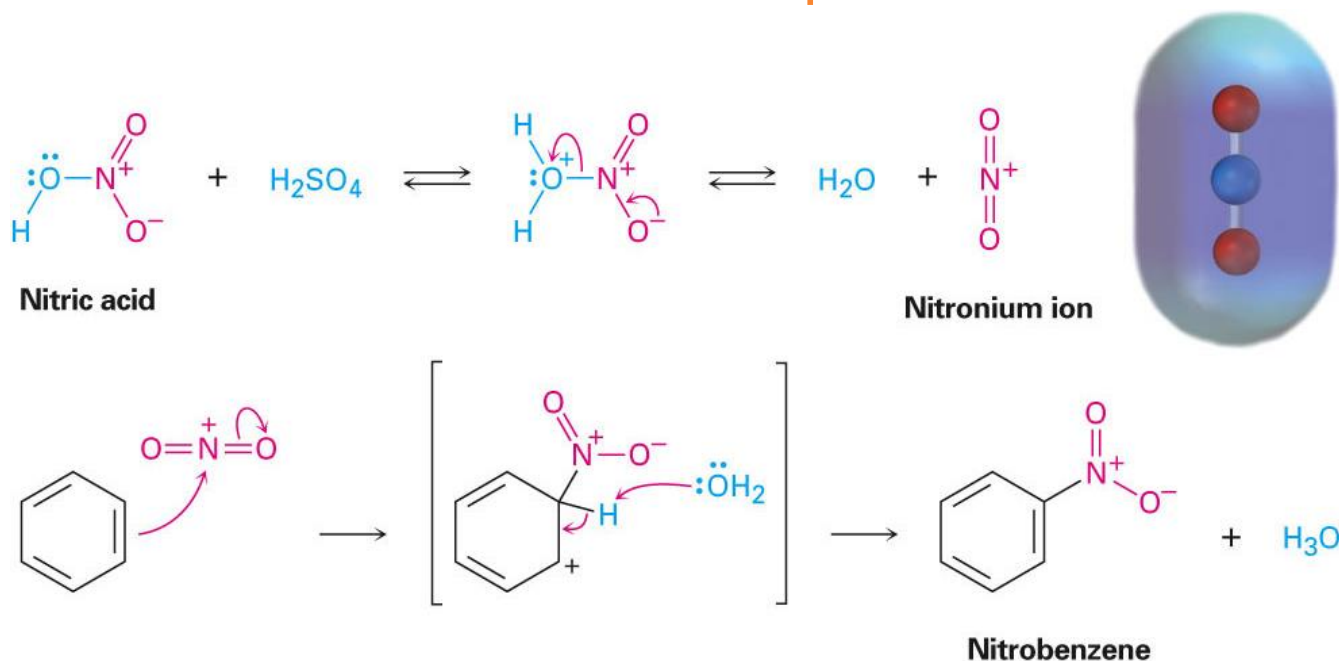
➢ Just what is the structure of this carbonium ion ? We find that we can represent

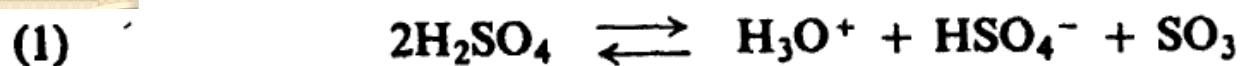➢ It by three structures (I, II, and III) that differ from each other only in position of double bonds and positive charge.

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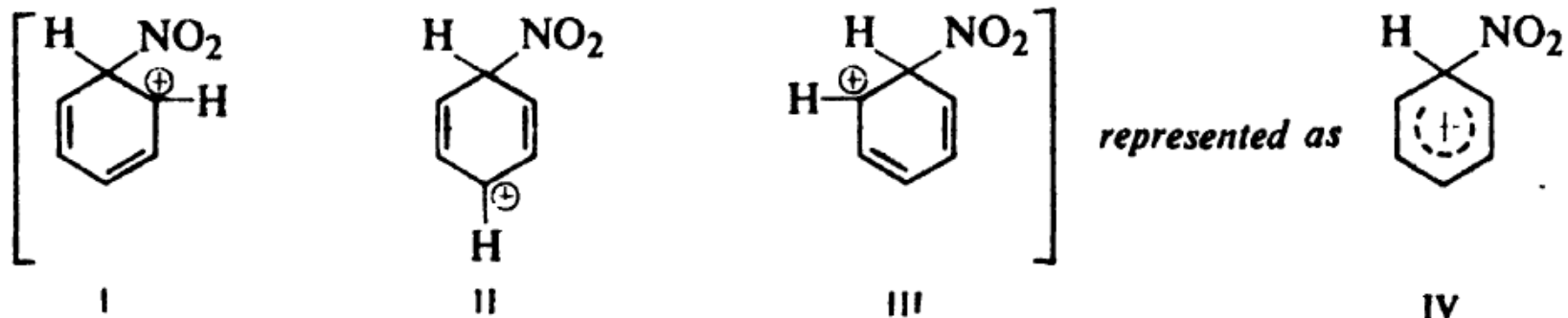
> **The Nitro group can be reduced to an Amino group if needed**

Nitrobenzene

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1. Fe, H_3O^+
2. HO^-

Aniline (95%)
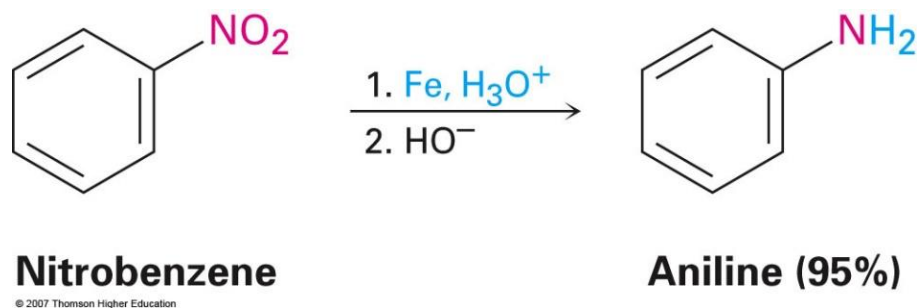
Mechanism of sulfonation

> Substitution of H by SO_3 (sulfonation)
> Reaction with a mixture of sulfuric acid and SO_3 ("Fuming H_2SO_4)
> Reactive species is sulfur trioxide or its conjugate acid

(1) $$2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$$

(2) $$SO_3 + C_6H_6 \rightleftharpoons C_6H_5\overset{\oplus}{\underset{SO_3^-}{\diagup}}\overset{H}{\diagup} \quad \textit{Slow}$$

(3) $$C_6H_5\overset{\oplus}{\underset{SO_3^-}{\diagup}}\overset{H}{\diagup} + HSO_4^- \rightleftharpoons C_6H_5SO_3^- + H_2SO_4 \quad \textit{Fast}$$

(4) $$C_6H_5SO_3^- + H_3O^+ \rightleftharpoons C_6H_5SO_3H + H_2O \quad \textit{Equilibrium far to the left}$$
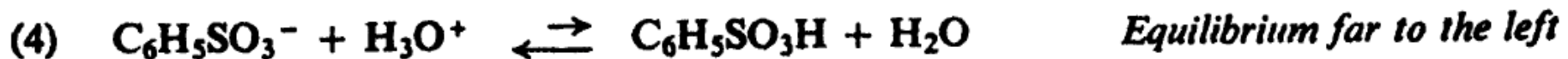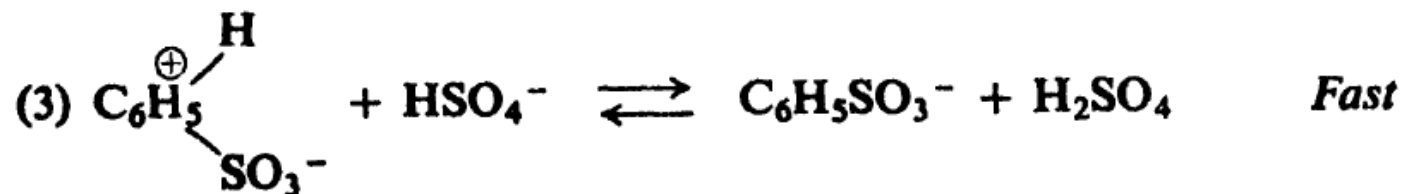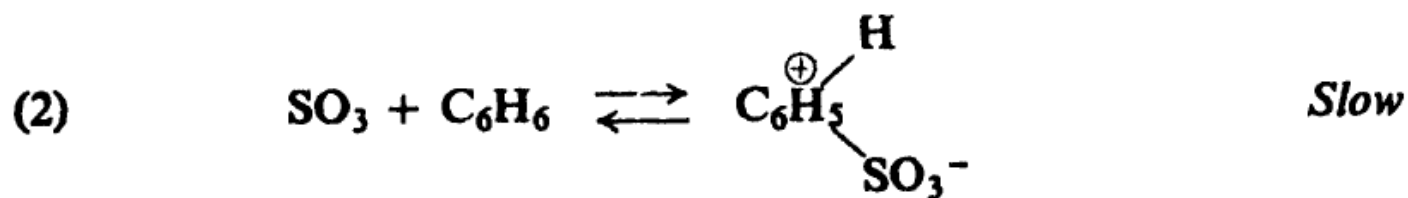
Mechanism of Friedel-Crafts alkylation

➢ Friedel-Crafts alkylation is an electrophilic aromatic substitution in cation acts as the eletrophile which an alkyl
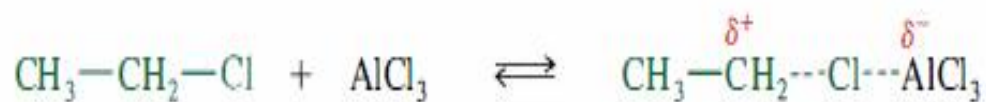
Step 1: Formation of a carbocation.

