Republic of Iraq Ministry of Higher
Education & Scientific Research
University of Al-Maarif
College of Dentistry

Aromatic Compounds

Lec(10)

First stage

By

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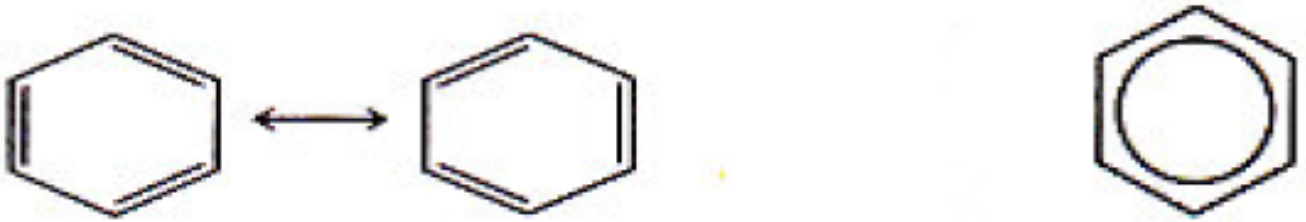
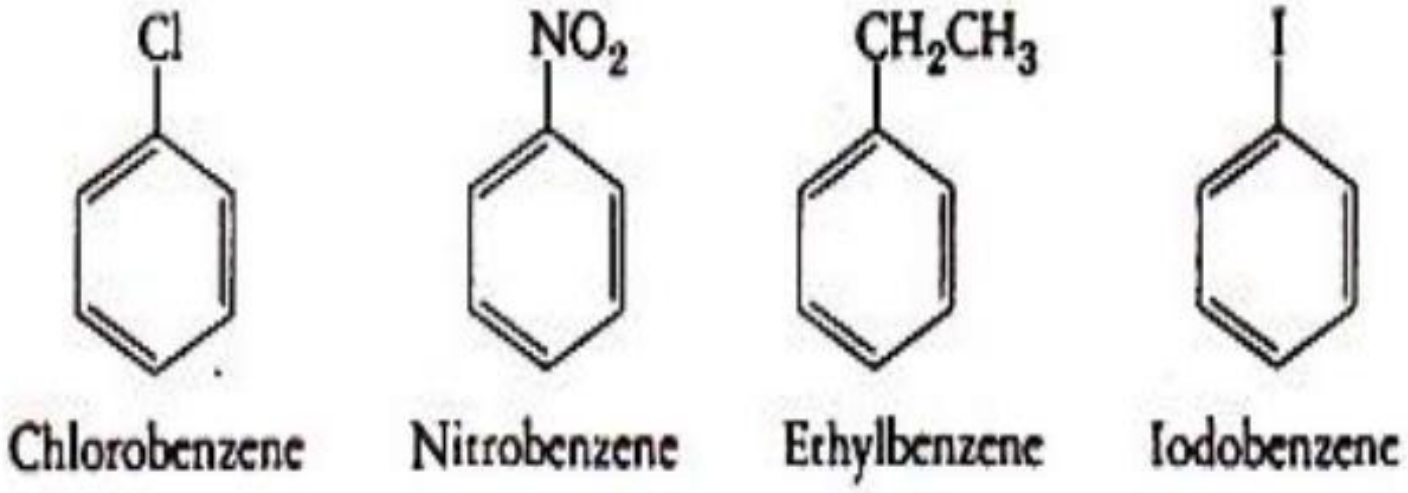
Aromatic Compounds

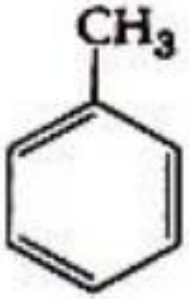
Benzene has a high degree of unsaturation but is unreactive.It does not undergo the usual addition reactions of alkenes and alkynes. It does react under more vigorous conditions(heat or catalysts) to form products of substitution. This difference in chemical reactivity is due to the structure of benzene.



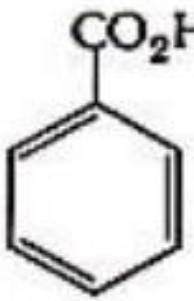
Naming Aromatic Compounds

When one group is attached to benzene, the compound is named by placing the name of the group as prefix to the benzene.

