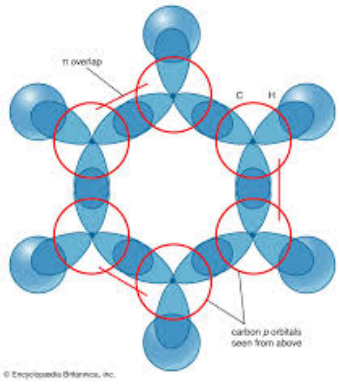
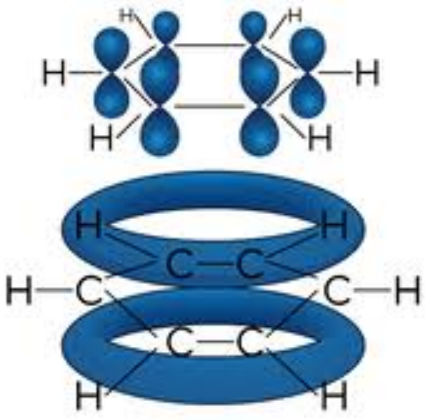
STUDY PACK 15.4

UNIVERSITY OF CAMBRIDGE



AROMATIC COMPOUNDS



ORGANIC CHEMISTRY

Since 2005
Chembase
School of Chemistry

First Edition Jan 2006
Second Edition Jun 2009
Third Edition Jun 2011
Fourth Edition Jun 2021 (Revised New Syllabus)

All Rights Reserved.
Unauthorized duplication contravenes applicable laws.

No part of this publication may be reproduced or utilized in any form or by electronic, mechanical or other means, now known or hereafter invented including photocopying & recording, without the prior permission in writing from the copyright owner.

PUBLISHED BY :

Since 2005 Chembase School of Chemistry

PRODUCER OF WORLD PRIZE & ISLAND TOP AWARD WINNERS SINCE 2005

Pearson Edexcel

UNIVERSITY OF CAMBRIDGE

COPYRIGHT OWNER :

Prof. IMRAN RAZEEK I.Chem.C(P1), M.Ed, Ph.D (Reading)

Honorary Professor | Founder, Chairman & Head of Department of Chembase School of Chemistry | Chief Chemistry Educator

CHEMBASE SCHOOL OF CHEMISTRY

34, 1/2, Galle Road, Dehiwela. SRI LANKA.

+94 754 456 456 | +94 776 534 233

info@chembase.lk

22 YEARS LEGACY OF EXCELLENCE Chembase School of Chemistry 2005-2026

ASIA PACIFIC EXCELLENCE AWARD 2025

JOIN LIVE CLASSES @ WWW.CHEMBASE.LK

ONLINE COURSES @ WWW.CHEMBASEACADEMY.COM

CHEMBASE.LK

CHEMBASE SCHOOL OF CHEMISTRY

CHEMBASE.LK

CHEMBASE SCHOOL OF CHEMISTRY

ACCREDITED & APPROVED BY :

UKIQ | UK International Qualifications

R·S·D·C·A Regional Skill Development & Certification Authority

AN ACCREDITED TEACHING INSTITUTE OF UK INTERNATIONAL QUALIFICATIONS.

Structure of benzene & Reactions of aromatic compounds.

1. Organic compounds can be divided into Three main categories, name & describe them.

   a. Aliphatic Compounds : compounds based on carbon chains (Compounds studied in previous units; Alkanes, Alkenes)

   b. Alicyclic Compounds : compounds where 'C' is bonded in a ring structure. Eg: Cyclic hydrocarbons (Cyclo hexane, Cyclopentane ect..)

   c. Aromatic Compounds : compounds based on ring structures with delocalized Electrons. (eg: Benzene)

2. Describe the structure of benzene which was proposed by August Kekule.

The molecular formula of benzene is C_6H_6, which can be experimentally shown by percentage composition by mass. Kekule proposed the structure which 'C' atoms in benzene forms a regular hexagon each 'C' is bonded with a 'sigma' bond to the other & alternatively with a 'pi' bond.

