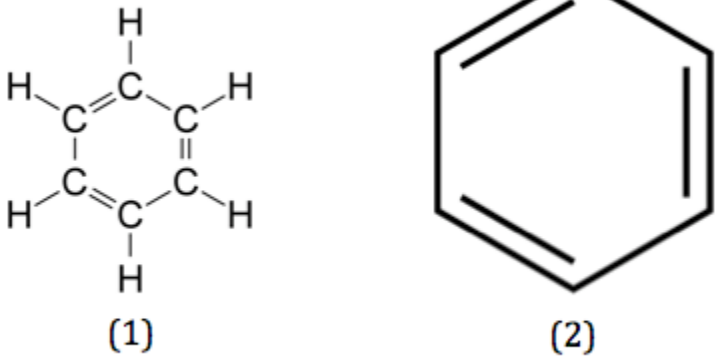
Lec. 2

Aromatic compounds

Are substances that consist of one or more rings that contain alternating single and double bonds in its chemical structure. In real life, many aromatic compounds have an odor, however, there are some compounds that are chemically aromatic, but do not have a distinct smell.

For example, benzene is an aromatic compound. The chemical structure of benzene, as illustrated here, contains a hexagon ring with alternating double bonds. Here, you'll see there are two ways to draw benzene. Structure 1 shows all the carbon (C) and hydrogen (H) atoms bonded together, and structure 2 shows a hexagon with alternating double bonds. In structure 2, the edges of the hexagon are the carbon atoms, and the hydrogen atoms are not shown.

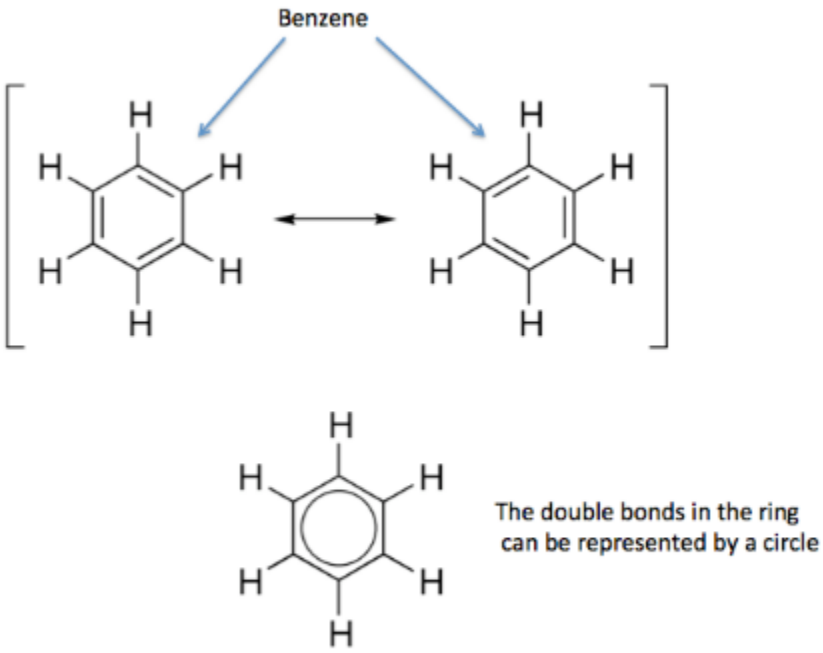


(1) (2)

Chemical structure of the aromatic compound benzene

For instance, the two structures show that the double bonds can be moved about the ring because the electrons are delocalized within the ring. This is why alternating double bonds in the ring can also be illustrated as a circle, as in this image.

Lec. 2



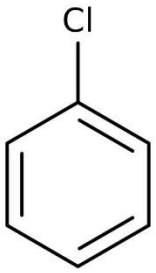
Benzene has delocalized electrons in the ring.

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

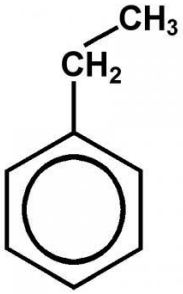
When one group is attached to benzene, the compound is named by placing the name of the group as prefix to the benzene.