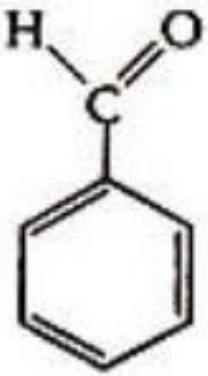




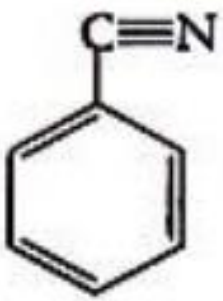
Toluene



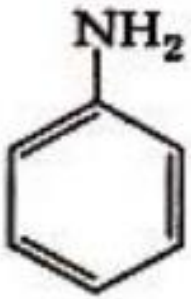
Benzoic acid



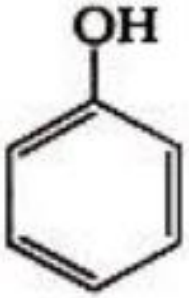
Benzaldehyde



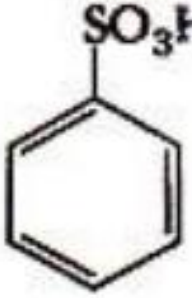
Benzonitrile



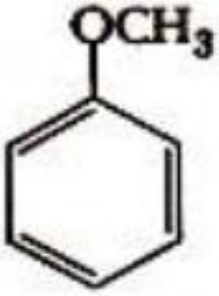
Aniline



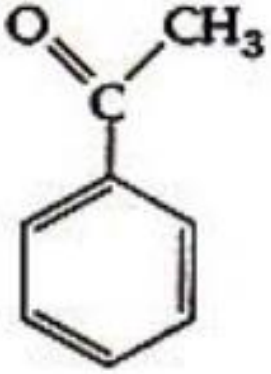
Phenol



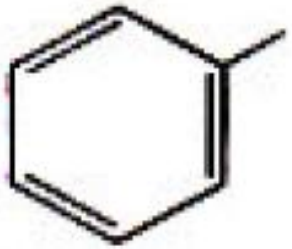
Benzenesulfonic acid



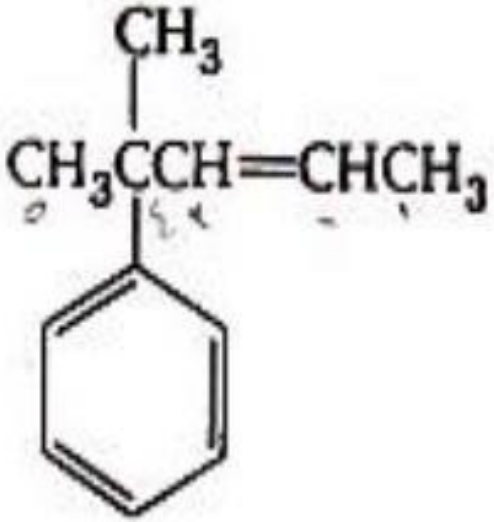
Anisole



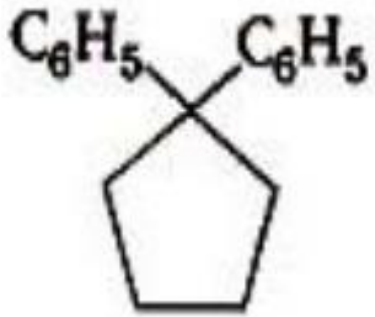
Acetophenone

C_6H_5— or 

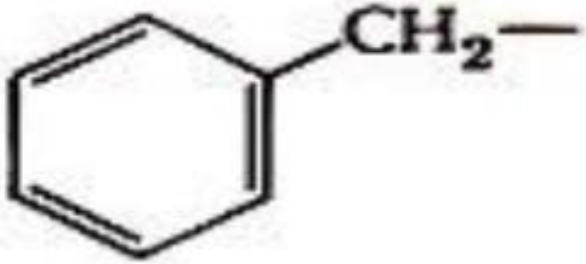
Phenyl group



4-Methyl-4-phenyl-2-pentene

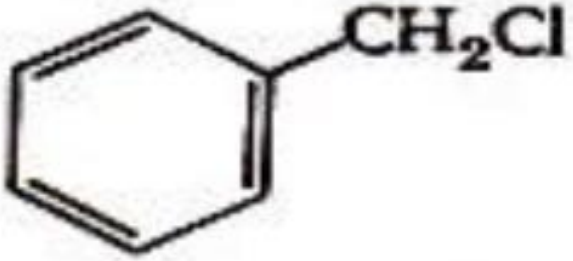


1,1-Diphenylcyclopentane

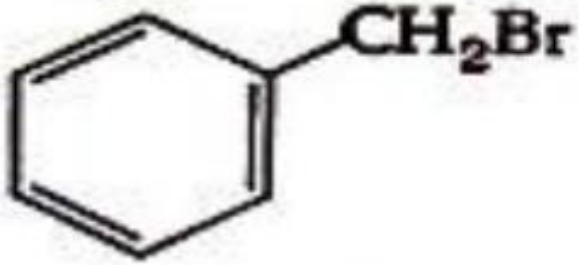


Benzyl group

For example:

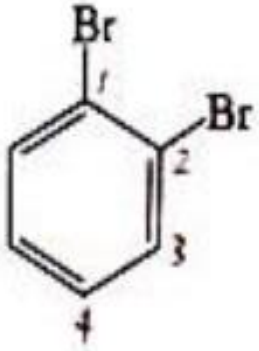


Benzyl chloride

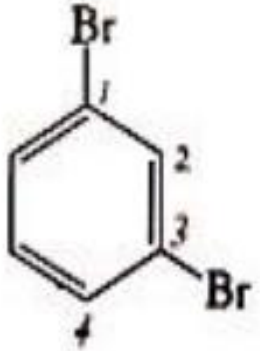


Benzyl bromide

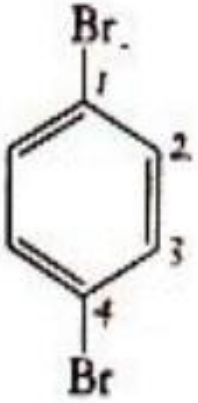
If two groups are attached to the benzene ring, the name must not only tell what groups are present, but also where they are located. We can differentiate the three possible isomers of a disubstituted benzene in two ways.