Which can be represented in the skeletal form as:

3. State why the Kekule's approach was unsuccessful

The Kekule structure does not explain the below behaviour of benzene.

i. The benzene molecule has a regular hexagonal shape & is planer. This is proven by x-ray diffraction. But the Kekule structure would not be a regular hexagon as the C-C & C=C bond lengths are not equal.

ii. The bond length of benzene is 0.139nm, which is roughly halfway of the C-C bond length in ethane (0.154nm) & that of C=C in ethene (0.134nm)

iii. Kekule structure is unsaturated. Therefore, benzene should undergo addition reactions as ethene, but this is not the case, instead it undergoes substitution. (benzene does not decolorize bromine)

iv. When a C=C is hydrogenated, it releases –120kJmol^{-1} energy. As benzene contains 3 C=C bonds as per the Kekule structure it should release -360kJmol^{-1} but in reality, benzene releases only -208 kJmol^{-1} energy.

4. How did Kekule overcome the above problems

Kekule suggested that the proposed structure of benzene exists as resonance structures

The double headed arrow is to represent the resonance structures which means the actual structure lies between the two representations. Therefore, each C-C bond is neither a single nor a double bond, but is an intermediate type. The 3 pi bonds are delocalized (shared) between the 'C' atoms; this concept overcomes the difficulties of the shape & the bond length of the benzene molecule.

5. Describe the molecular orbital explanation of the structure of benzene

Each of the six atoms in benzene is sp^2 hybridized. Each 'C' has 3 sp^2 orbitals in 120^0 angle. Each carbon uses two sp^2 orbitals to bond to two other 'C' atoms. Its 3rd sp^2 orbital overlaps with the s orbital of 'H' atom to form a sigma bond. The linear overlap between hybrid 'C' leads to a planer hexagonal structure where 'C' atoms are linked in sigma bonds. Also, each 'C' atom has an unhybrid 'p' orbital containing a single electron. The six 'p' orbitals are parallel to each other. Each of these 'p' orbitals overlaps laterally with the two 'p' orbitals on either side of it, as a result overlapping of 'p' orbitals forms a continuous ring-shaped cloud of pi electrons above & below the plane of the hexagonal benzene ring. Therefore, benzene cannot be named as 1,3,5 cyclohexatriene as the pi electron cloud is delocalized to form a cloud above & below the ring.

The benzene structure may be represented as below, but in mechanisms one may use the Kekule structure or the delocalized structure.

6. Prove comparing enthalpy changes of hydrogenation that benzene does not exist as 1,3,5 cyclohexatriene.

7. Explain, in terms of bonding in benzene, why the enthalpy change of hydrogenation of benzene is not –360 $kJmol^{-1}$ but –208 $kJmol^{-1}$

The pi electron cloud of benzene is delocalized between the six 'C' atoms. Therefore, there is no C=C double bonds in benzene. This is due to the overlap of the six 'p' orbitals. As a result, benzene is more stable due to delocalization & more energy is needed to break the pi cloud compared with having 3 separate pi bonds as cyclohexatriene.

8. State the physical properties of benzene.

Benzene is a non-polar liquid. The intermolecular forces in benzene are induced dipole-induced dipole attractions. (Dispersion / London forces) Hence it has a low boiling point.

Benzene is immiscible in water due to the absence of ionic nature. It is also less dense compared to water.

9. Explain why benzene undergo electrophilic substitution reactions

The high electron density in the delocalized electron cloud attracts electrophiles. But it requires more activation energy than the alkenes due to the stability of the delocalized system.

The benzene ring is thermodynamically very stable. Therefore, addition reactions are not favourable. But substitution reactions (by substituting the 'H') can occur so that the stability of the benzene ring is maintained.

Benzene will undergo addition reactions only under extremely forced conditions (eg: U.V radiation ect.)

Nomenclature of Benzene compounds.

- **Naming when only one substituent is attached.**

It does not matter to which '*C*' the substituent is attached; the substituent is named before benzene.

- **Naming when more than one substituent is attached.**

The '*C*' atoms in the ring are numbered starting from the side chain. (The substituent attached to the ring via a '*C*' atom is known as a side chain) The substituent is named according to the alphabetical order also by indicating the number of the carbon atom which is attached to.

- **Naming benzene as phenyl (-Ph)**

Phenyl is the name given to the radical formed by removing one 'H' atom from benzene ($-C_6H_5$) When benzene is attached to a main functional group it is named as phenyl.