Lec. 2

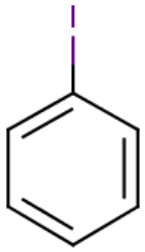


Chlorobenzene

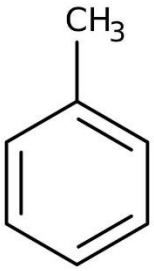




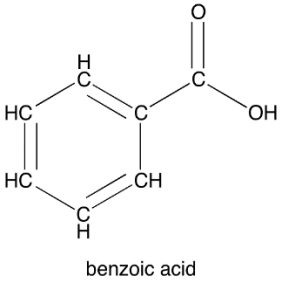
Ethylbenzene

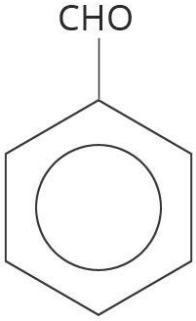


Iodobenzene

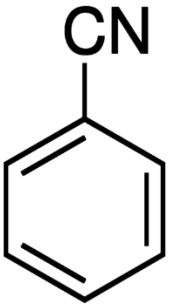


Toluene

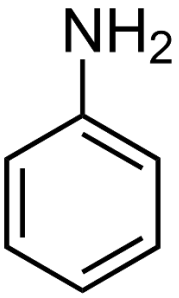




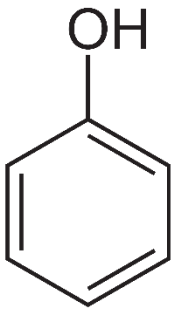
Benzaldehyde



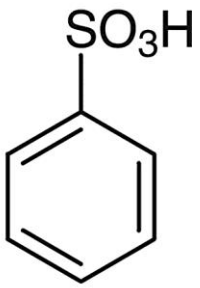
benzonitrile



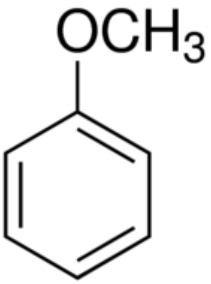
Aniline



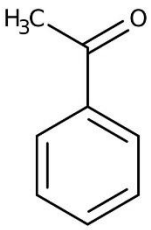
Phenol



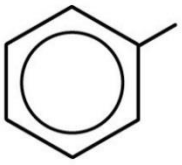
Benzenesulfonic acid



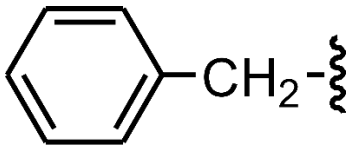
Anisole



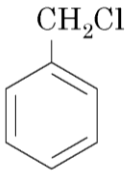
Acetophenone



phenyl group

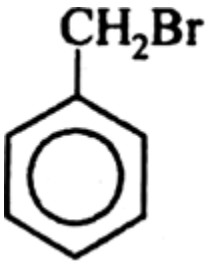


benzyl group



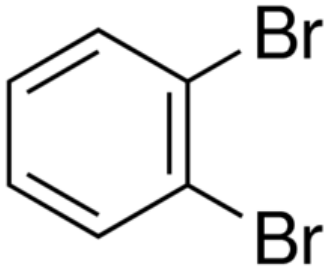
benzyl chloride

Lec. 2



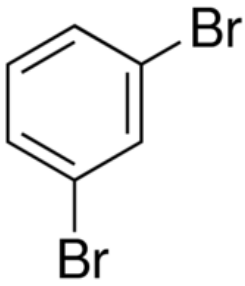
Benzyl bromide

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 di substituted benzene in two ways.



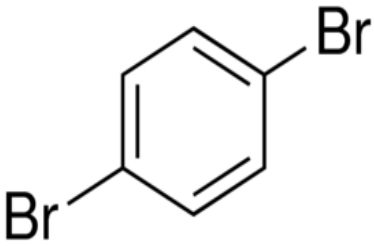
o-dibromobenzene

1,2-dibromobenzene



m-dibromobenzene

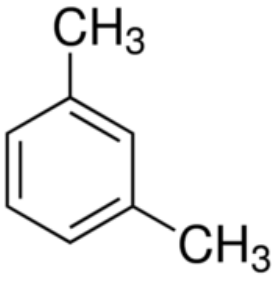
1,3-dibromobenzene



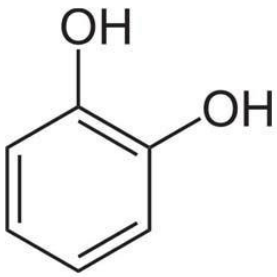
p-dibromobenzene

1,4-dibromobenzene

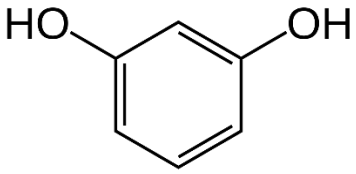
Several di substituted benzene have been given name that, give no indication of the kind of groups attached to the ring.