o-Dibromobenzene
1,2-Dibromobenzene

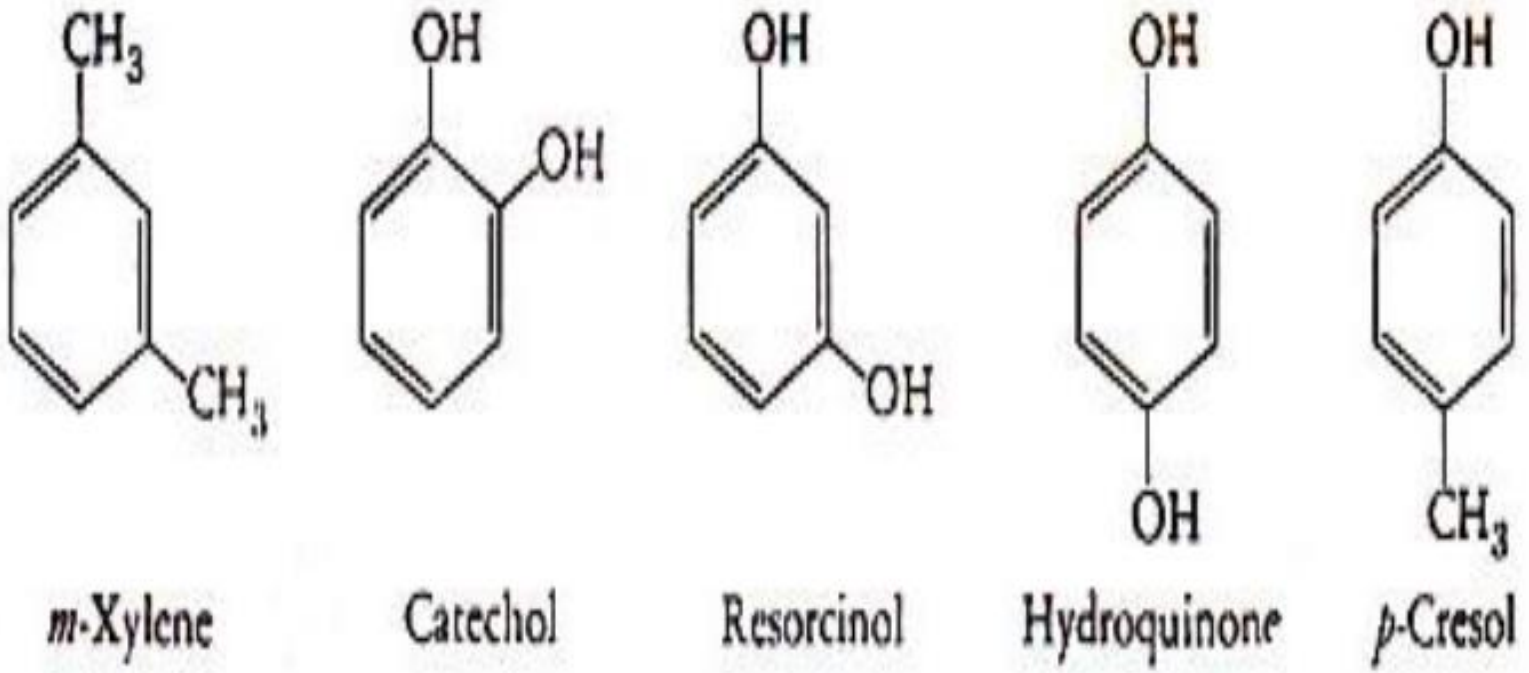


m-Dibromobenzene
1,3-Dibromobenzene



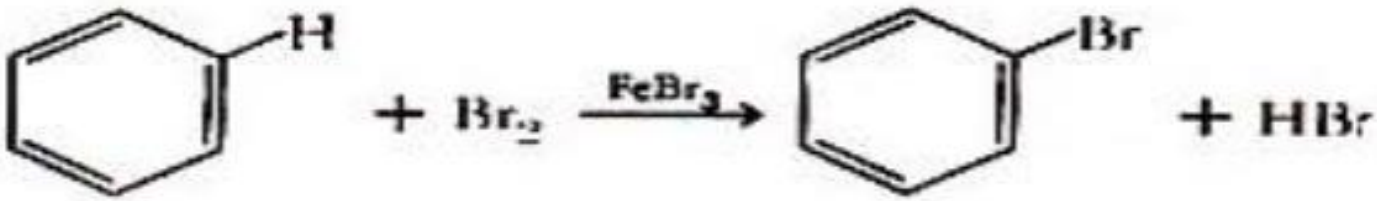
p-Dibromobenzene
1,4-Dibromobenzene

Several disubstituted benzenes have been given names that, give no indication of the kind of groups attached to the ring.

