BENZENE

AROMATICITY

Structure of BENZENE:

Bond line structure

Molecular orbital diagram:

2D  3D
Since there are three $\sigma$-bonds present in Benzene in alternate position due to which the process of conjugation takes place and delocalisation of $\pi$-electrons occurs.

Since $\pi$-electrons delocalised, resonance hybrid is from

Resonance hybridised is more stable form as compare to another canonical structure (resonating structure) hence the energy difference between canonical structure and resonance hybrid is known as Resonance Structure

Bond order

Since in Benzene Resonating Structure are forming, the $C-C$ bond order not perfectly single or not perfectly double hence the bond order in $C-C$ in Benzene will be
\[ B.O. = \frac{\text{No. of bond due bonded atoms}}{\text{Resonating structure}} \]

\[ B.O. = \frac{3}{6} = \frac{1}{2} = 1.5^- \]

**Bond length**

Since the bond order C-C in Benzene like blur single bond and double bond, therefor bond length also like blur single bond and double bond.

Hence the bond length blur C-C in Benzene is 1.04 Å < 1.4 Å.

**Benzene derivatives**

When one or more one H-atom of Benzene is replaced by another atom or group of atom, Benzene derivative are formed.

\[ \text{H} \quad \text{G-group} \quad \text{Benzene derivative} \]
The most important benzene derivatives are:

1) Methyl benzene

2) Toluene

3) Phenol

4) Benzoic acid

Methods of preparation of Benzene:

1) From ethene:

\[ \text{HC} + \text{HC} \xrightarrow{\text{Reductant}} \text{CH} \xrightarrow{\text{Fe tube}} \text{HC} \xrightarrow{\text{III}} \text{CH} \xrightarrow{\text{II}} \]

2) Method A

From sodium benzoate:

When sodium benzoate treated with soda lime, the formation of benzene will take place and \( \text{Na}_2\text{CO}_3 \) also form due to some CO\(_2\) gas. This can also known as diazotization seen:

\[ \text{C} \xrightarrow{\text{NaOH}} \text{C} + \text{Na}_2\text{CO}_3 \]
Method III

\[ \text{From Benzene Sulphonic Acid} \]

\[
\text{From Benzene Diazonium chloride} \]

\[ \text{Benzene Hydriphosphonic acid chloride} \]

\[ \text{From Normal hexene} \]

\[ \text{From phenol} \]
Physical properties of Benzene:

1. It is a colourless mobile liquid having pleasant odour.
2. It is insoluble in water, highly soluble in another organic solvent.
3. It self is a good solvent.
4. Fat, kerosene, oil etc. Can dissolvent.

Chemical properties of Benzene:

Electrophilic Substitution Reaction:

When one electrophile replace another electrophyl. Rxn is known as electrophilic substitution Rxn.

There are following types of electrophilic substitution Rxn:

1. Halogenation
2. Nitration
3. Sulphonation
4. Friedel-Craft Alkyl Rxn
5. Friedel-Craft Acylation Rxn

1. Halogenation:

\[
\text{C}_6\text{H}_6 + \text{X}_2 \xrightarrow{\text{AlCl}_3/FeCl_3} \text{C}_6\text{H}_5\text{X}
\]

\(X = \text{Cl, Br}\)
Nitrilation

\[ \text{Conc \text{HNO}_3} \]

\[ \text{Conc \text{H}_2\text{SO}_4} \]

\[ \text{STEP-1} \]

\[ \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{H} + \text{H}_2\text{SO}_4^- \rightarrow \text{H}_2\text{O} + \text{NO}_2^- + \text{H}_2\text{SO}_4^- \]

\[ \text{STEP-2} \]

\[ \text{STEP-3} \]

\[ \text{STEP-4} \]

\[ \text{H}_2\text{O} + \text{NO}_2^- + \text{HSO}_4^- \rightarrow \text{H}_2\text{O} + \text{NO}_2^- + \text{H}_2\text{SO}_4^- \]

\[ \text{H}_2\text{O} + \text{HSO}_4^- \rightarrow \text{H}_2\text{O} + \text{H}_2\text{SO}_4^- \]
**Sulphonation of Benzene**

1. **STEP-1**
   
   \[ \text{C}_6\text{H}_5 \overset{\text{SO}_3}{\longrightarrow} \text{C}_6\text{H}_5\text{SO}_3\text{H} + \text{HSO}_4^- \]

2. **STEP-2**
   
   \[
   \begin{align*}
   \text{C}_6\text{H}_5 \quad &\quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \\
   \end{align*}
   \]

3. **STEP-3**
   
   \[
   \begin{align*}
   \text{C}_6\text{H}_5 \quad &\quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \\
   \end{align*}
   \]

4. **STEP-4**
   
   \[
   \begin{align*}
   \text{C}_6\text{H}_5 \quad &\quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \\
   \end{align*}
   \]

5. 

   \[
   \begin{align*}
   \text{C}_6\text{H}_5 \quad &\quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \quad \overset{\text{SO}_3\text{H}}{\longrightarrow} \\
   \end{align*}
   \]

Benzene Sulphonation
Friedel-Craft Alkylation Reaction

When benzene reacts with alkyl chloride in the presence of anhydrous AlCl₃, the formation of alkyl benzene takes place.