t-butyl chloride

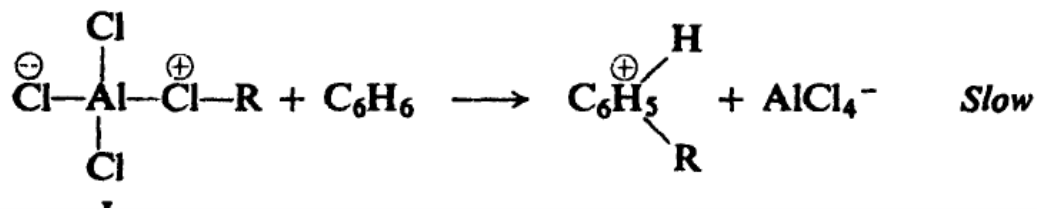t-butyl cation
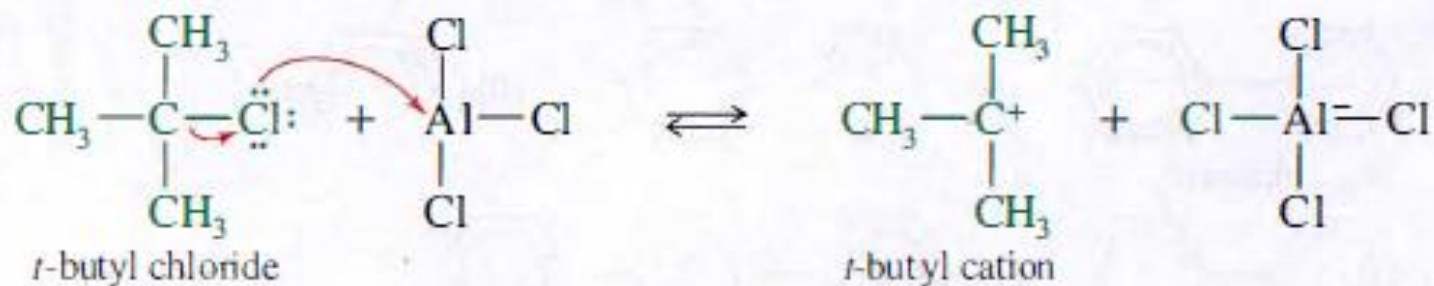
Step 2: Electrophilic attack forms a sigma complex.

sigma complex
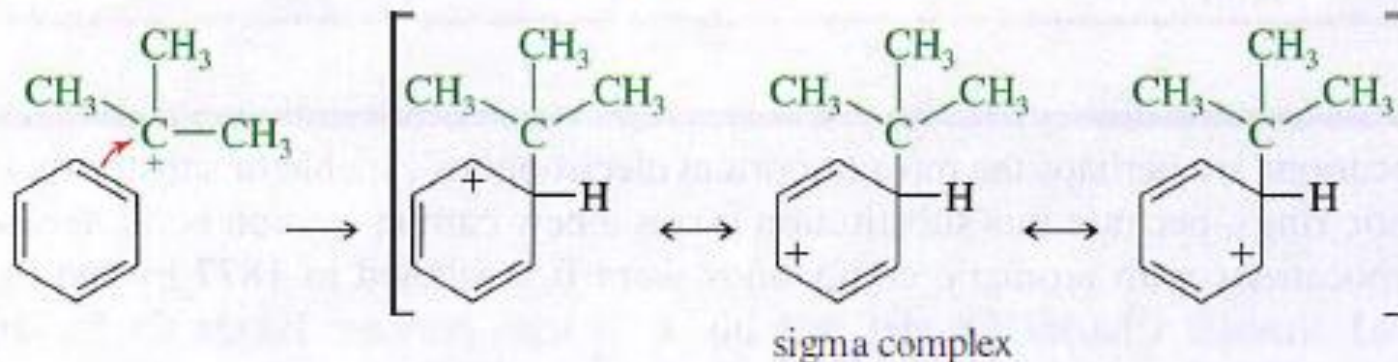
Step 3: Loss of a proton regenerates the aromatic ring and gives the alkylated product.
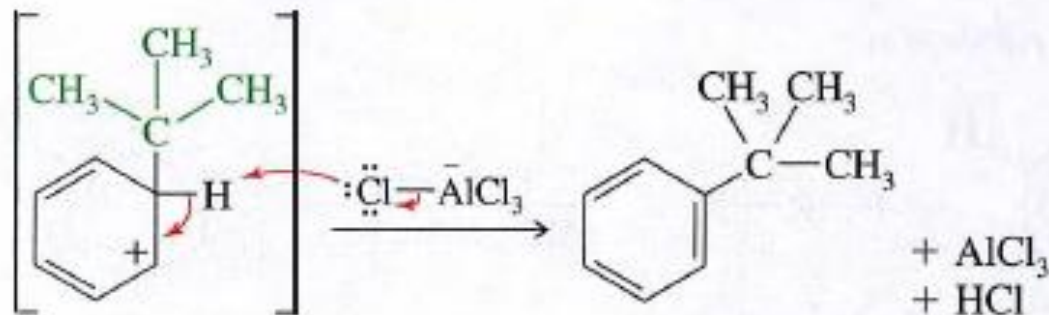

+ AlCl₃
+ HCl

> In certain cases, there is no free carbonium ion involved. Instead, the alkyl group is transferred -without a pair of electrons- directly to the aromatic ring from the polar complex, I, between $AlCl_3$ and the alkyl halide:
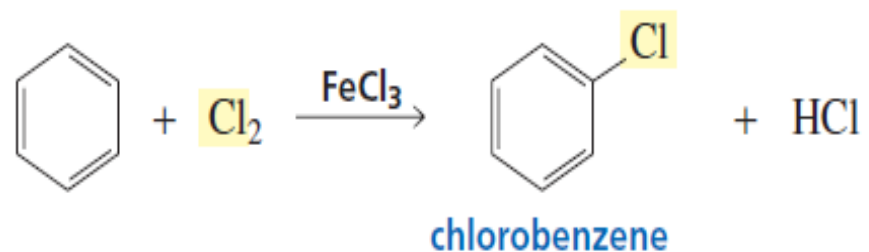
$$Cl-\overset{\ominus}{Al}-\overset{\oplus}{Cl}-R + C_6H_6 \longrightarrow C_6H_5\overset{H}{\underset{R}{\overset{\oplus}{\diagdown}}} + AlCl_4^- \qquad \textit{Slow}$$

$$CH_3-CH_2-Cl + AlCl_3 \rightleftharpoons CH_3-CH_2\cdots\overset{\delta^+}{Cl}\cdots\overset{\delta^-}{AlCl_3}$$

sigma complex

$$Cl-\bar{A}lCl_3$$

$$\text{---}CH_2CH_3 + H-Cl + AlCl_3$$

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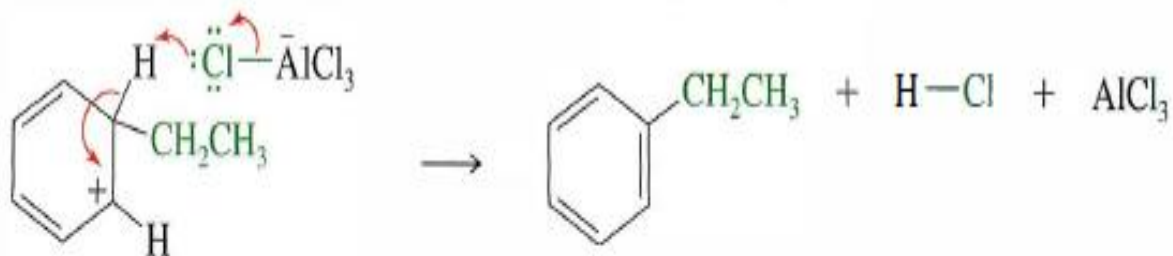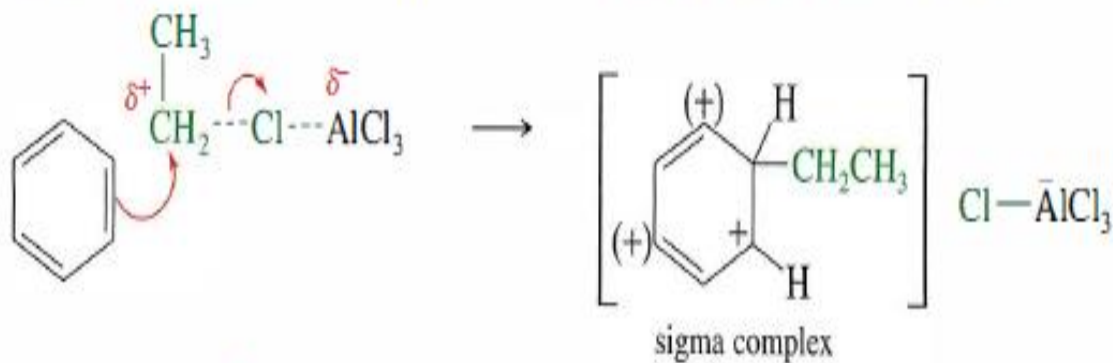
Mechanism of halogenation

➢ The bromination or chlorination of benzene requires a Lewis acid such as ferric bromide or ferric chloride

bromination

bromobenzene

chlorination

chlorobenzene
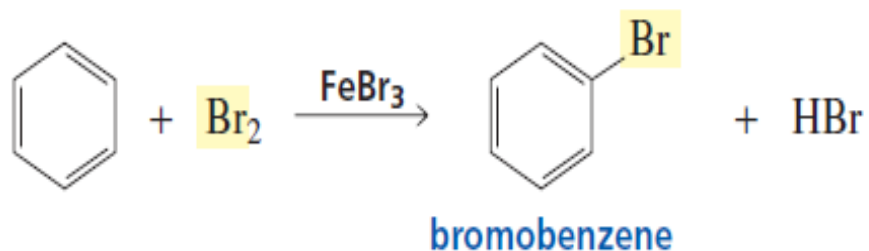
➢ In the first step of the bromination reaction, bromine donates a lone pair to the Lewis acid. This weakens the Br-Br bond, thereby providing the electrophile necessary for electrophilic aromatic substitution.