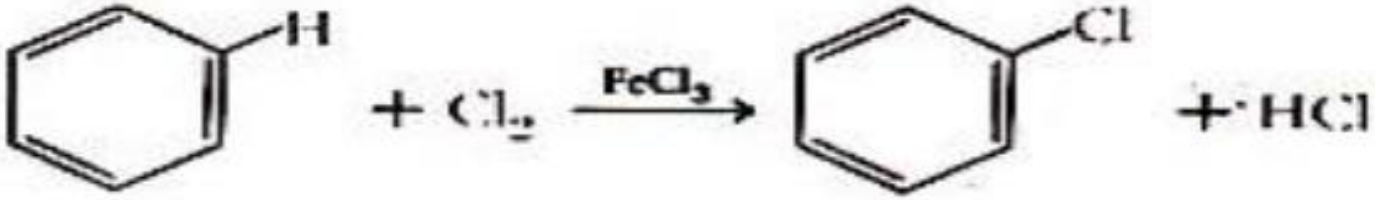


Substitution Reactions Of Aromatic Compounds

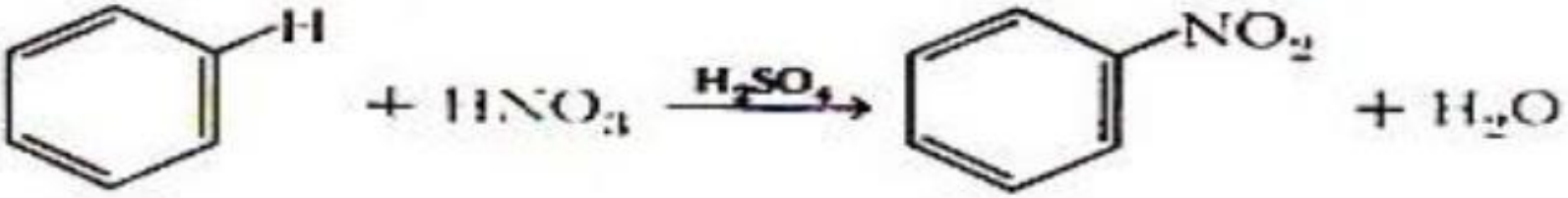
Bromination



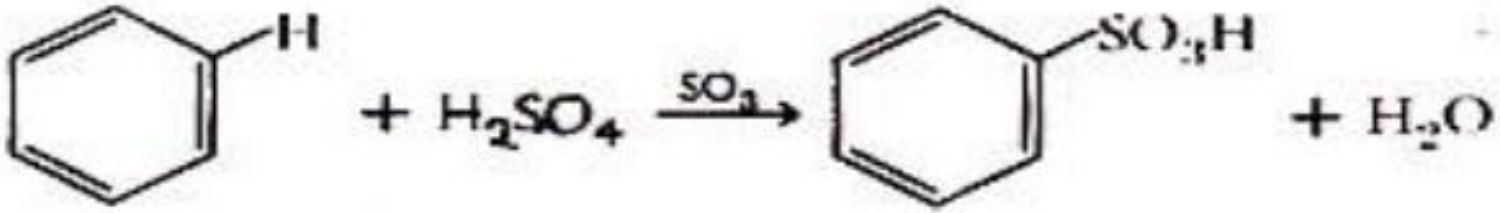
Chlorination



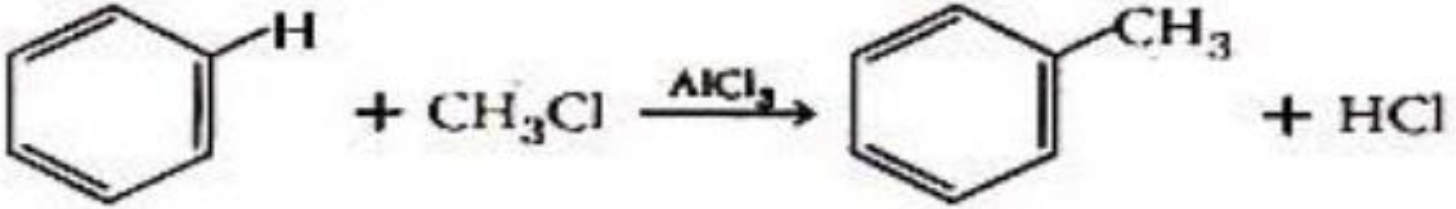
Nitration



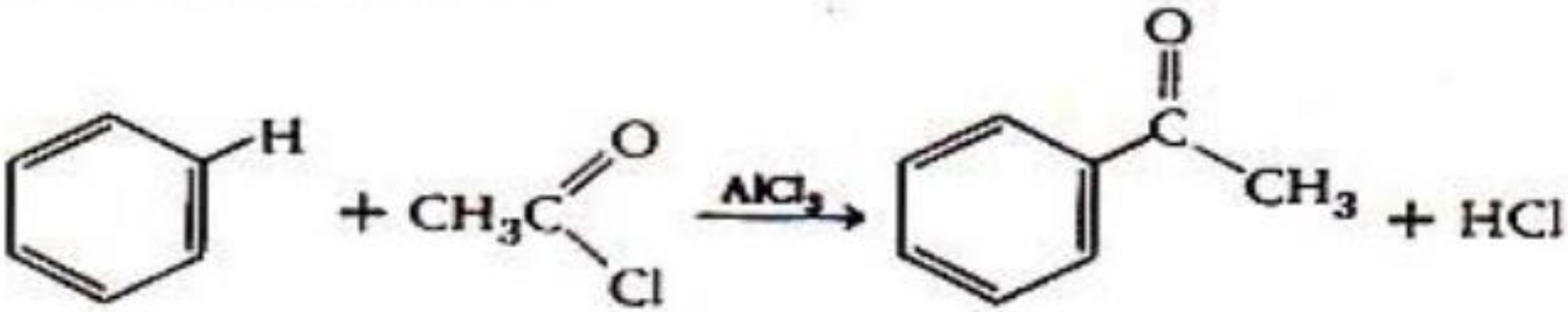
Sulfonation



Friedel-Crafts alkylation

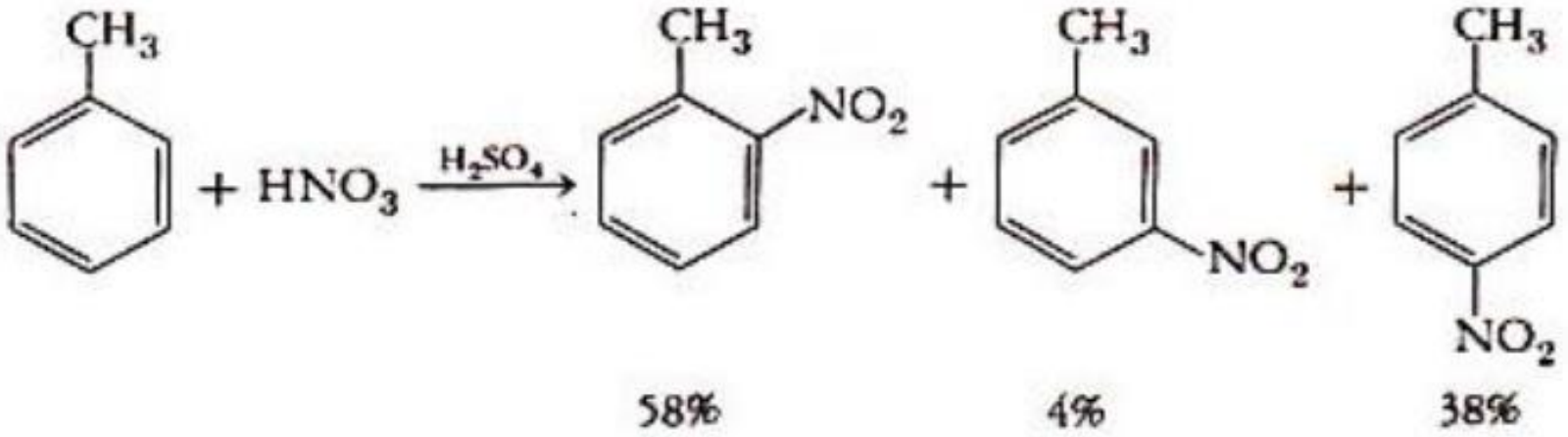


Friedel-Crafts acylation



Toluene,nitrobenzene,chlorobenzene and many other aromatic compounds also undergo substitution reactions. These compounds differ from benzene in that they already have a substituent on the benzene ring. The remaining five hydrogens are not equivalent. When these hydrogens undergo substitution reactions, **isomers** can be formed depending on which hydrogen is replaced.

Examples:


CH3
+ HNO3