m-xylene

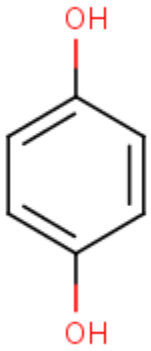


Catechol



Resorcinol

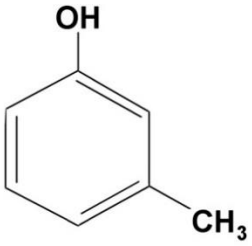
Lec. 2



Hydroquinone



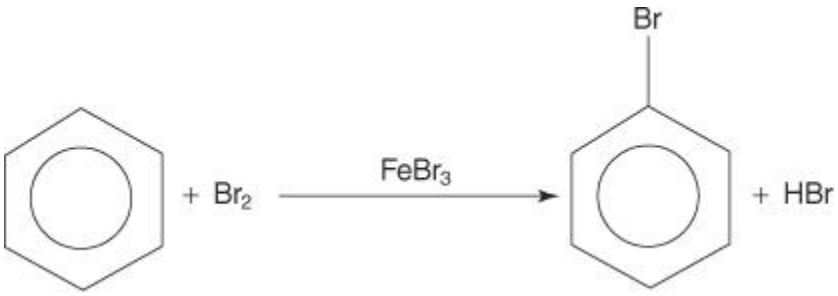
p-cresol



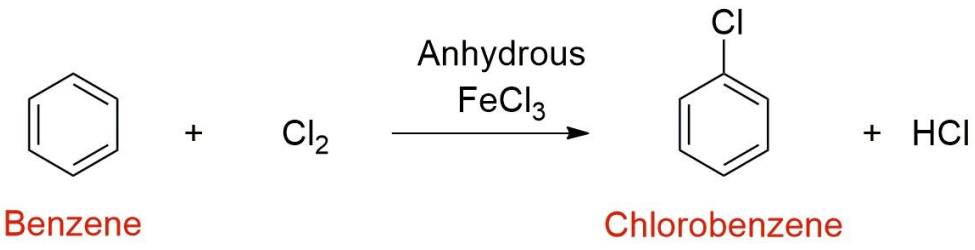
m-cresol

Substitution reaction of aromatic compounds

Bromination

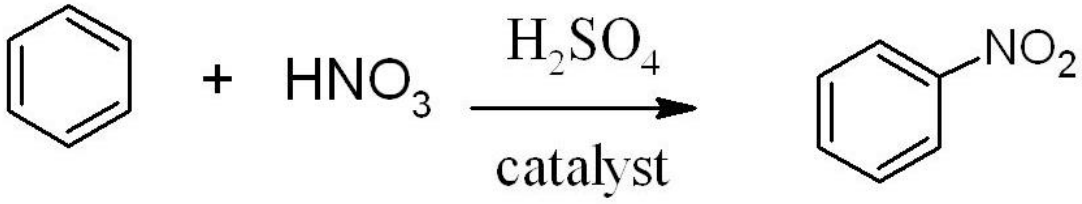


Chlorination

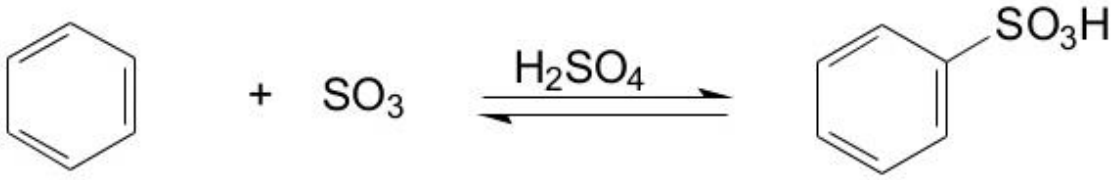


Nitration

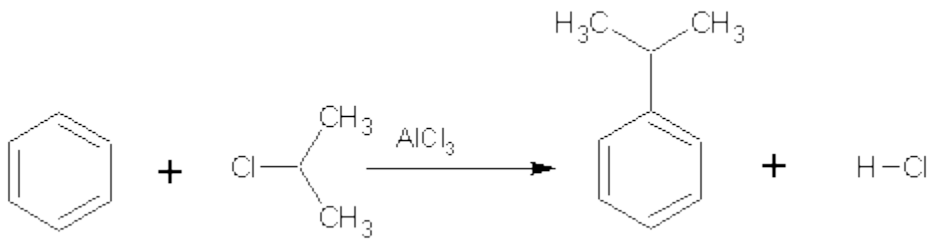
Lec. 2



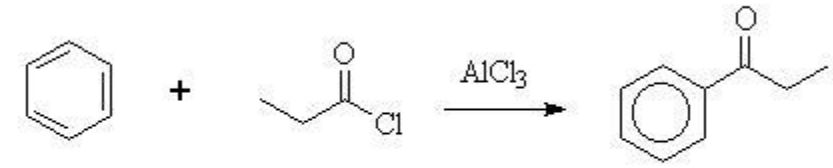
Sulfonation