➢ In the last step of the reaction, a base from the reaction mixture
➢ Removes a proton from the carbocation intermediate. The
➢ following equation shows that the catalyst is regenerated:

$$:\ddot{B}r-\ddot{B}r: \quad + \quad FeBr_3 \quad \longrightarrow \quad :\ddot{B}r-\overset{..+}{\ddot{B}r}-\bar{F}eBr_3$$

$$+ \quad \bar{F}eBr_4$$
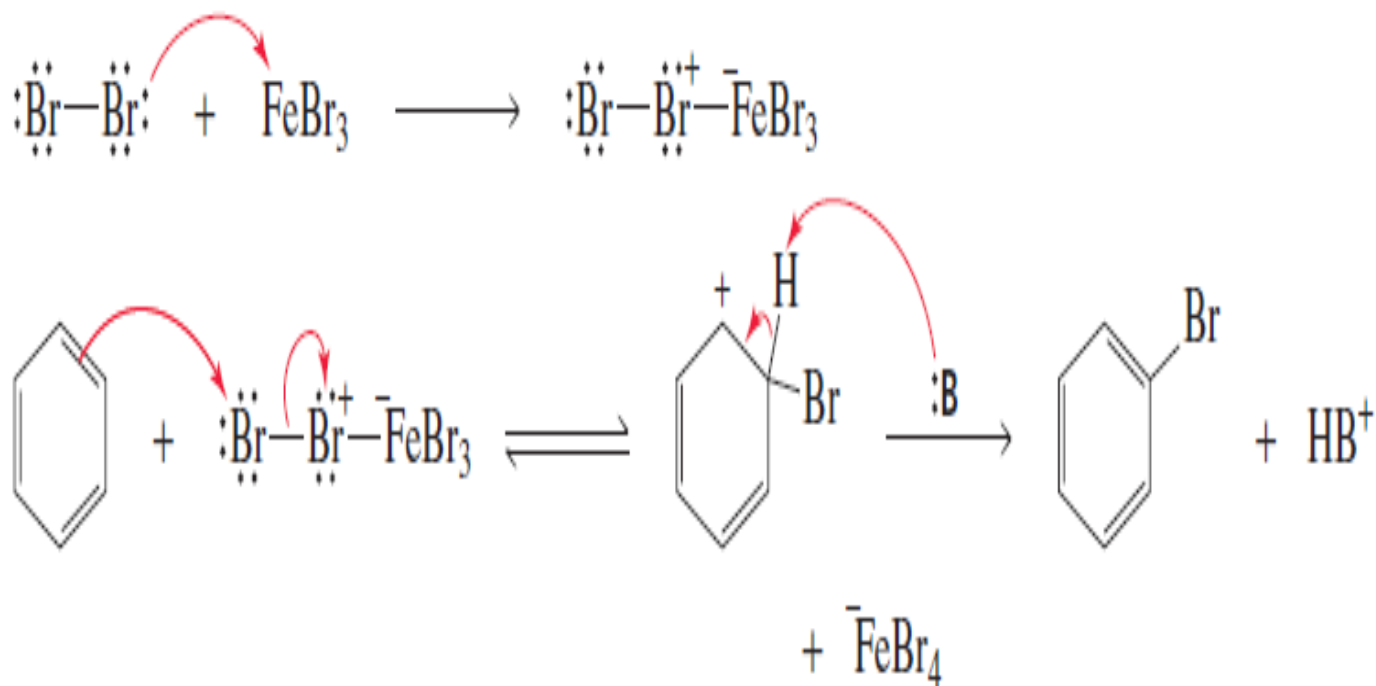
Mechanism of Friedel-Crafts Acylation

- ➤ Similar to alkylation
- ➤ Reactive electrophile: resonance-stabilized acyl cation
- ➤ An acyl cation does not rearrange
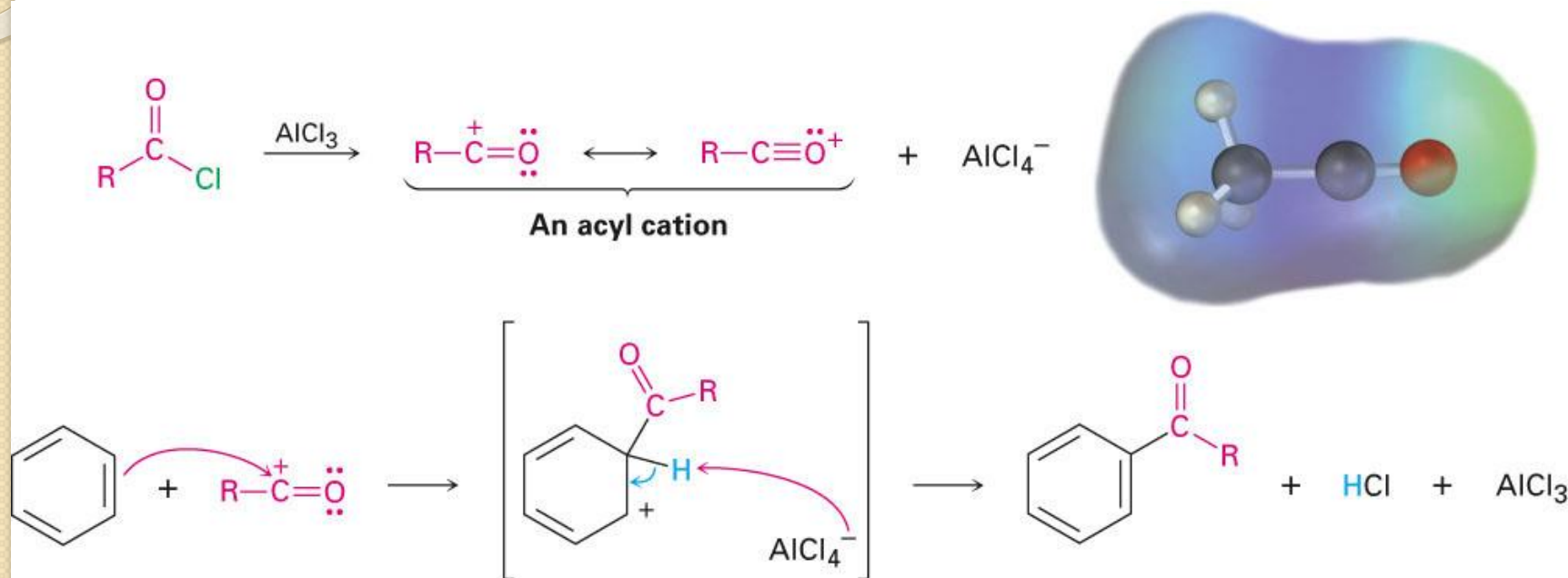
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- ➤ Can reduce carbonyl to get alkyl product

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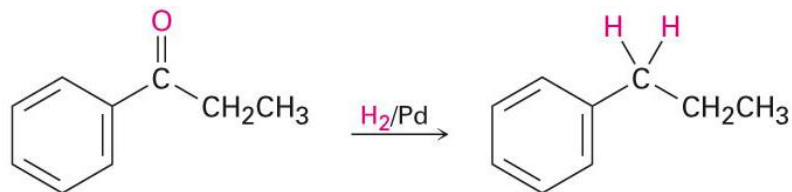
Reactivity and orientation

➢ We have seen that certain groups activate the benzene ring and direct substitution to **ortho** and **para** positions,and that

➢ Other groups deactivate the ring and (except halogens) direct substitution to **meta** positions.

➢ Methyl is said to activate the ring because it makes the ring reacts *faster* than benzene; it causes **ortho, para** orientation because it makes the **ortho** and **para** positions react faster than the **meta** positions.

➢ ***The rate of electrophilic aromatic substitution is determined by the same slow step-attack of the electrophile on the ring to form **a carbonium ion**:

$$C_6H_6 + Y^+ \longrightarrow C_6H_5 \overset{H}{\underset{Y}{<}} \quad \text{Slow: } rate\text{-}determining$$
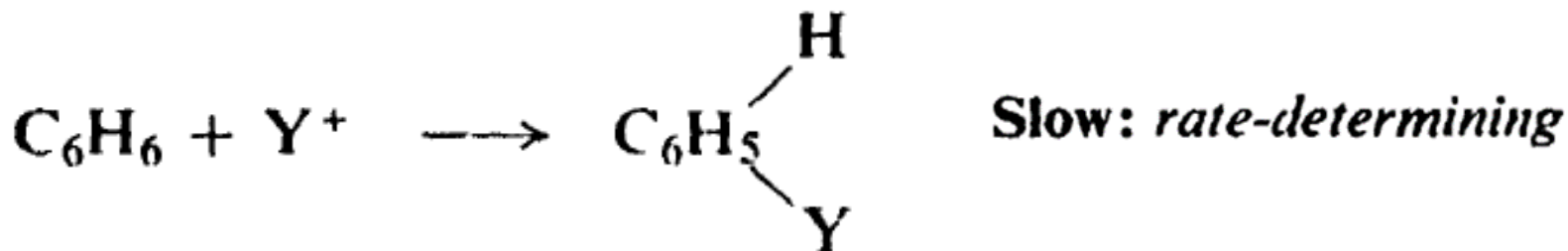
➢ ****Any differences in rate of substitution must therefore be due to differences in the rate of this step.

➢ In electrophilic aromatic substitution the intermediate carbonium ion is a hybrid of structures I, II, and III, in which the positive charge is distributed about the ring, being strongest as the positions **ortho** and **para** to the carbon atom being attacked.
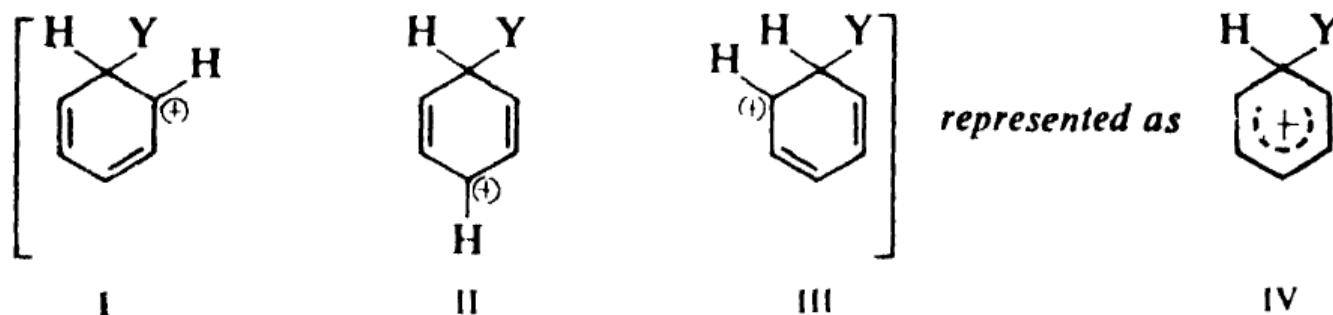
➢ ***A group already attached to the benzene ring should affect the stability of the carbonium ion by dispersing or intensifying the positive charge, depending upon its electron-releasing(activating) or electron-withdrawing nature (deactivating).