H2SO4
CH3
NO2
CH3
NO2
CH3
NO2
58%
4%
38%

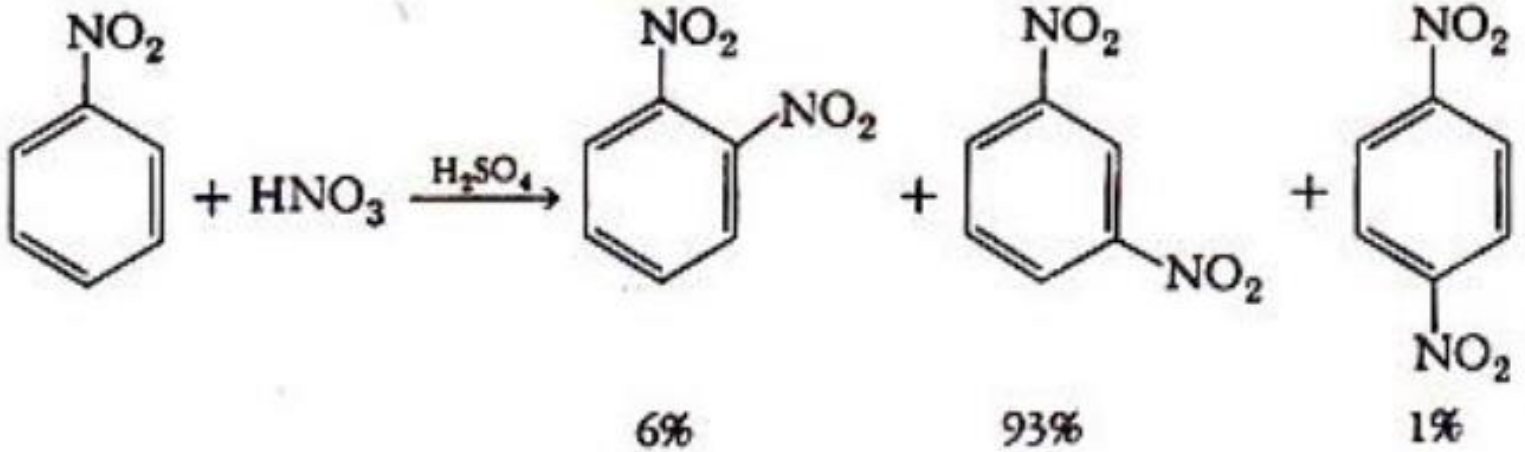

NO2
+ HNO3
H2SO4
NO2
NO2
NO2
NO2
NO2
NO2
6%
93%
1%

Table 13-1. Directing Effect of Substituents[a]

Predominant Directing	
o, *p*	*m*
$-NH_2$, $-NHR$, $-NR_2$	$-NO_2$
$-NH_2$, $-NHAr$, $-N(Ar)_2$	$-CN$
$-OH$, $-OR$, $-OAr$	$-CO_2H$, $-CHO$, $-C(=O)R$, $-CO_2R$, $-CO_2Ar$
$-NHC(=O)R$, $-NHC(=O)Ar$	$-SO_3H$
Alkyl groups	$-\overset{+}{N}H_3$, $-\overset{+}{N}H_2R$, $-\overset{+}{N}HR_2$, $-\overset{+}{N}R_3$
Halogens	$-\overset{+}{N}H_3$, $-\overset{+}{N}H_2Ar$, $-\overset{+}{N}H(Ar)_2$, $-\overset{+}{N}(Ar)_3$

[a] R = alkyl groups; Ar = aryl groups.

Table 13-2. Directive Influence and Effect on Reactivity of Substituents[a]

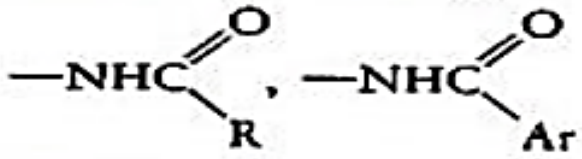
I. Activating and *ortho* and *para* directing

