



# Aromatic Hydrocarbons

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### Aromatic hydrocarbons



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## **Aromatic Hydrocarbons**

#### Arenes

- Aromatic hydrocarbons are also known as arenes
- Benzene is parent aromatic compound
- There are large number of arenes in which alkyl, alkenyl or alkynyl groups are present on benzene ring



### Benzene

#### **Representation of benzene**

- Regular hexagon containing a circle
- > The circle denotes cloud of pi electrons



#### Nomenclature of benzene derivatives

- Benzene nucleus
- Side chain





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### Benzene

#### **Isomerism in benzene derivatives**

- Only one Monosubstituted benzene derivative
- Three isomers of disubstituted benzene derivative



RE of 151 KJ/mol  $\geq$ 

**Evidence** 

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 $\geq$ 

 $\checkmark$ 

### **Structure of Benzene**

### Orbital structure of Benzene

- Each carbon is sp<sub>2</sub> hybridized
- sp<sub>2</sub> hybrid orbitals form sigma bonds
- Unhybridized 2pz orbitals form pi bonds
- Continuous overlap above and below the ring resulting in two continuous rings of pi electrons

### Evidence

- Flat ring structure
- > Stability
- Resist addition reactions
- Undergo electrophilic substitution reactions
- Number of mono and disubstituted products



## **Aromatic Hydrocarbons**

### **Aromaticity**

- The aromatic compounds are highly unsaturated but they resist addition reactions and undergo electrophilic substitution reactions
- > This special characteristic is known as aromatic character or aromaticity.
- > The aromatic compounds are flat and have unusual stability.

### Huckel's Rule

> The compounds which are planer, cyclic and have delocalized pi electron cloud above and below the plane of ring and contain (4n+2)  $\pi$  electrons are aromatic in character.

### **Methods for Preparation of Benzene**

### From Phenol

By distillation with Zinc dust



#### **From Benzoic acid**

> By decarboxylation of sodium benzoate by heating it with soda lime (CaO + NaOH)

$$O - COONa + NaOH - CaO + Na_2CO_3$$
  
Sod benzoate Benzene

### **Methods for Preparation of Benzene**

#### **From Acetylene**

> By trimerization of acetylene by passing it through red hot tube

$$H = \begin{array}{c} CH \\ H \\ H \\ H \\ H \end{array} \qquad Oh \\ 3C_2H_2 \\ Acetylene \\ H \\ Benzene \\ \end{array}$$

**From Benzene sulphonic acid** 

$$\langle O \rangle$$
-SO<sub>3</sub>H + H<sub>2</sub>O  $\xrightarrow{HCl}_{423-473K}$   $\langle O \rangle$  + H<sub>2</sub>SO<sub>4</sub>



- **Electrophilic substitution reactions contd.**
- Nitration
- Replacement of H with Nitro group

$$H_0 - N_{0_1} \xrightarrow{H_0 - N_{0_1}} + H_1 O_3 \text{ (conc.)} \xrightarrow{H_2 S O_4} O + H_2 O$$
Nitrobenzene

#### Sulphonation

Replacement of H with sulphonic acid group

- **Electrophilic substitution reactions contd.**
- Freidel-Craft's reactions
- **1. Alkylation**
- Replacement of H with alkyl group



#### **2. Acylation**

Replacement of H with acyl group



**General pattern of mechanism of electrophilic substitution reactions** 

#### Three Steps

**1. Generation of electrophile** 



- 2. Attack of electrophile on benzene ring to form carbocation
- Carbocation is also known as Arenium ion, or sigma  $\sigma$  complex or Wheland intermediate which is non aromatic. It has only 4π electrons delocalised over five sp<sub>2</sub> hybrid carbons



3. Abstraction of proton by base to restore aromatic character



### Evidence for mechanism

- Isotopic tracer technique
- With the help of this technique, we can show that the second step ie Attack of electrophile on benzene ring to form carbocation, is slow and rate determining step.
- > If we take deuterated benzene then it is seen that the rate of the reaction is not affected at all

$$C_{6}H_{6} \xrightarrow{\text{Electrophilic}} C_{6}H_{5}E \\ \text{substitution} \xrightarrow{\text{C}_{6}H_{5}E} \\ C_{6}D_{6} \xrightarrow{\text{Electrophilic}} C_{6}D_{5}E \\ \text{substitution} \xrightarrow{\text{C}_{6}D_{5}E} \\ \end{array} \\ Both proceed at the same rate$$

- If third step is slow and rate determining then the rate of the substitution reaction should have decreased because there is cleavage of C-H bond.
- Since no isotope effect is observed so we can safely say that the mechanism is three step and second step is slow and rate determining. Concerted mechanism can not be there.

### The 2<sup>nd</sup> TS involves the loss of proton and it T.S.1 T.S.2

needs little Activation energy Ea<sub>2</sub>.