Theory of reactivity

➢ To compare rates of substitution in benzene, toluene, and nitrobenzene, we compare the structures of the carbonium ions formed from the three compounds:
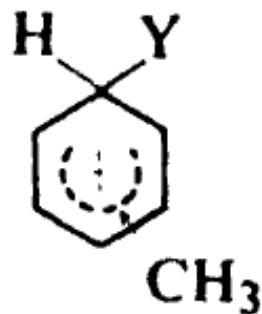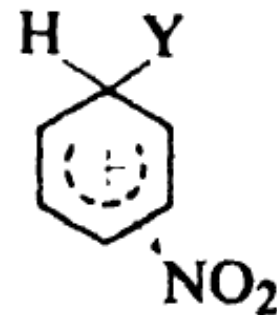
➢ By releasing electrons, the methyl group (II) tends to neutralize the positive charge of the ring and so become more positive itself; this dispersal of the charge stabilizes the carbonium ion. In the same way the inductive effect stabilizes the developing positive charge in the transition state and thus leads to a faster reaction.

Transition state.
developing positive charge

Carbonium ion:
full positive charge
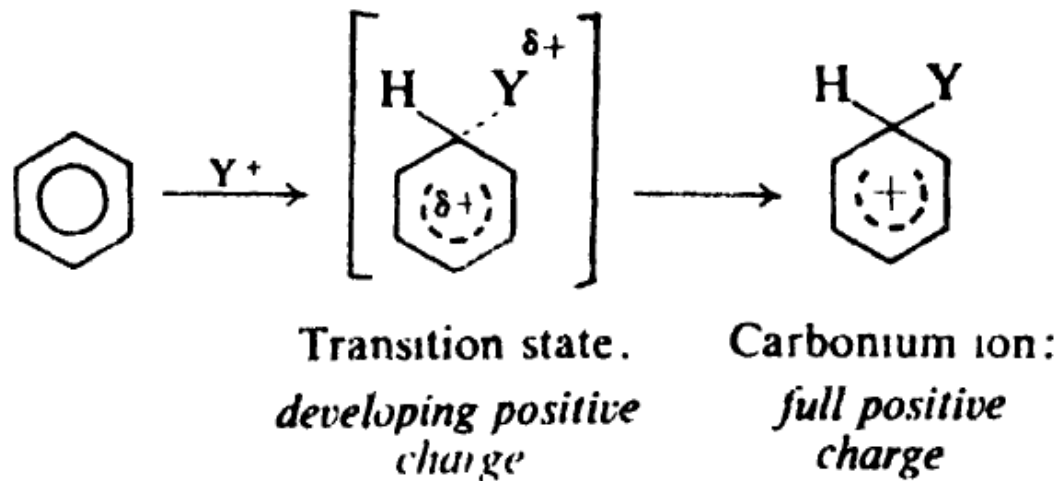
➢ The -NO$_2$ group, on the other hand, has an electron-withdrawing inductive effect (III); this tends to intensify the positive charge, destabilizes the carbonium ion, and thus causes a slower reaction

➢ *Reactivity in electrophilic aromatic substitution depends, then, upon the tendency of a substituent group to release or withdraw electrons.* **A group that releases electrons activates the ring; a group that withdraws electrons deactivates the ring.**

Electrophilic Aromatic Substitution
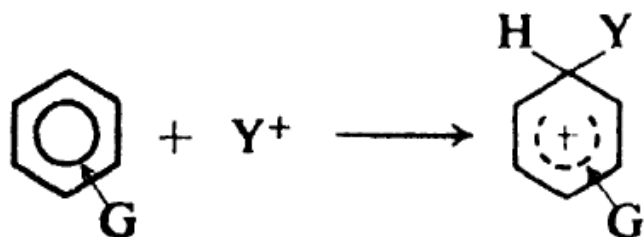
G *releases electrons.*
stabilizes carbonium ion,
activates

$G = -NH_2$
$--OH$
$--OCH_3$
$--NHCOCH_3$
$-C_6H_5$
$--CH_3$
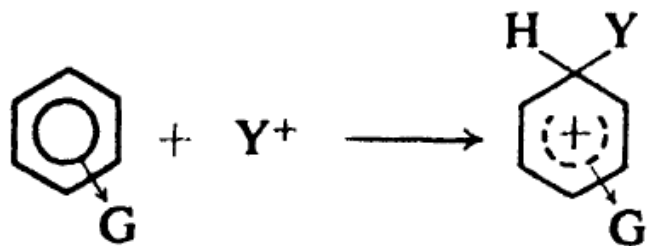
G *withdraws electrons*
destabilizes carbonium ion,
deactivates

$G = -N(CH_3)_3^+$
$--NO_2$
$--CN$
$--SO_3H$
$---COOH$
$--CHO$
$--COR$
$-X$

➤ We might expect replacement of hydrogen in -CH$_3$ by halogen to decrease the electron-releasing tendency of the group, and perhaps to convert it into an electron-withdrawing group.
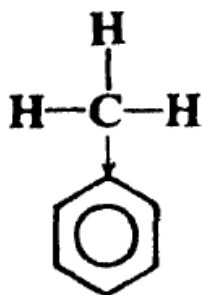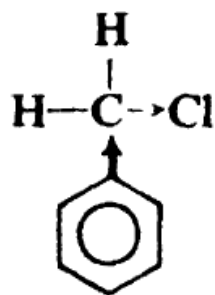
Activating   Weakly deactivating   Moderately deactivating   Strongly deactivating
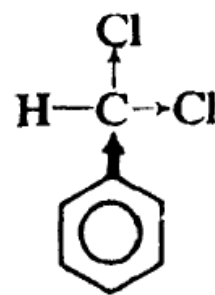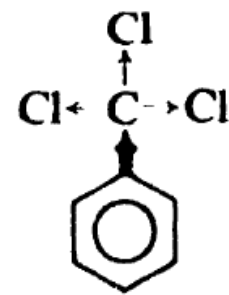
Theory of orientation

- ➤ An activating group activates all positions of the benzene ring; even the positions meta to it are more reactive than any single position in benzene itself. It directs *ortho* and *para* simply because it activates the *ortho* and *para* positions much more than it does the *meta*

- ➤ A deactivating group deactivates all positions in the ring, even the positions *meta* to it. It directs *meta* simply because it deactivates the *ortho* and *para* positions even more than it does the *meta*.

- ➤ Thus both *ortho, para* orientation and *meta* orientation arise in the same way: **the effect of any group whether activating or deactivating is strongest at the *ortho* and *para* positions**.
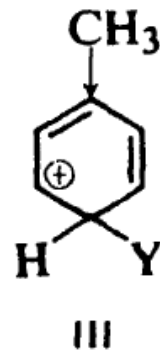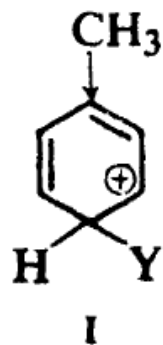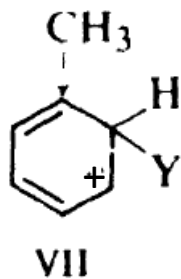
Para attack
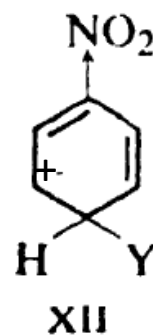
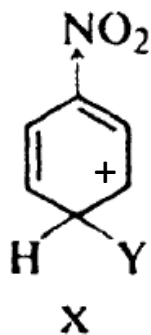Especially stable:
charge on carbon
carrying substituent
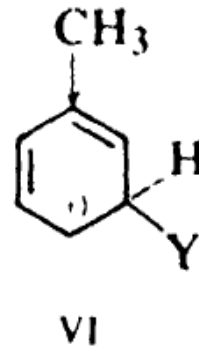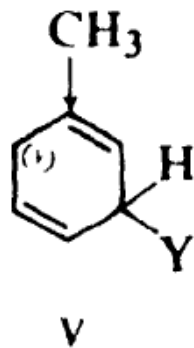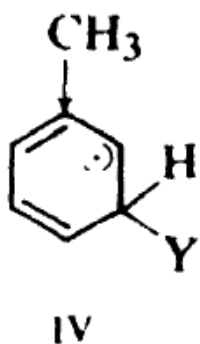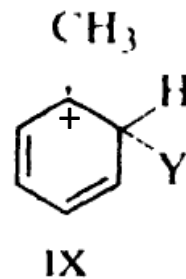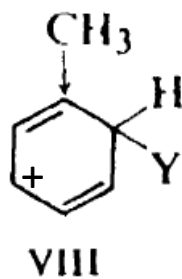
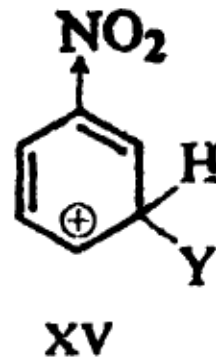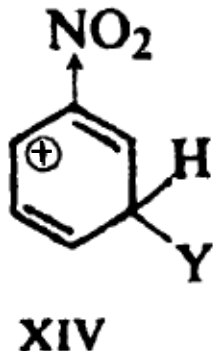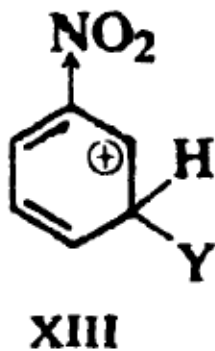*Meta* attack

Ortho attack

Especially stable:
charge on carbon
carrying substituent

➢ compare the carbonium ions formed by attack at the **para** and **meta** positions of nitrobenzene

➢ Each of these is a hybrid of three structures, X-XII for para attack, XI II-XV for **meta** attack. In one of the six structures, XI, the positive charge is located on the
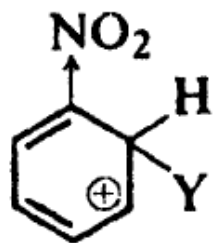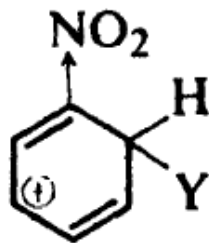

Para attack

X   XI   XII

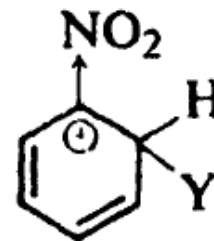*Especially unstable: charge on carbon carrying substituent*

Meta attack

XIII   XIV   XV

XVI **XVII** **XVIII** *Ortho* attack

Especially unstable:
charge on carbon
carrying substituent

➤ In nitrobenzene, ***ortho. para*** substitution is thus slower than ***meta*** substitution because electron withdrawal by -NO$_2$ is more effective during attack at the positions ***ortho*** and ***para*** to it.