A. Strongly activating

$-NH_2$, $-NHR$, $-NR_2$, $-NHAr$, $-N(Ar)_2$

$-OH$, $-OR$, $-OAr$

B. Moderately activating



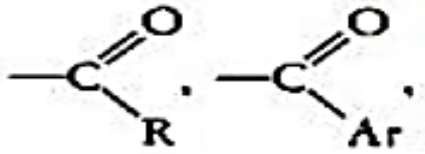
C. Weakly activating

Alkyl groups

II. Strongly deactivating and *meta* directing

$-NO_2$

$-CN$

$-CO_2H$, $-CHO$,  , $-CO_2R$, $-CO_2Ar$

$-SO_3H$

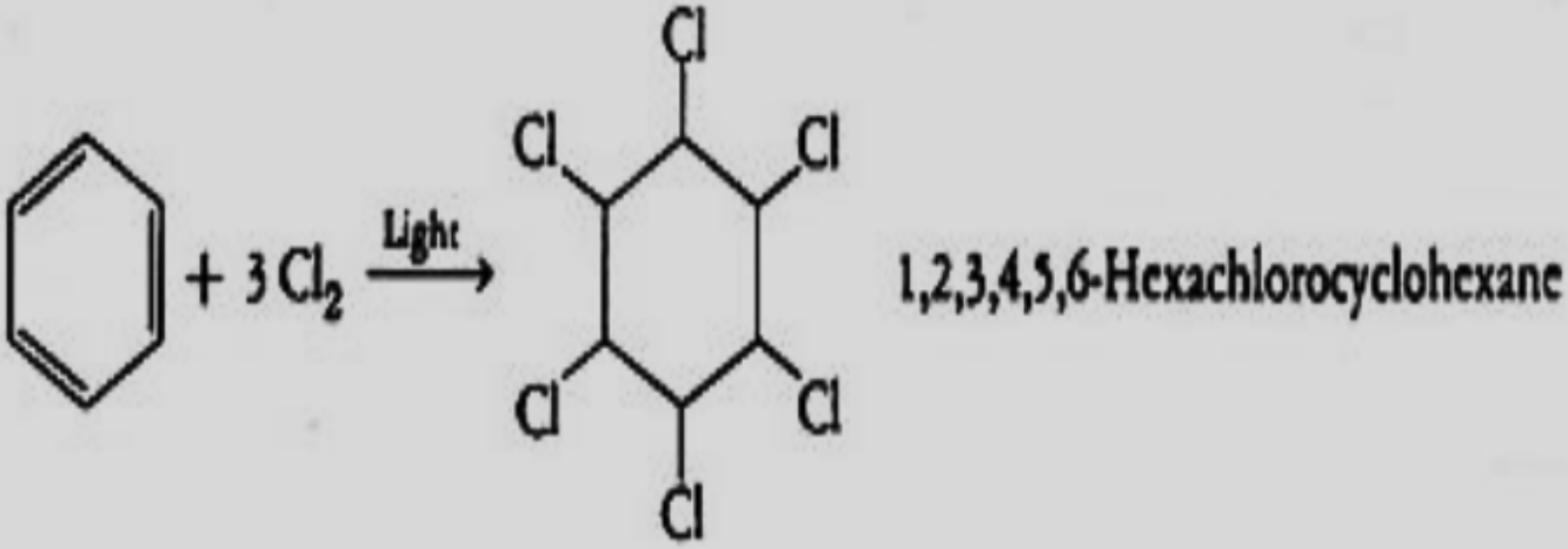
$-\overset{+}{N}H_3$, $-\overset{+}{N}H_2R$, $-\overset{+}{N}HR_2$, $-\overset{+}{N}R_3$, $-\overset{+}{N}H_2Ar$, $-\overset{+}{N}H(Ar)_2$, $-\overset{+}{N}(Ar)_3$