Friedel-Crafts alkylation



Friedel-Crafts acylation

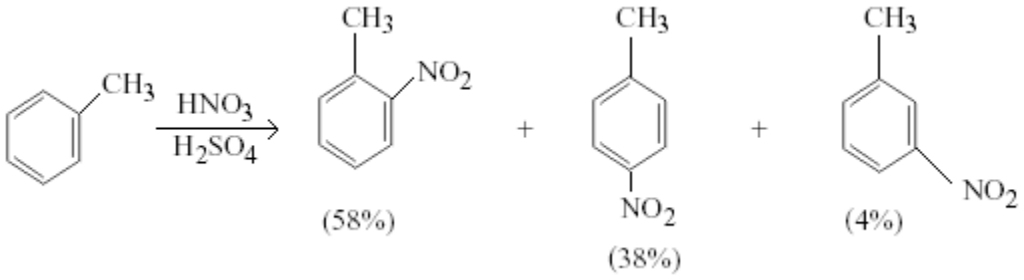


Benzene acetyl chloride acetophenone

Toluene, nitrobenzene, chlorobenzene and many other aromatic compounds also undergo substitution reaction. These compounds differ from benzene in that they already have a substituent on the benzene ring. The remaining five hydrogens are not equivalent.

Lec. 2

When these hydrogens undergo substitution reactions, isomers can be formed depending on which hydrogen is replaced.