Electron release via resonance

Groups (-NH$_2$ and -OH, and their derivatives) act as powerful activators toward electrophilic aromatic substitution, even though they contain electronegative atoms and can be shown in other ways to have electron-withdrawing inductive effects.

➢ They are believed to do this by a resonance effect

➢ That nitrogen and oxygen can share more than a pair of electrons with the ring and can accommodate a positive charge.
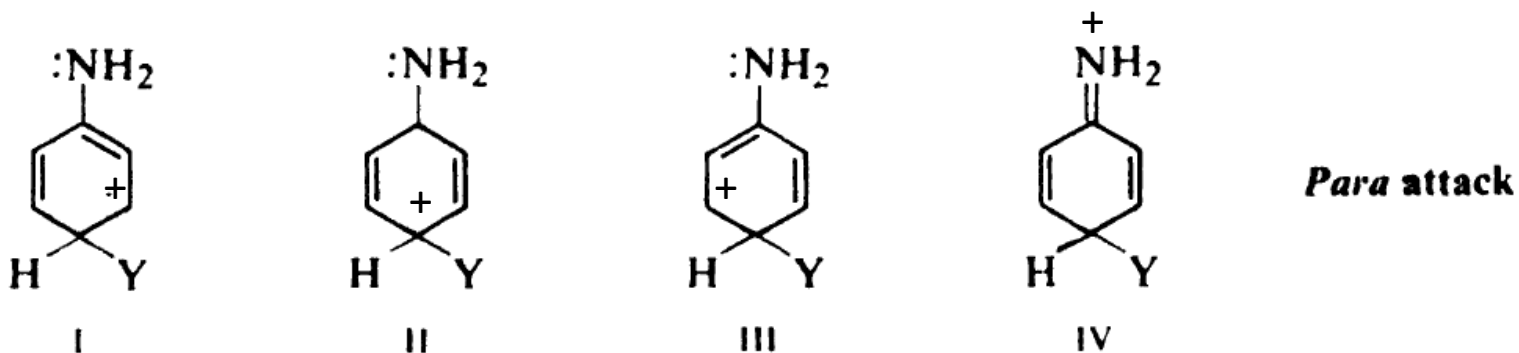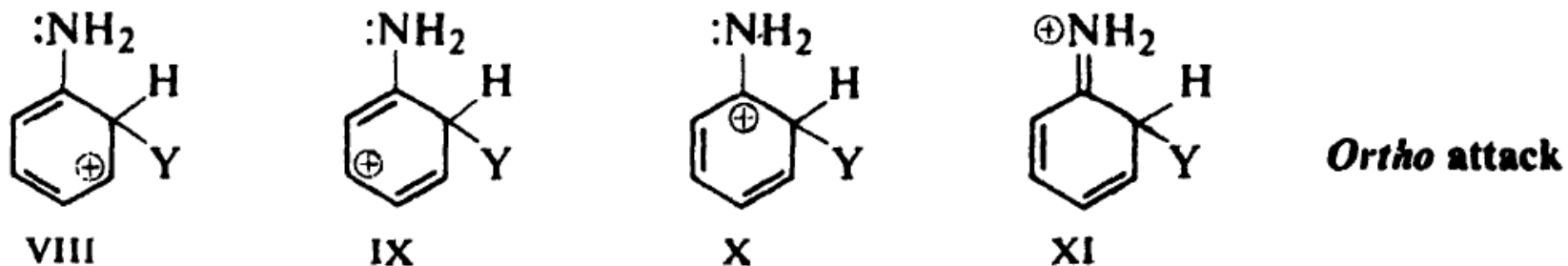

Para attack

*Especially stable:*
every atom has octet
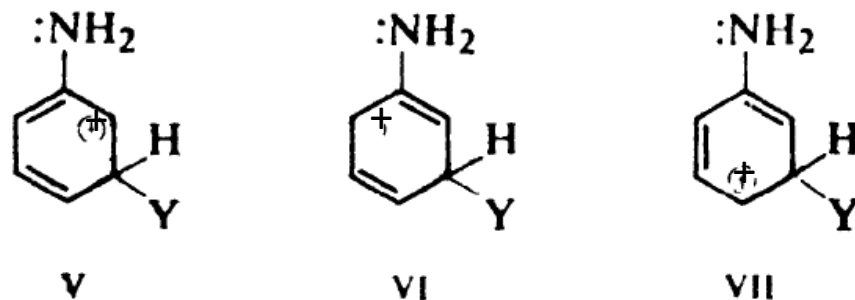
Meta attack

➢ Examination of the corresponding structures (VIII-XI) shows that **ortho** attack is much like para attack:



VIII   IX   X   XI

Ortho attack

Especially stable:
every atom has octet

➢ Thus substitution in aniline occurs faster than substitution in benzene, and occurs predominantly at the positions ortho and para to -NH$_2$.

➢ In the same way activation and **ortho**, **para** orientation by the -OH group is accounted for by contribution of structures like XII and XIII, in which every atom has a complete octet of electrons:
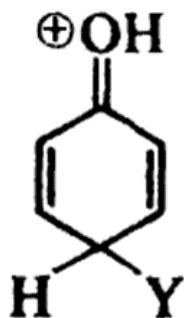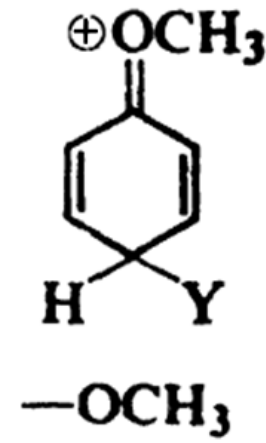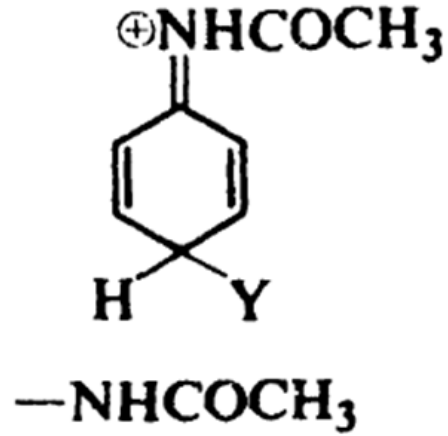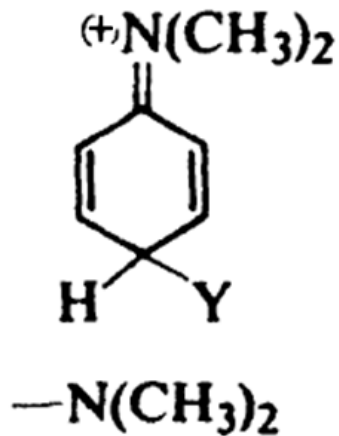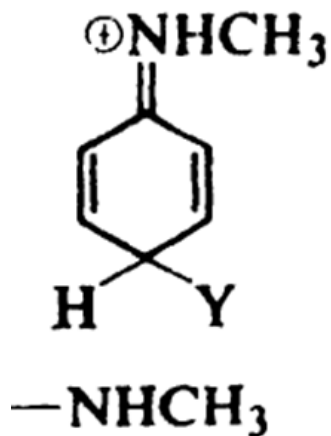
XII
Para attack
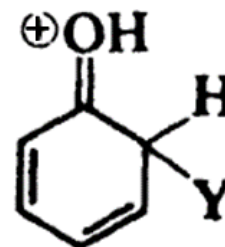
XIII
Ortho attack

➤ The similar effects of the derivatives of -NH$_2$ and -OH are accounted for by similar structures (shown only for para attack):

—NHCH$_3$ —N(CH$_3$)$_2$ —NHCOCH$_3$ —OCH$_3$

Effect of halogen on electrophilic aromatic substitution

➤ Halogens are unusual in their effect on electrophilic aromatic substitution: they are deactivating yet ortho, para-directing

➤ Can halogen both withdraw and release electrons?

➤ Halogen withdraws electrons through its inductive effect, and releases electrons through its resonance effect.

➤ but there the much stronger resonance effect greatly outweighs the other.
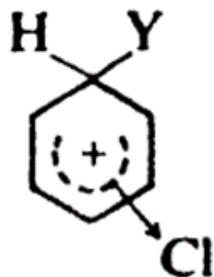
— Cl withdraws electrons: destabilizes carbonium ion, deactivates ring

I   II

➢ The electron withdrawing inductive effect of chlorine intensifies the positive charge in carbonium ion II, makes the ion less stable, and causes a slower reaction.

➢ To understand orientation, we compare the structures of the carbonium ions formed by attack at the para and meta positions of chlorobenzene.

Para attack

III   IV   V
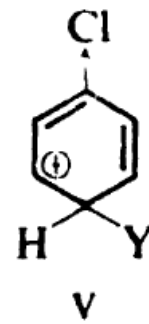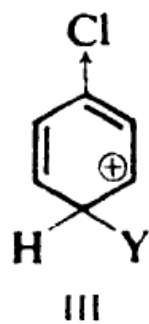
Especially unstable:
charge on carbon
bearing substituent

Meta attack

VI   VII   VIII
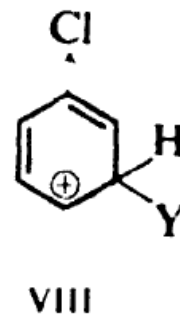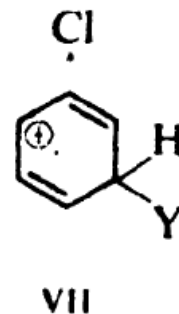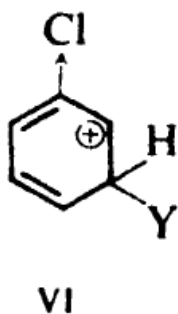
➤ the existence of halonium ions has shown us that halogen can share more than a pair of electrons and can accommodate a positive charge.
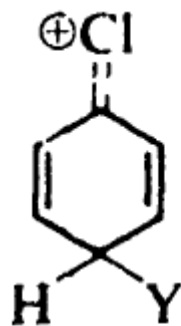
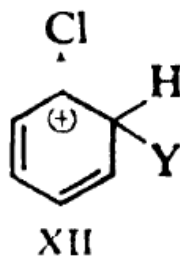**Para attack**

IX
Comparatively stable: every atom has octet

➤ This structure should be comparatively stable, since in it every atom (except hydrogen, of course) has a *complete octet of electrons*.