III. Deactivating and *ortho* and *para* directing

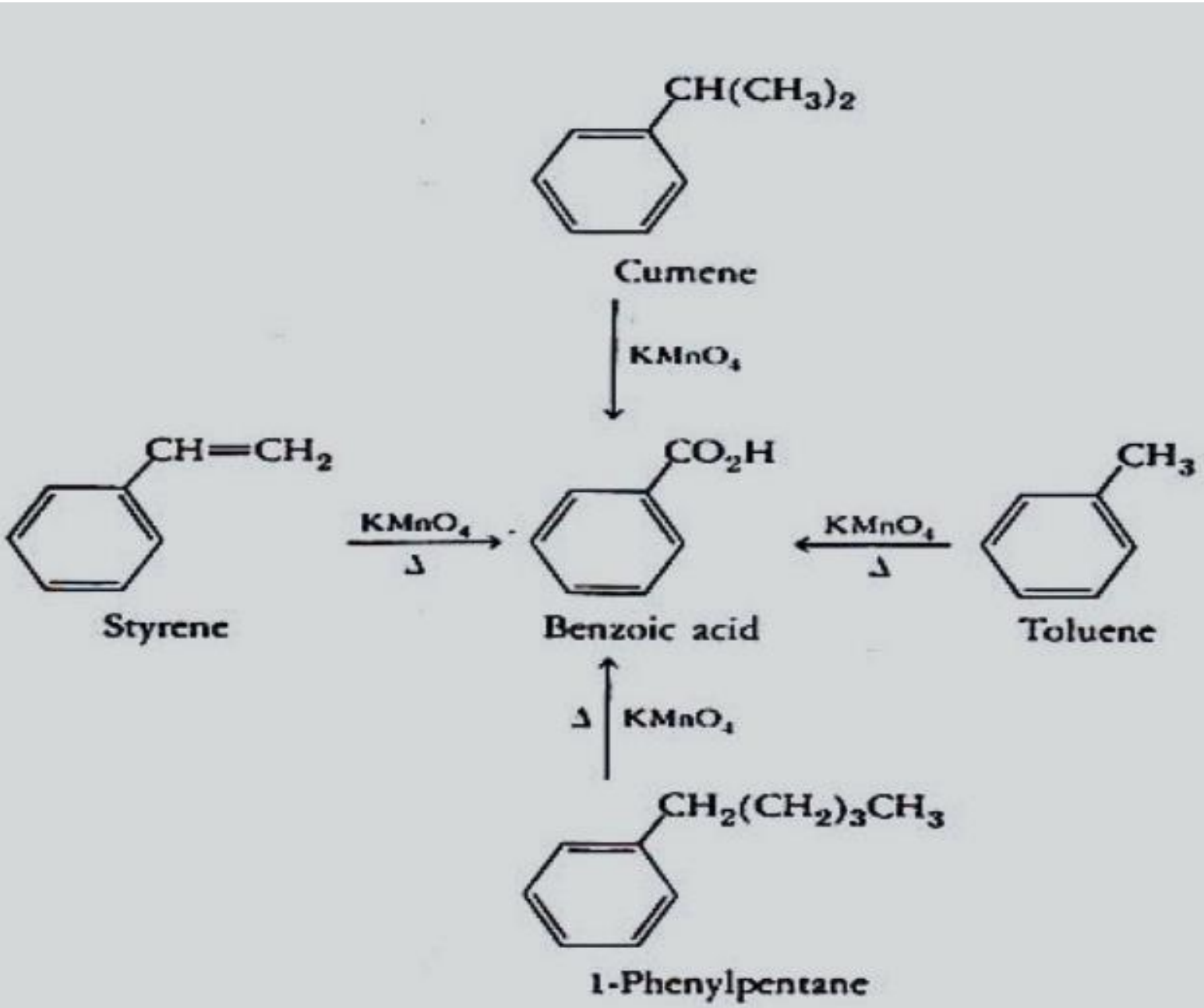
Halogens

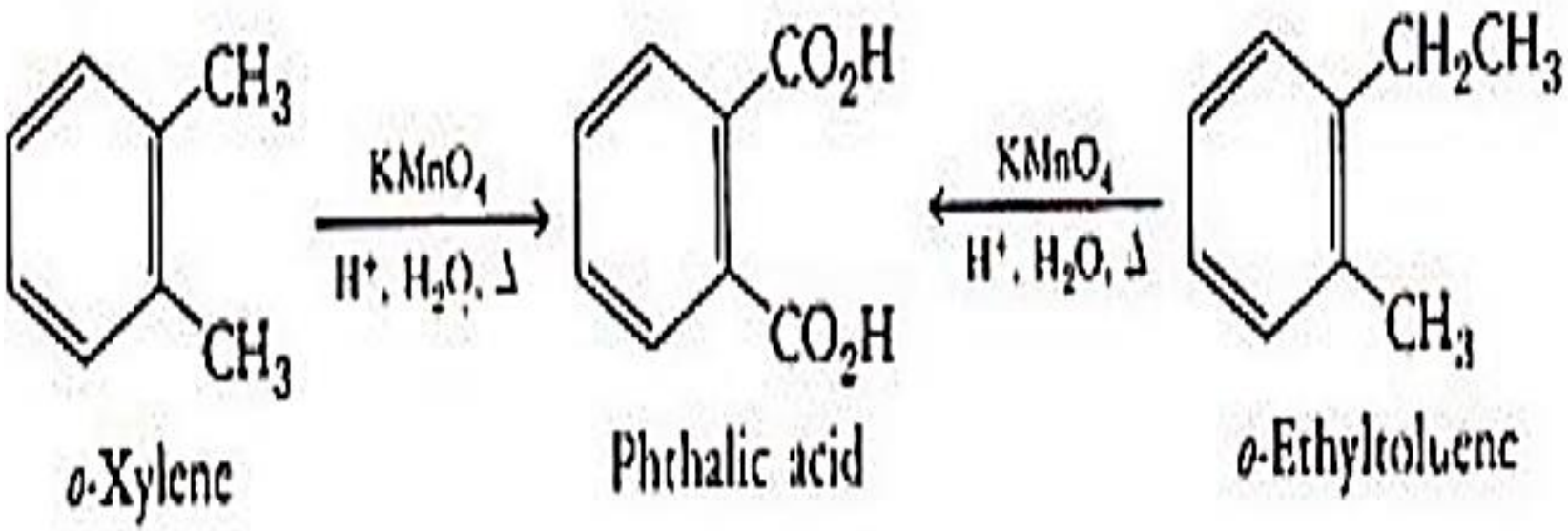
[a] R = alkyl groups; Ar = aryl groups.

Other Reactions Of Aromatic Compounds

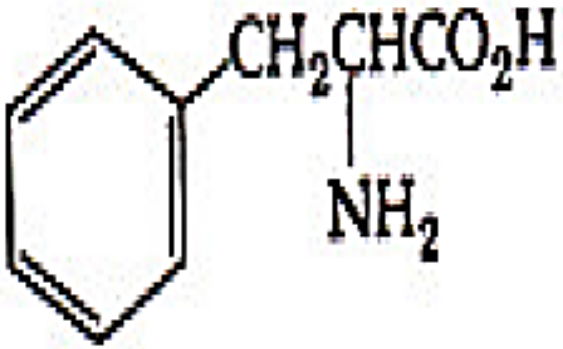


1,2,3,4,5,6-Hexachlorocyclohexane

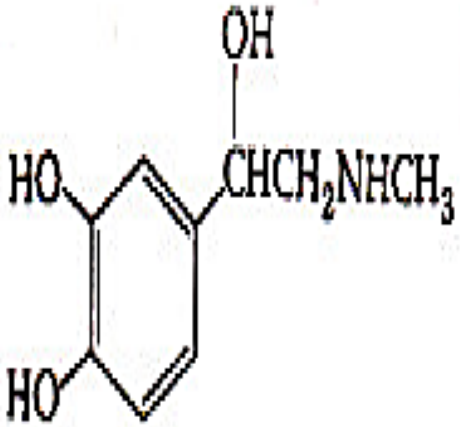

CH(CH3)2
Cumene
KMnO4
CH=CH2
CO2H
CH3
KMnO4
Δ
KMnO4
Δ
Styrene
Benzoic acid
Toluene
Δ
KMnO4
CH2(CH2)3CH3
1-Phenylpentane