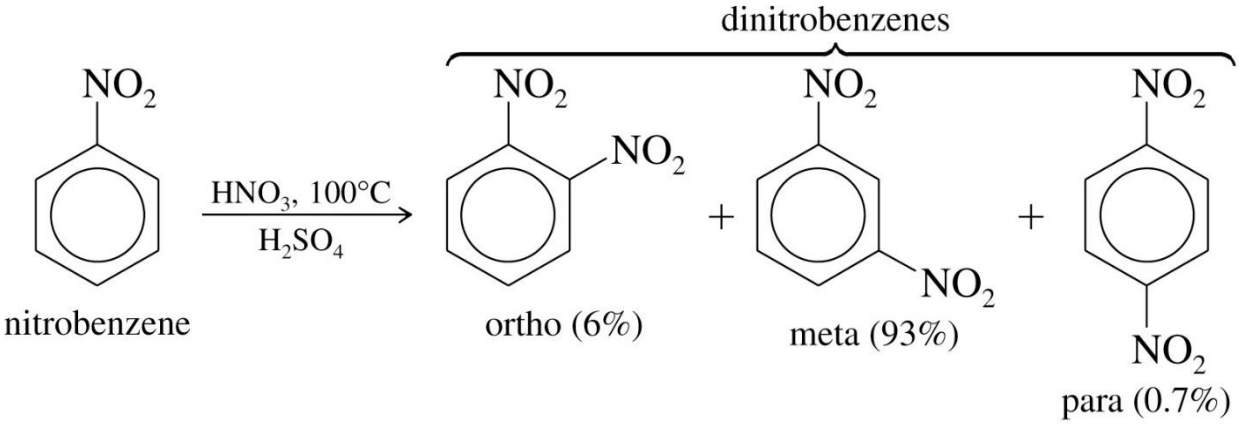


Table 1 Directing effect of substituents

	Predominant directing
O,P	**m**
$-NH_2$, $-NHR$, $-NR_2$	**$-NO_2$**
$-NH_2$, $-NHAr$, $-N(Ar)_2$	**$-CN$**
$-OH$, $-OR$, $-OAr$	**$-CO_2H$, $-CHO$, $-COR$, $-CO_2Ar$**
$-NHCOR$, $-NHCOAr$	**$-SO_3H$**
Alkyl groups	**$-{}^{+}NH_3$, $-{}^{+}NH_2R$, $-{}^{+}NHR_2$, $-{}^{+}NR_3$**
Halogens	**$-{}^{+}NH3$, $-{}^{+}NH_2Ar$, $-{}^{+}NH(Ar)_2$, $-{}^{+}N(Ar)_3$**
R=alkyl groups	**Ar= aryl group**

Lec. 2

Table 2 Directive influence and effect on reactivity of substituents

1. **Activating and ortho and para directing**
   a. **Strongly activating**
      -NH_2, -NHR, -NR_2, -NHAr, -$N(Ar)_2$
      -OH, -OR, -OAr

   b. **Modcrately activating**

      -NHCOR, -NHCOAr

   C. **Weakly activating**

      Alkyl groups

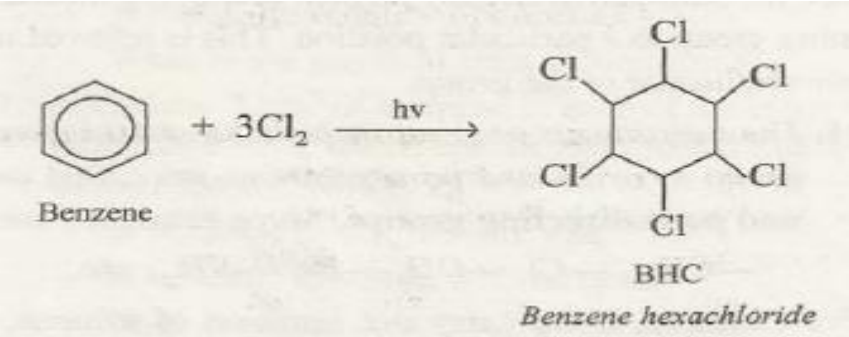
2. **Strongly deactivating and meta (m) directing**
   -NO_2
   -CN
   -CO2H, -CHO, -COR, -COAr, CO_2R, -CO_2Ar
   -SO_3H
   -$^+NH_3$, -$^+NH_2R$, -$^+NHR_2$, -$^+NR_3$, -$^+NH3$, -$^+NH_2Ar$, -$^+NH(Ar)_2$, -$^+N(Ar)_3$

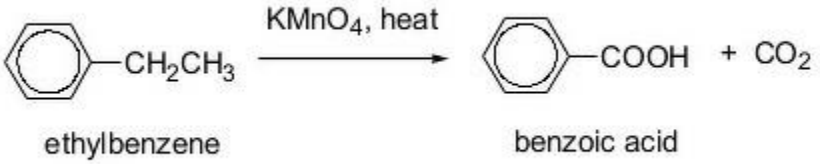
3. **Deactivating and ortho and para directing**