➤ In the same way it can be seen that attack at an ortho position also yields an ion (X-X1II) that can be stabilized by accommodation of the positive charge by chlorine
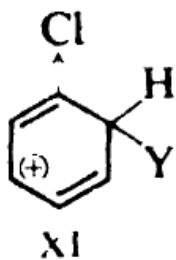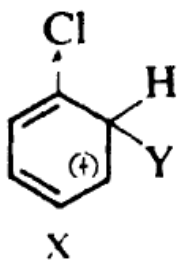
Ortho attack

XII
Especially unstable·
charge on carbon
bearing substituent

XIII
Comparatively stable·
every atom has octet
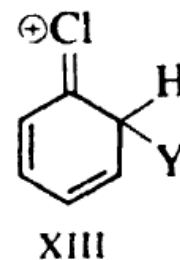
Arenes

➢ Aliphatic-aromatic hydrocarbons

❖ Important compounds are contain both aliphatic and aromatic units; hydrocarbons of this kind are known collectively as arenes for example:

$$CH_2CH_3$$
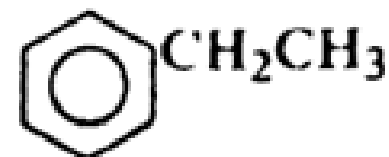
Ethylbenzene

❖ The ring of ethylbenzene should undergo the electrophilic substitution characteristic of benzene, and the side chain should undergo the free radical substitution characteristic of ethane

CH_2CH_3 $\xrightarrow{HNO_3, H_2SO_4}$ CH_2CH_3 NO_2 and O_2N CH_2CH_3 *More readily than for benzene*

o-Nitroethylbenzene   p-Nitroethylbenzene

Chief products

CH_2CH_3 $\xrightarrow{Br_2, \text{ light}}$ CHCH$_3$ | Br
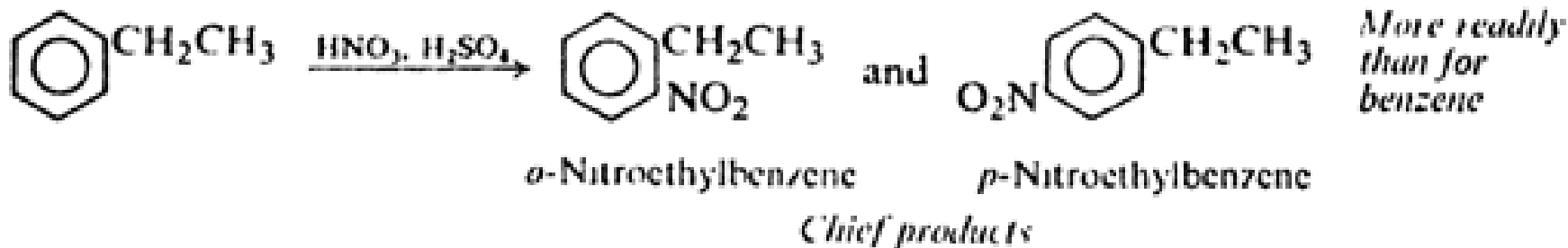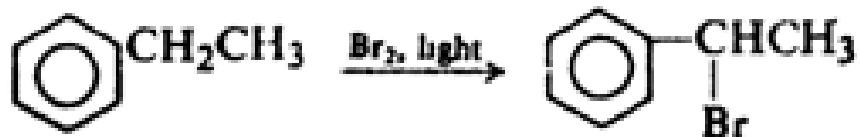
More readily than for ethane

1-Bromo-1-phenylethane
(α-Phenylethyl bromide)
Only product

❖ Thus each portion of the molecule affects the reactivity of the other portion and determines the orientation of attack

➢ **Structure and nomenclature**

❖ The simplest of the alkylbenzenes, methylbenzene, is given the special name of toluene
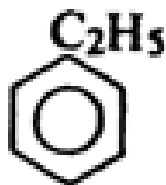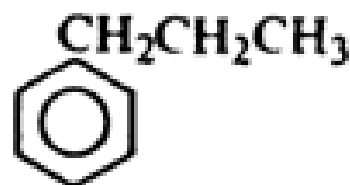
CH_3

Toluene

❖ Compounds containing longer side chains are named by prefixing the name of the alkyl group to the word -*_benzene_*

Toluene   Ethylbenzene   *n*-Propylbenzene   Isobutylbenzene
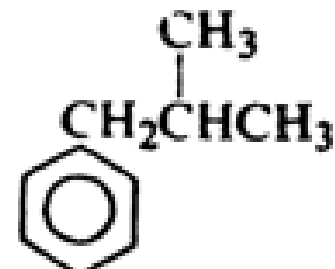
❖ The simplest of the dialkylbenzenes, the dimethylbenzenes, are given the special names of xylenes
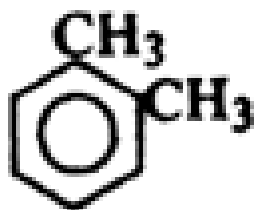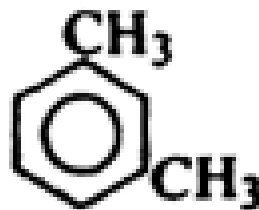
o-Xylene   *m*-Xylene   *p*-Xylene

❖ Dialkylbenzenes containing one methyl group are named as derivatives of toluene

❖ Others are named by prefixing the names of both alkyl groups to the word -benzene

❖ A compound containing a very complicated side chain might be named asa phenylalkane (C_6H_5 = phenyl)
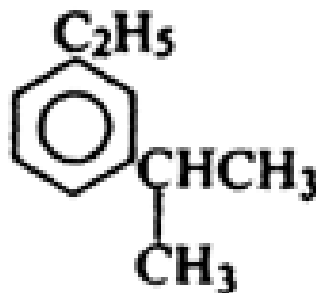
p-Ethyltoluene   m-Ethylisopropylbenzene   2-Methyl-3-phenylpentane
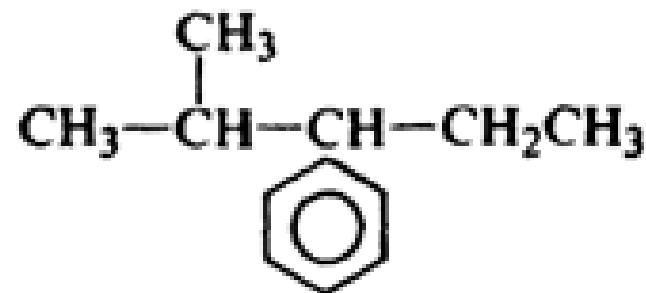
❖ Compounds containing more than one benzene ring are nearly always named as derivatives of alkanes
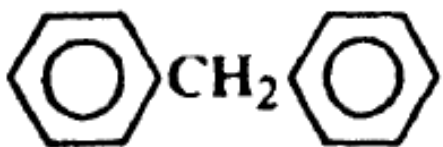
Diphenylmethane
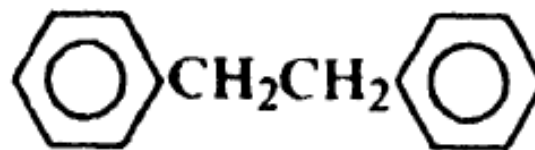
1.2-Diphenylethane

❖ The simplest alkenylbenzene has the special name styrene. Others are generally named as substituted alkenes, occasionally as substituted benzenes. Alkynylbenzenes are named as substituted alkynes

Physical properties

❖ As compounds of low polarity, the alkylbenzenes possess physical properties that are essentially the same as those of the hydrocarbons

❖ They are insoluble in water, but quite soluble in non-polar solvents like ether, carbon tetrachloride

❖ They are almost always less dense than water

❖ Boiling points rise with increasing molecular weight, the boiling point increment being the usual 20-30° for each carbon atom

➢ Preparation of alkylbenzenes

1. Attachment of alkyl group: Friedel-Crafts alkylation.
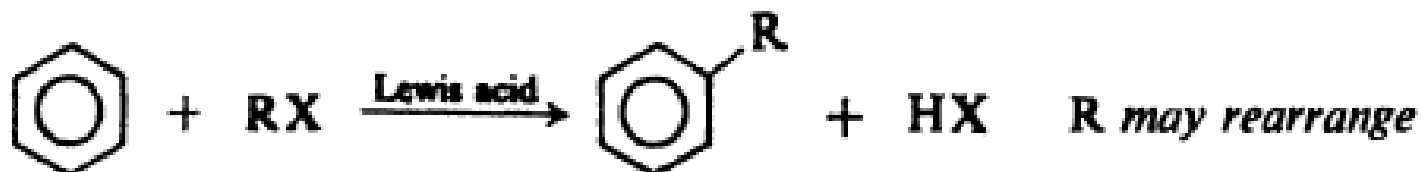
Lewis acid: $AlCl_3$, BF_3, HF, etc.
Ar-X *cannot be used in place of* R-X

❖ polyhalogenated alkanes it is possible to prepare compounds containing more than one aromatic ring

$$2C_6H_6 + CH_2Cl_2 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + 2HCl$$
Diphenylmethane

$$2C_6H_6 + ClCH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5CH_2CH_2C_6H_5 + 2HCl$$
1,2-Diphenylethane

$$3C_6H_6 + CHCl_3 \xrightarrow{AlCl_3} C_6H_5-\underset{\underset{H}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-C_6H_5 + 3HCl$$

Triphenylmethane

$$3C_6H_6 + CCl_4 \xrightarrow{AlCl_3} C_6H_5-\underset{\underset{Cl}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-C_6H_5 + 3HCl$$