CH3
CH3
KMnO4
H+, H2O, Δ
CO2H
CO2H
KMnO4
H+, H2O, Δ
CH2CH3
CH3
o-Xylene
Phthalic acid
o-Ethyltoluene

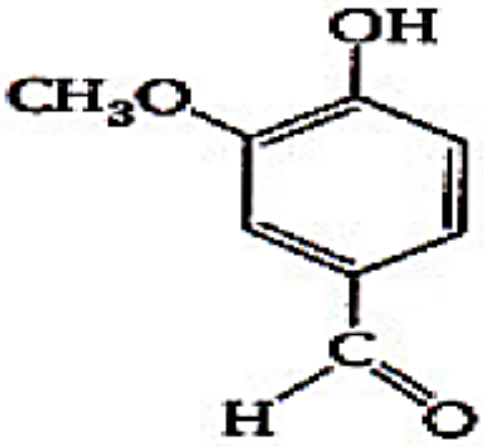
Aromatic Compounds in Nature



Phenylalanine



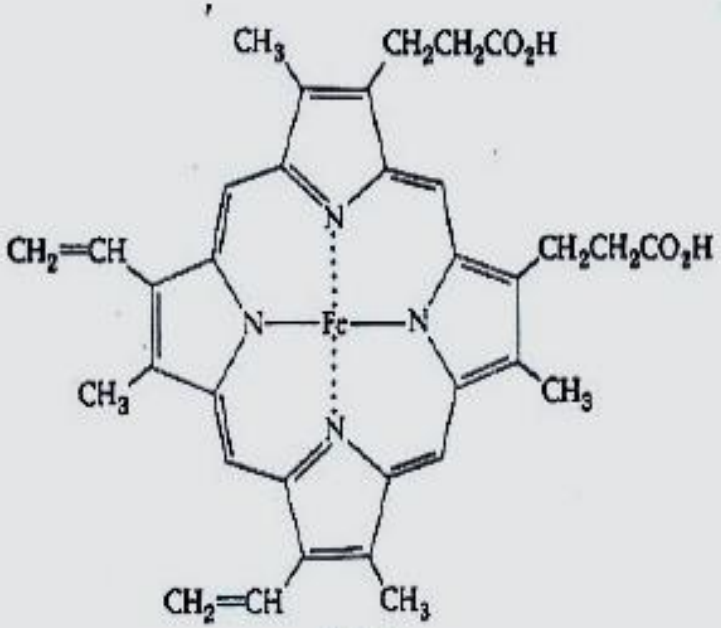
Epinephrine



Vanillin

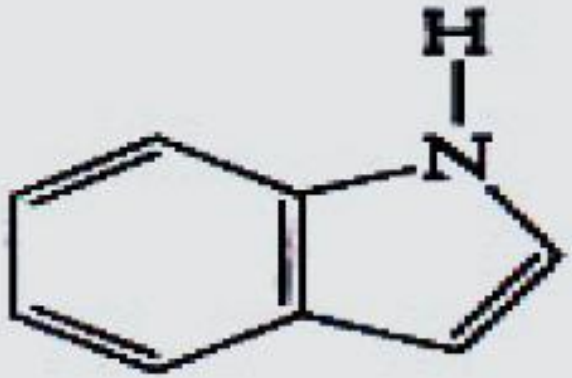
Aromatic Heterocyclic compounds

Unlike benzene, they contain at least one element other than carbon or hydrogen, usually nitrogen. These compounds, called aromatic heterocyclic compounds, contain a ring (or rings) in which one or more of the atoms of the ring are elements other than carbon. The other elements are called heteroatoms.

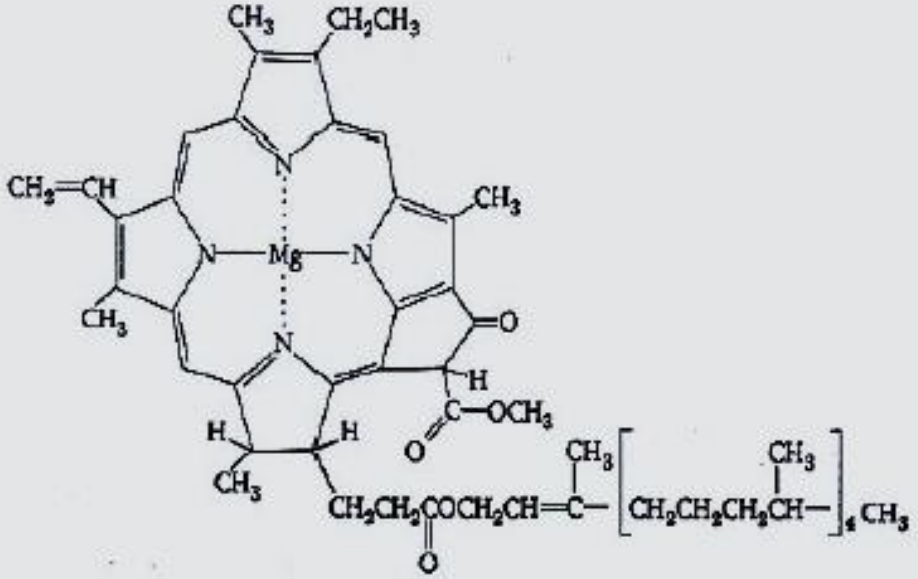


Heme

Pyridine



Indole



Chlorophyll a