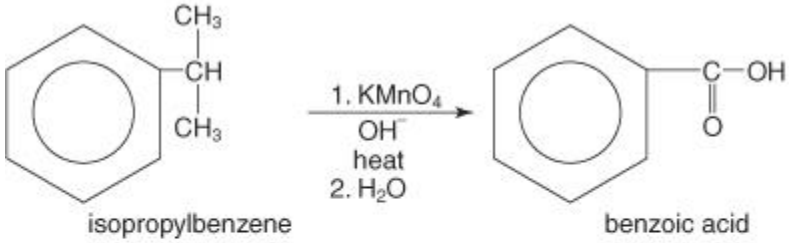
   Halogens

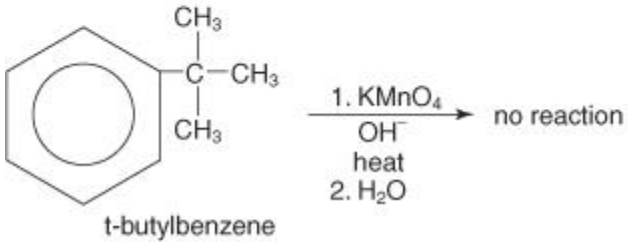
Other reaction of aromatic compounds

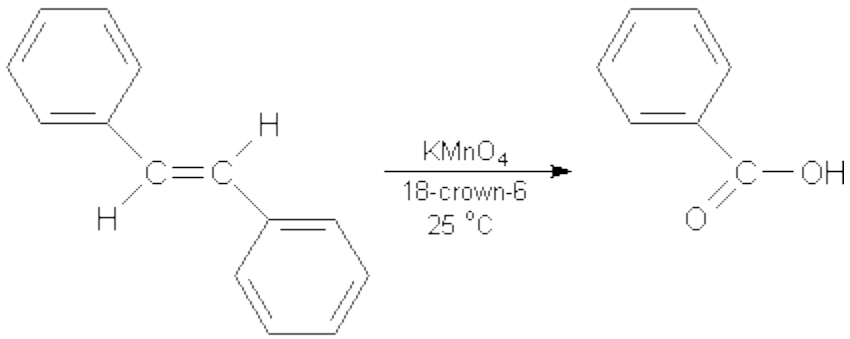
Lec. 2


Cl
Cl
Cl
Cl
Cl
Cl
+ 3Cl2
hv
Benzene
BHC
Benzene hexachloride

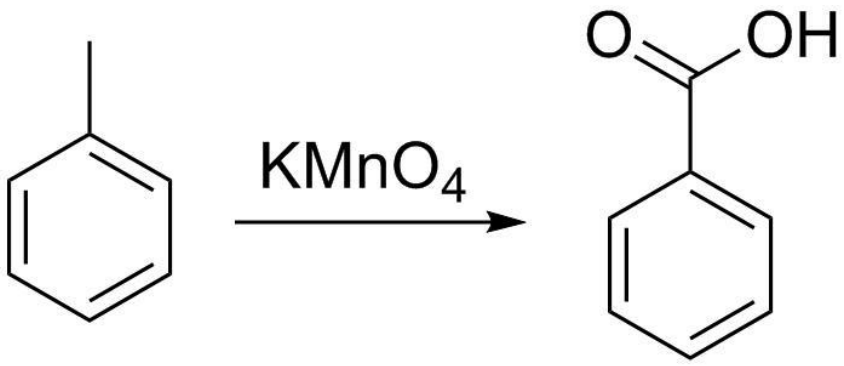

KMnO4, heat
CH2CH3
COOH
+ CO2
ethylbenzene
benzoic acid

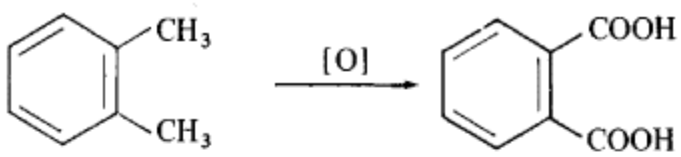

CH3
CH
CH3
1. KMnO4
OH⁻
heat
2. H2O
C
OH
O
isopropylbenzene
benzoic acid


CH3
C
CH3
CH3
1. KMnO4
OH⁻
heat
2. H2O
no reaction
t-butylbenzene

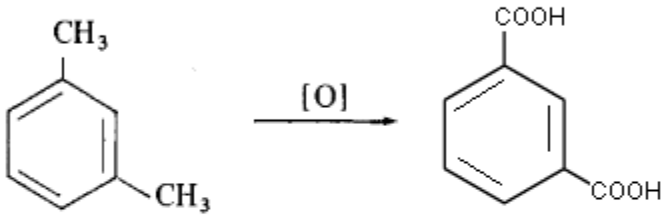

H
C
C
H
KMnO4
18-crown-6
25 °C
C
OH
O

Lec. 2

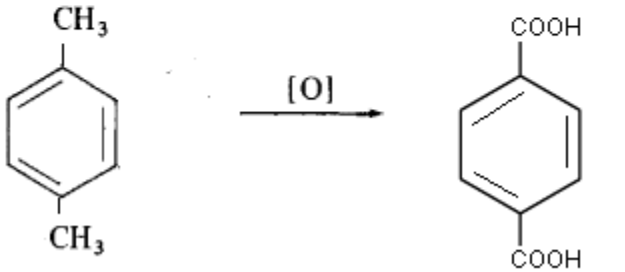