Triphenylchloromethane
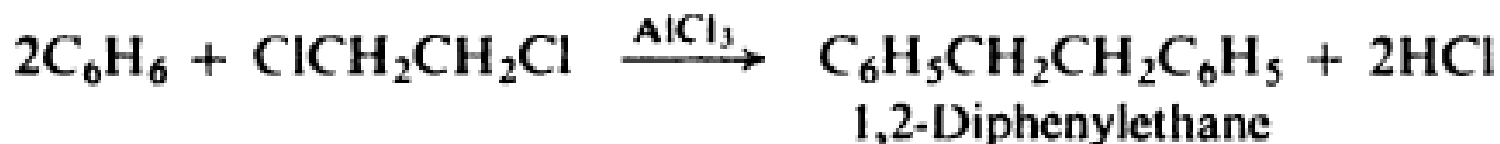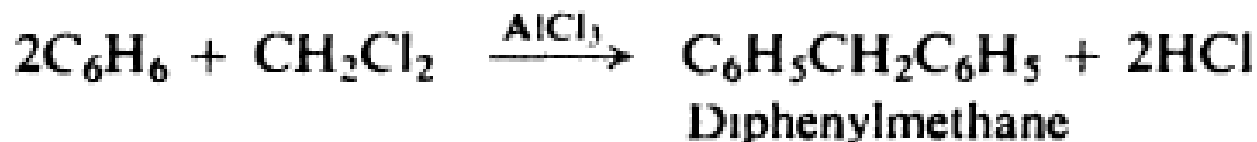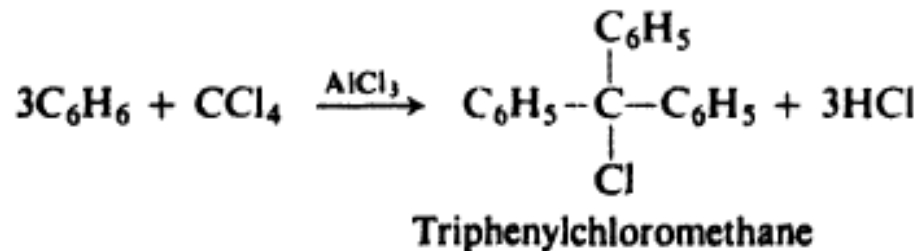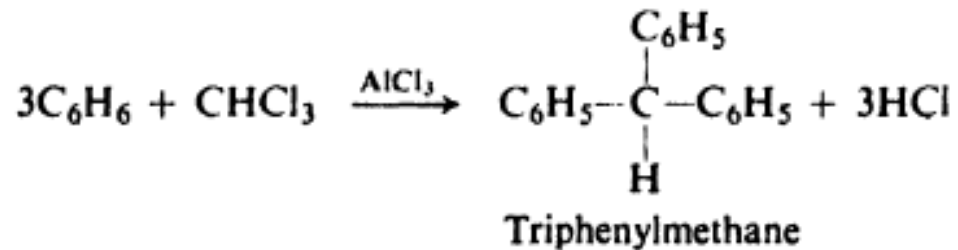
❖ **mechanism for Friedel-Crafts alkylation involves the following steps**

(1) $\qquad\qquad RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$

(2) $\qquad\qquad R^+ + C_6H_6 \rightleftharpoons C_6H_5\underset{H}{\overset{R}{<}}$

(3) $\qquad\qquad C_6H_5\underset{H}{\overset{R}{<}} + AlCl_4^- \rightleftharpoons C_6H_5R + HCl + AlCl_3$
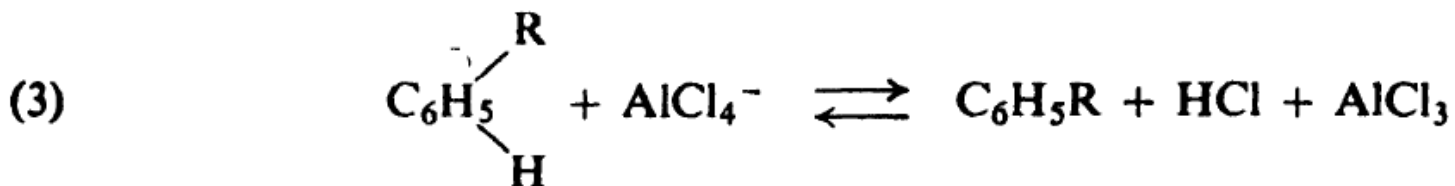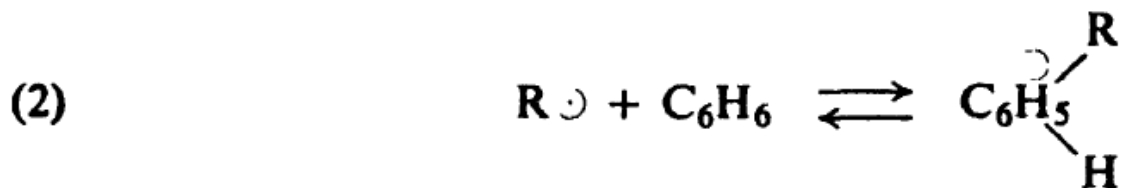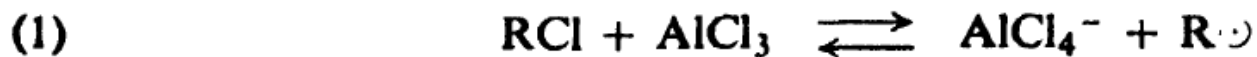
❖ We might expect the benzene ring to be attacked by carbonium ions generated in other ways: by the action of acid on alcohols and on alkenes.

$$ROH + H^+ \rightleftarrows ROH_2^{\oplus} \rightleftarrows R^{\oplus} + H_2O$$

$$-\overset{|}{C}=\overset{|}{C}- + H^+ \rightleftarrows -\overset{|}{\underset{H}{C}}-\overset{|}{C}^{\oplus}$$
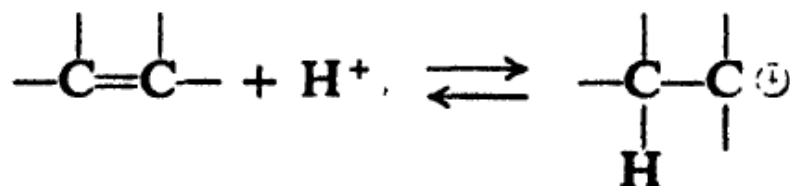
Carbonium ions from alcohols and from alkenes

$$C_6H_6 + (CH_3)_3COH \xrightarrow{H_2SO_4} C_6H_5-C(CH_3)_3$$

tert-Butyl alcohol   *tert*-Butylbenzene

$$C_6H_6 + (CH_3)_2C=CH_2 \xrightarrow{H_2SO_4} C_6H_5-C(CH_3)_3$$

Isobutylene   *tert*-Butylbenzene
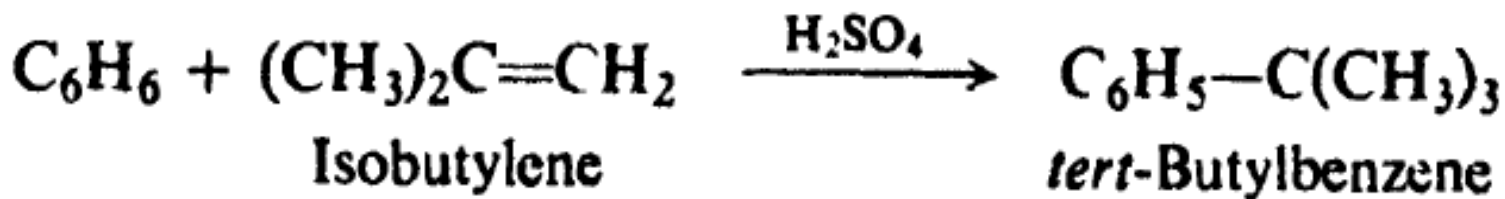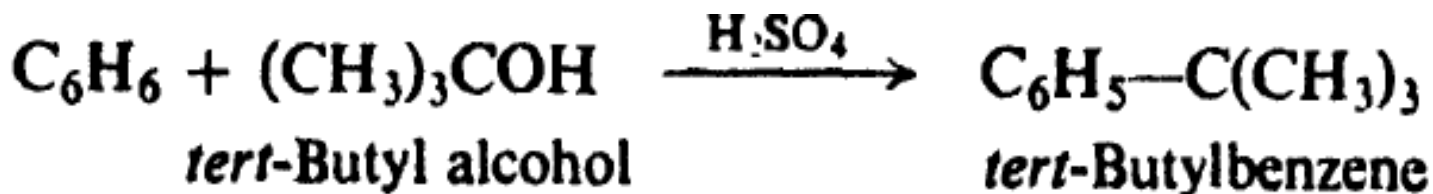
❖ We might expect Friedel-Crafts alkylation to be accompanied by the kind of rearrangement that is characteristic of carbonium ion reactions

$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow[-18° \text{ to } 80°]{AlCl_3} C_6H_5CH_2CH_2CH_3 \quad and \quad C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

n-Propyl chloride ⟶ n-Propylbenzene 35–31% Isopropylbenzene 65–69%

$$C_6H_6 + CH_3CH_2CH_2CH_2Cl \xrightarrow[0°]{AlCl_3} C_6H_5CH_2CH_2CH_2CH_3 \quad and \quad C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

n-Butyl chloride ⟶ n-Butylbenzene 34% sec-Butylbenzene 66%

$$C_6H_6 + CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2Cl \xrightarrow[-18° \text{ to } 80°]{AlCl_3} C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3$$

Isobutyl chloride ⟶ tert-Butylbenzene
Only product

$$C_6H_6 + CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2OH \xrightarrow[60°]{BF_3} C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_3$$

Neopentyl alcohol ⟶ tert-Pentylbenzene
Only product

2. Conversion of side chain.

A ketone

Clemmensen or Wolff-kishner
reaction
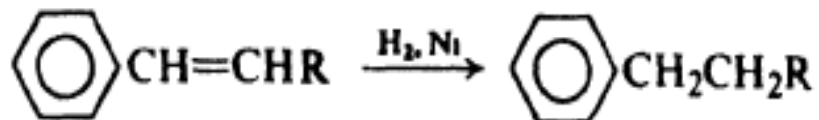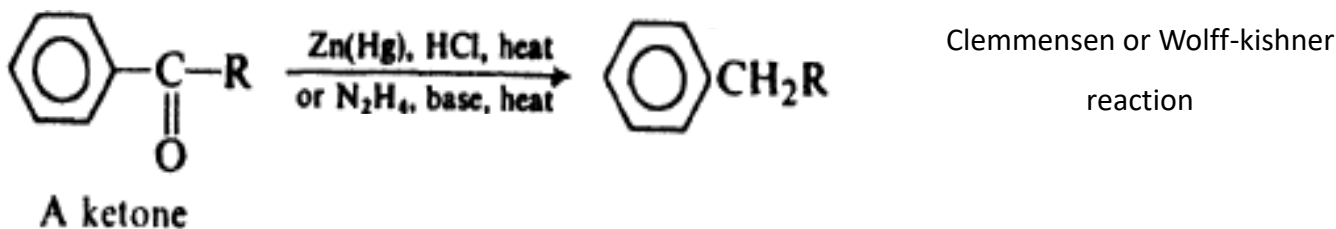
Reactions of alkylbenzenes