When TS<sup>2</sup> changes to product, large amount of energy is released because aromatic character is restored

and it requires higher Activation energy Ea<sub>1</sub>

### Two transition states are involved Ist TS<sup>1</sup> leads to the formation of arenium ion $H \bigvee E^{\delta^+} E = E^{\delta^+}$

**Energy Profile diagrams for Aromatic Electrophilic substitution** 

**T.S.1**  $E_{a_1} \smile$ Energy Progress of reaction

### Formation of $\sigma \& \pi$ - complexes during Aromatic Electrophilic substitution

- > When electrophile approaches benzene ring, there is formation of  $\pi$  complex in which electrophile is held close to ring by pi electron cloud
- $\blacktriangleright$  Pi complex then changes to  $\sigma$ -complex



### Formation of $\sigma \& \pi$ - complexes during Aromatic Electrophilic substitution

- $\succ$  Formation of both  $\pi$ -complex and  $\sigma$ -complex may be rate determining
- > Then there will be different energy profile diagrams as shown



formation of  $\sigma$ -complex as rate determining step

Progress of reaction formation of  $\pi$  -complex as rate determining step

Halogenation (Chlorination)

$$\bigcirc + Cl_2 \xrightarrow{FeCl_3 \text{ or } AlCl_3} \bigcirc + HCl$$
  
Chlorobenzene

1. Generation of electrophile(Chloronium ion)

$$CI - CI + FeCl_3 \longrightarrow CI \dots Cl_{rec} FeCl_3$$

2. Attack of electrophile(Chloronium ion) on benzene ring



3. Abstraction of proton by base



Sulphonation  $H_2SO_4 (conc.) \longrightarrow O^{SO_3H} + H_2O$ 

1. Generation of electrophile(Sulphur trioxide)



- **Galarian Sulphonation contd.**
- 2. Attack of electrophile



3. Abstraction of proton by base



4. Proton transfer from hydronium ion to benzene sulphonate ion



#### **Friedel Craft's Alkylation**



1. Generation of electrophile (Alkyl cation)

$$R-Cl + AlCl_{3} \longrightarrow R^{+} + AlCl_{4}^{-}$$
  
Alkyl cation

2. Attack of electrophile on benzene ring



3. Abstraction of proton by base



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### Role of catalyst in electrophilic substitution reactions

- We have seen that the catalysts like FeCl<sub>3</sub>, AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> etc are used during electrophilic substitution reactions
- > Powerful electrophile is needed to attack benzene ring because on attack it will loose aromatic character
- Catalyst causes polarization of the attacking molecule to generate positive charge on one of the atoms which makes attack on benzene ring easy

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### **Effect of substituents on further substitution in benzene**

- Directive influence or orientation
- > It is the ability of the group already present to direct the incoming group to a particular position in benzene
- **Electron releasing groups direct the incoming group to ortho and para positions**
- Called as o- and p- directing groups
- -R, C<sub>6</sub>H<sub>5</sub>, -OH, -SH, -OR, -NH<sub>2</sub>, -NHR, -NR<sub>2</sub>, -Cl, -Br, -I etc are electron releasing groups so they are o- & pdirectors



- Electron withdrawing groups direct the incoming groups to meta position
- Called as meta directing groups
- Groups containing multiple bonds such as -NO<sub>2</sub>, -SO<sub>3</sub>H, -CN, -CHO, -COR, -COOH & -COOR etc. are electron withdrawing in nature and are meta directing



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### **Effect of substituents on further substitution in benzene**

- **Directive influence or orientation contd....**
- > For example. –OH group releases electrons in to the ring by resonance effect
- > Electron density on O- & P- positions increases (-ve charge on O- & P- positions)



> So electrophile preferably attacks O- & P- positions



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### **Effect of substituents on further substitution in benzene**

- **Directive influence or orientation contd.....**
- > Electron withdrawing group such as –CHO withdraws electrons from benzene ring
- Partial positive charge is developed on O- & P- positions and meta positions have more electron densities in comparison.



- So electrophile can not attack on O- & P- positions
- Hence it attacks meta position preferably.

### **Effect of substituents on reactivity in benzene**

#### Activating groups

- Electron releasing groups increase reactivity of benzene towards further substitution and are called as activating groups
- > These groups increase electron density in benzene ring
- -R, C<sub>6</sub>H<sub>5</sub>, -OH, -SH, -OR, -NH<sub>2</sub>, -NHR, -NR<sub>2</sub>, -Cl, -Br, -I etc are electron releasing groups & hence activating
- > Activating groups are O- & P- directing in nature

#### Deactivating groups

- Electron withdrawing groups decrease reactivity of benzene ring towards further substitution and are known as deactivating groups.
- > These groups decrease electron density in benzene ring
- Groups containing multiple bonds such as -NO<sub>2</sub>, -SO<sub>3</sub>H, -CN, -CHO, -COR, -COOH & -COOR etc. are electron withdrawing in nature & hence deactivating.
- > Deactivating groups are m- directing in nature.

### Side chain oxidation of alkyl benzenes

**Oxidising agents such as alk. KMnO**<sub>4</sub> or Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidise side chain to carboxylic acid group



### Side chain oxidation of alkyl benzenes

### **Etard's Reaction**

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Solution of toluene in CCl<sub>4</sub> is treated with mild oxidising agent Chromyl chloride



### Questions

- Give mechanism of nitration of benzene
- > What is the role of catalyst in electrophilic substitution reactions in benzene?
- > How will you prepare the following compounds from benzene
  - 1. Toluene 2. Bromobenzene 3. Acetophenone
- Discuss general mechanism for electrophilic substitution reactions in benzene. Give evidence for the proposed mechanism.
- What happens when
- 1. O-Xylene is treated with alkaline KMnO<sub>4</sub>
- 2. N-Propyl benzene is oxidised with Acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution
- 3. Sodium benzoate is heated with soda lime
- 4. Phenol is distilled in the presence of Zinc dust
- > Draw the energy profile diagram for electrophilic aromatic substitution reactions.
- > How will you convert benzene to benzene sulphonic acid? Explain by giving mechanism