phthalic acid

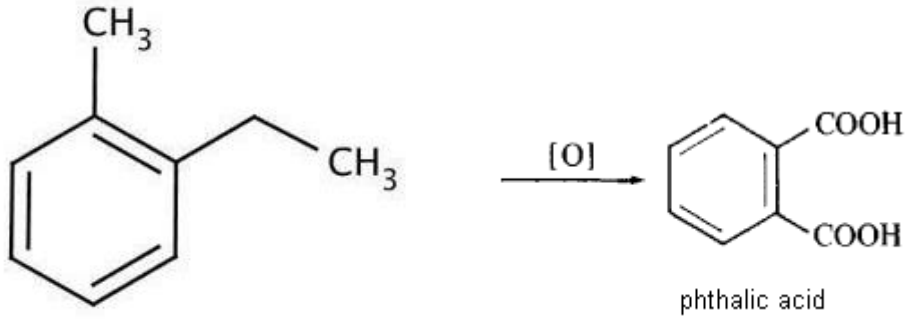


isophthalic acid



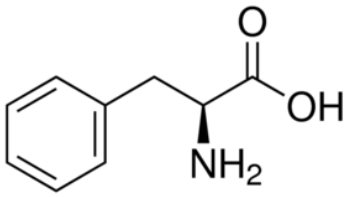
terephthalic acid

Lec. 2

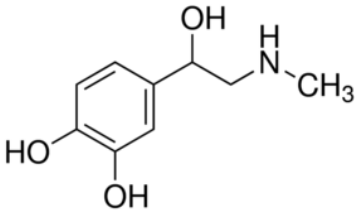


phthalic acid

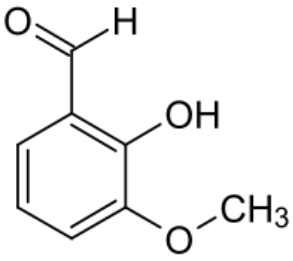
Aromatic compounds in Nature



Phenylalanine



Epinephrine

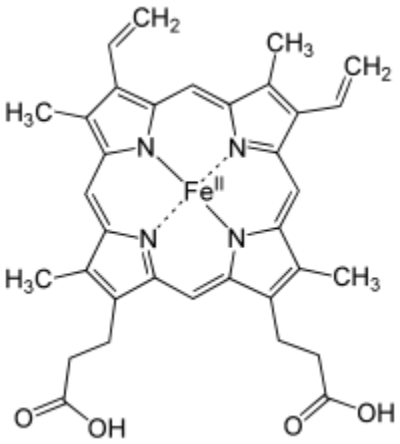


Vanillin

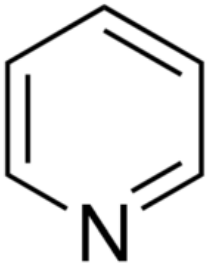
Aromatic heterocyclic compounds

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

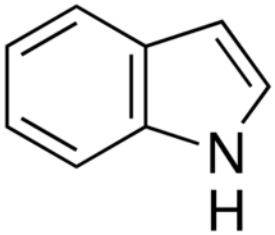
Lec. 2



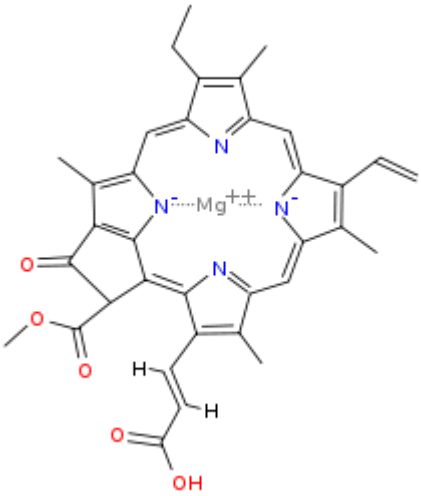
Heme



Pyridine



Indole



Chlorophyll