1. Hydrogenation

Ethylbenzene   Ethylcyclohexane

2. Oxidation.

Ethylbenzene $\xrightarrow[\text{or dil. HNO}_3)]{\substack{\text{KMnO}_4 \\ \text{(or K}_2\text{Cr}_2\text{O}_7,}}$ Benzoic acid $(+ CO_2)$
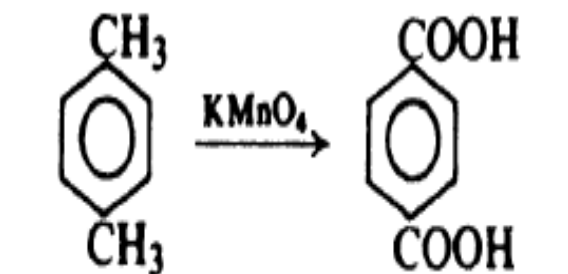
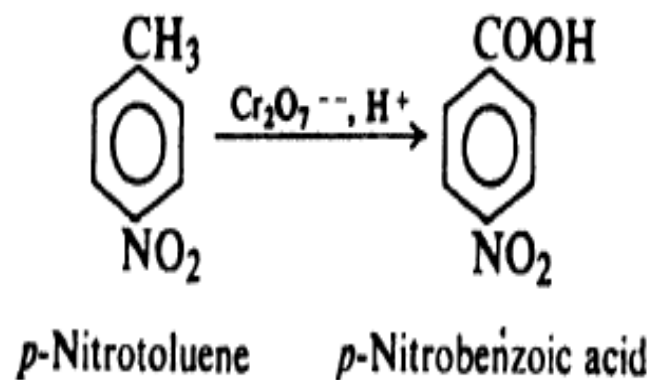n-Butylbenzene $\xrightarrow{\text{hot KMnO}_4}$ Benzoic acid and CO_2

❖ This reaction is used for two purposes:

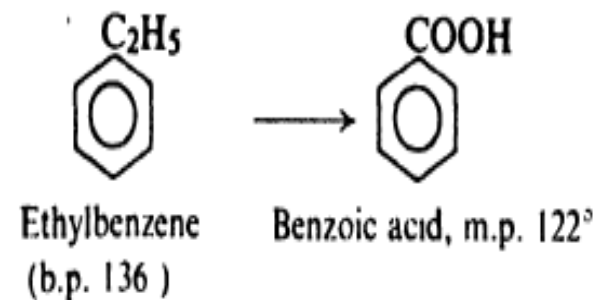Synthesis of carboxylic acids

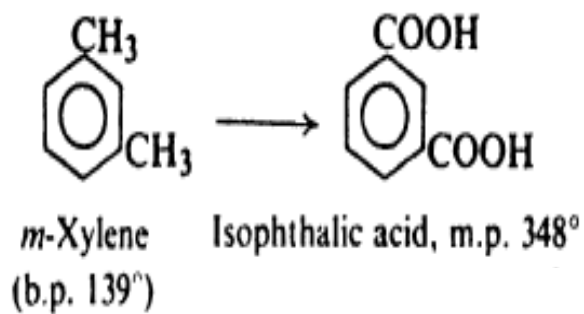p-Xylene $\xrightarrow{\text{KMnO}_4}$ Terephthalic acid (1,4-Benzenedicarboxylic acid)

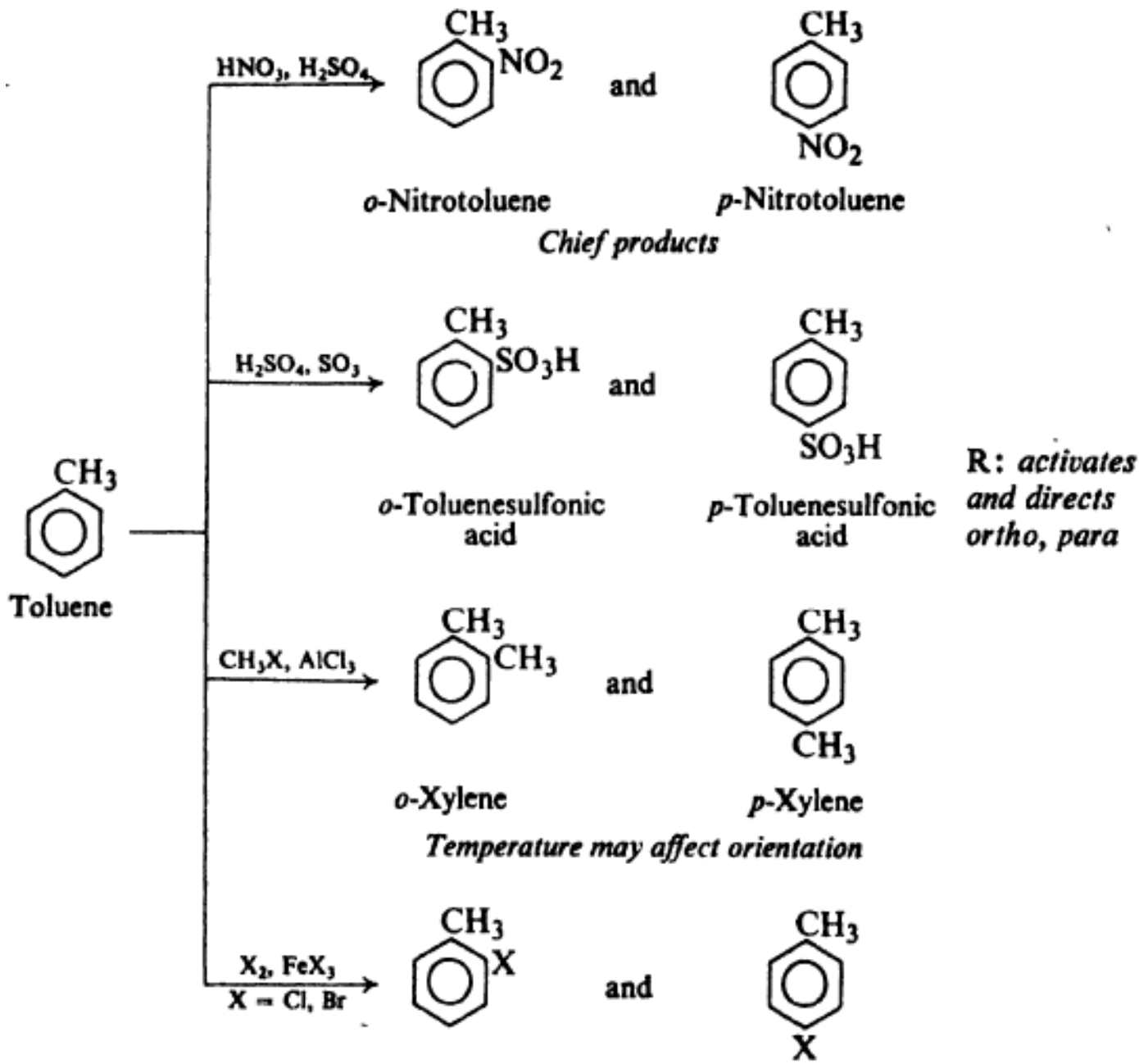p-Nitrotoluene $\xrightarrow{Cr_2O_7^{--}, H^+}$ p-Nitrobenzoic acid

Identification of alkylbenzenes

o-Xylene → Phthalic acid, m.p. 231°
(b.p. 144°)

p-Xylene → Terephthalic acid, m.p. 300° subl.
(b.p. 138°)

m-Xylene → Isophthalic acid, m.p. 348°
(b.p. 139°)

Ethylbenzene → Benzoic acid, m.p. 122°
(b.p. 136)
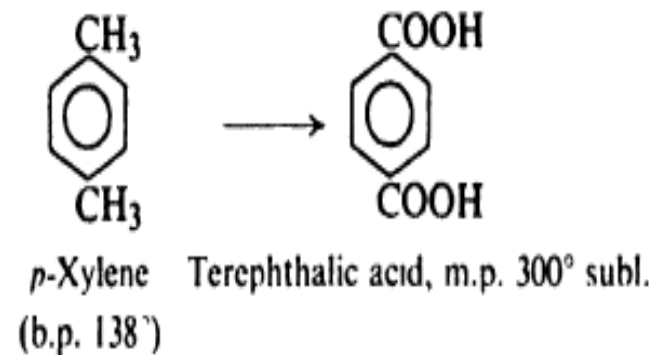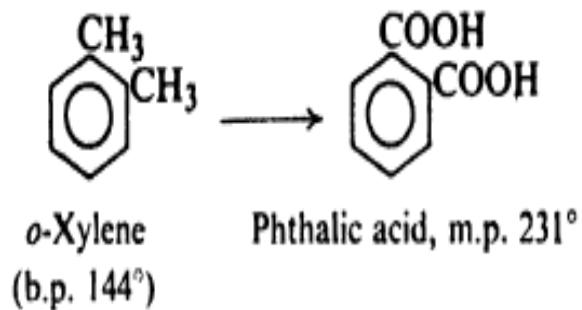
3. Substitution in the ring. Electrophilic aromatic substitution.

Toluene → (HNO$_3$, H$_2$SO$_4$) →

CH_3 NO_2 (*o*-Nitrotoluene) **and** CH_3 / NO_2 (*p*-Nitrotoluene)

Chief products

→ (H$_2$SO$_4$, SO$_3$) →

CH_3 SO_3H (*o*-Toluenesulfonic acid) **and** CH_3 / SO_3H (*p*-Toluenesulfonic acid)

R: *activates and directs ortho, para*

→ (CH$_3$X, AlCl$_3$) →

CH_3 CH_3 (*o*-Xylene) **and** CH_3 / CH_3 (*p*-Xylene)

Temperature may affect orientation

→ (X$_2$, FeX$_3$; X = Cl, Br) →

CH_3 X **and** CH_3 / X

4. Substitution in the side chain. Free-radical halogenation.

❖ The ring and the side chain. We can control the position of attack simply by choosing the proper reaction conditions

Free radical substitution

Electrophilic substitution

Toluene   Benzyl chloride   Benzal chloride   Benzotrichloride

Ethylbenzene   α-Phenylethyl chloride   β-Phenylethyl chloride

Chief product