The reaction goes through the following mechanism:

\[
\text{C}_{6}\text{H}_6 + R-\text{Cl} \xrightarrow{\text{Anhydrous AlCl}_3} \text{C}_{6}\text{H}_5\text{R} + \text{AlCl}_4^-
\]

**STEP 1:**

\[
R-\text{Cl} + \text{AlCl}_3 \rightarrow R^+ + \text{AlCl}_4^-
\]

(Electrophile) Carbocation

**STEP 2:**

Carbocation rearrangement.

**STEP 3:**

Resonance of

**STEP 4:**

Stable Carbocation Attack.
STEP 1

\[ \text{C}_6H_5 + \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl} \xrightarrow{\text{Anh AlCl}_3} \]

STEP 2

\[ \text{C}_6H_5 + \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Cl} + \text{AlCl}_3 \rightarrow \text{C}_6H_5 + \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3 + \text{AlCl}_4^- \]

STEP 3

\[ \text{C}_6H_5 + \text{CH}_3\text{CH} = \text{CH}_2 \rightarrow \text{C}_6H_5 + \text{CH}_3-\text{CH} = \text{CH}_3 \]

STEP 4

\[ \text{C}_6H_5 + \text{CH}_3+\text{CH} = \text{CH}_3 + \text{AlCl}_4^- \rightarrow \text{C}_6H_5 + \text{CH}_3+\text{CH} = \text{CH}_3 + \text{HCl} + \text{AlCl}_3 \]

**Question**

\[ \text{C}_6H_5 \xrightarrow{\text{Anh AlCl}_3} \text{C}_6H_5 \]

**STEP 1**

\[ \text{CH}_3-\text{CH} = \text{CH} + \text{CH}_3 + \text{AlCl}_3 \rightarrow \text{CH}_3-\text{CH} = \text{CH} + \text{AlCl}_3 \]

**STEP 2**

\[ \text{CH}_3-\text{CH} = \text{CH} - \text{Cl} \rightarrow \text{CH}_3-\text{CH} = \text{CH} - \text{Cl} \]
Friedel–Craft Acylation Reaction

\[
\text{C}_{6}H_{5} + R - C - Cl \underset{\text{AlCl}_{3}}{\overset{\text{Acid Chloride}}{\rightleftharpoons}} R - C_{6}H_{5} - C - Cl
\]

**STEP 1**

\[
R - C - Cl + \text{AlCl}_{3} \rightarrow R - \text{C}_{6}H_{5} + \text{AlCl}_{4}^{-}
\]

**STEP 2**

\[
\text{C}_{6}H_{5} + R - C - Cl \rightarrow \text{C}_{6}H_{5} + \text{AlCl}_{3}
\]

**STEP 3**

\[
\text{C}_{6}H_{5} + R - C - Cl \rightarrow \text{C}_{6}H_{5} + \text{AlCl}_{3}
\]
Additions Reaction

1) Hydrozination of

\[ R - \text{H} + \text{H}_2\text{O} \rightarrow R\text{-OH} \]

2) Helozination in the presence of Sun light

\[ \text{C}_6\text{H}_6 + 3\text{Cl}_2 \rightarrow \text{Product} \]

\[ \text{C}_6\text{H}_6\text{Cl}_6 \]

Gammarane

It is a powerfull insecticide.

It is not eco-friendly.

Ozonolysis of

\[ \text{C}_6\text{H}_6 + \text{O}_3 \rightarrow \text{Product} \]

\[ \text{C}_6\text{H}_6 \rightarrow 3\text{CHO} \]
Orientiation of Artho, Para, and Meta Position

If one H-atom of \( \text{C}_6 \) is replaced by functional group, the formed compound is known as Benzene derivative. The general representation of Benzene derivative:

The left, right location of functional group in Benzene Derivative known as meta position:

The opposite position of \( f-G \) in Benzene Derivative is known as para position:

The remaining location dicord in Artho, and Para in Benzene Derivative known as meta position.

When an electrophile attack in Benzene Derivative, the position of electrophile in the Benzene ring decided by functional group - present in Benzene Derivative.
When the position of $E^1$ ortho and para given by Benzene Directives, the Benzene Derivative is known as Ortho-Para Director.

If electrophile square meta reaction,

The Benzene Derivative is known as meta Director.

The ortho and para Director decided by the help of meta metric effect.
Answer: Identify the ortho, para, meta direction.

(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi)
Birch Reduction

When Ditiz perenynhe reacts with Na/CO3/H2O in the presence of liquid ammonia, the formation of cyclic amines takes place.

\[
\text{Cyclic Amine} \xrightarrow{\text{Birch Reduction}} \text{Cyclic Amine}
\]