

Aromatic Compounds

Benzene and compounds resembling benzene in chemical behavior.

Structure of Benzene

- C_6H_6
- 1858 Friedrich August Kekule' proposed that carbon atoms joint to form chains
- 1865 Carbon chains sometimes close to form rings
- Benzene yields only one monosubstitution product C_6H_5Y
- Benzene yields three disubstitution products

Stability of Benzene

- Undergoes substitution rather than addition
- Heats of hydrogenation and combustion are lower than expected
- All C-C bonds are equal and are intermediate in length between single and double bonds









A Resonance Hybrid







Aromatic Character

 Hückel 4n+2 rule: Aromatic compounds must contain cyclic clouds of delocalized π electrons above & below the plane of the molecules and the π clouds must contain a total of (4n+2) π electrons

Nomenclature





Nitrobenzene



Toluene

Nomenclature



Aniline



Phenol



Benzoic Acid















Nomenclature

1,2,4-tribromobenzene

3-bromo-5-chloronitrobenzene



CYCLOHEXENE vs. BENZENE

Reagent	Cyclohexene gives	Benzene gives
KMnO ₄ (cold, dilute, aqueous)	Rapid oxidation	No reaction
Br_2/CCl_4 (in the dark)	Rapid addition	No reaction
HI	Rapid addition	No reaction
$H_2 + Ni$	Rapid hydrogenation @ 25°C, 20 lb/in ²	Slow hydrogenation @ 100-200°C, 1500 lb/in ²

REACTIONS OF BENZENE

1. Nitration. Discussed in Sec. 15.8.

 $C_6H_6 + HONO_2 \xrightarrow{H_2SO_4} C_6H_5 - NO_2 + H_2O$ Nitrobenzene

2. Sulfonation. Discussed in Sec. 15.9.

 $C_6H_6 + HOSO_3H \xrightarrow{SO_3} C_6H_5 \xrightarrow{SO_3}H + H_2O$ Benzenesulfonic acid

3. Halogenation. Discussed in Sec. 15.11.

 $C_6H_6 + Cl_2 \xrightarrow{Fe} C_6H_5 \xrightarrow{-Cl} + HCl$ Chlorobenzene

$$C_6H_6 + Br_2 \xrightarrow{Fe} C_6H_5 - Br + HBr$$

Bromobenzene

4. Friedel-Crafts alkylation. Discussed in Secs. 15.10 and 16.7.

 $C_6H_6 + RCl \xrightarrow{AlCl_3} C_6H_5 - R + HCl$ An alkylbenzene

5. Friedel-Crafts acylation. Discussed in Sec. 18.5.

 $\begin{array}{ccc} C_6H_6 + RCOCl & \xrightarrow{AlCl_3} & C_6H_5 \hline COR + HCl \\ An acyl chloride & A ketone \end{array}$





AB: HONO₂ or HOSO₃H or Cl₂ or RCl or RCOCl

Polynuclear Aromatic Hydrocarbons

Naphthalene



Naphthalene







2-Naphthol or β-Naphthol



2,4-Dinitro-1-naphthylamine

Other Fused-ring Hydrocarbons



Anthracene



Phenanthrene