- Meanings of alkyl, aryl, acyl & arene

Alkyl :Radical obtained by the removal of a 'H' atom from an alkane. Symbolized by –R (methyl, ethyl)

Aryl :Aromatic radical obtained by the removal of a 'H' atom. Symbolized by –Ar (Phenyl)

Acyl :The group obtained by removal of a –OH group from a carboxylic acid. RCO-, ArCO

Arene : Hydrocarbon with one or more benzene rings

Substitution Reactions of Benzene

1. Nitration of benzene:

Benzene in the Presence of conc. H_2SO_4 & HNO_3 introduce a $-NO_2$ substituent to benzene when heated under reflux at temperature between 25 ^0C - 60 ^0C

The equal volumes of conc. H_2SO_4 & conc. HNO_3 added is known as nitrating mixture. Nitro compounds are widely used to make explosive such as tri nitro toluene (TNT)

2. Bromination of Benzene:

Benzene in the presence of a Br_2 & iron under dry conditions substitutes a –Br atom to the benzene ring at room temperature. Bromine converts the iron to $FeBr_3$ catalyst which then reacts with the benzene ring. (Note: 'Fe' is not the catalyst, rather its FeBr3 which will be elaborated under the mechanism) Alternatively, AlCl3 or AlBr3 may also be used as the catalysts. These catalysts are known as "halogen carriers".

3. Benzene with chloroalkanes (Alkylation) –Friedel Crafts reaction

Benzene is mixed with chloro alkanes in the presence of anhydrous aluminum chloride (catalyst) under perfectly anhydrous conditions to produce alkyl benzene at room temperature. The introduction of an alkyl group to benzene is known as alkylation & the reaction is known as Friedel crafts reaction. Anhydrous conditions are required as $AlCl_3$ is sensitive to water.

4. Benzene with acid chlorides (Acylation) –Friedel Craft Reaction

Benzene is mixed with acid chloride (acyl halide) in the presence of anhydrous $AlCl_3$ under perfectly anhydrous conditions at 50 ^0C to produce phenyl alkanone. The introduction of an acid chloride group to benzene is known as acylation & the reaction is known as Friedel crafts reaction.

- **Oxidation by alkaline $KMnO_4$: (Side chain oxidation reactions)**

Any substituent attached to the benzene ring via a '*C*' atom is called a side chain. When benzene is heated under reflux with alkaline potassium per manganite (VII) solution and then acidified with sulfuric acid, it oxidizes all side chains to carboxylic groups resulting benzoic acid.

R= any substituent which is attached to benzene ring via '*C*'
Eg: (R = $-C_2H_5$ / $-CH_2CH{=}CH_2$ / $-CH_2CH_2OH$ / $-CH_2COCH_2$ / any '*C*' containing group)

Addition Reactions of Benzene

I. **Reaction with Hydrogen:**

When benzene is mixed with hydrogen in the presence of finely divided 'Ni' catalyst at a temperature of 150^0C will undergo addition reaction resulting a cyclohexane.

With Methyl benzene, the product would be methyl cyclohexane:

Phenol

- **Nomenclature:**

When the –OH group is directly attached to the benzene nucleus the compounds are named as phenol & others are named as derivatives of phenol

- **Chemical properties of phenol:**

Phenols are more acidic than alcohols. This is because the anion which is formed (phenate ion/ phenoxide ion) is more stable. The stability is due to the delocalization of the negative charge, which overlaps with the π benzene ring.

The pH of phenol is slightly below 5. Therefore, it cannot decompose Na_2CO_3 or $NaHCO_3$ to liberate CO_2. Solid phenol is soluble in strong alkalis & can be re precipitated by strong acids.

- **Physical properties of phenol:**

- Crystalline solid at room temperature which melts at 43^0C
- Has a strong antiseptic smell.
- In contact with water forms oil.
- It burns the skin & highly toxic. (eye protection & gloves must be worn when handling phenol)

- **Reactions of Phenol:-**

1. **Reaction with Sodium hydroxide / Anhydrous Na:**

Phenol reacts with NaOH & form the salt sodium phenate & water.

Phenol reacts in a similar manner with 'Na' under perfectly anhydrous conditions to form sodium phenate & hydrogen gas. Anhydrous conditions are required because 'Na' reacts with water.

2. **Reaction with Bromine:**

Phenol reacts with aqueous bromine to form the white precipitate of 2,4,6 tri bromo phenol. Similar reaction is observed with chlorine & iodine. This can be used as a qualitative test to show the presence of phenol group.

3. Reaction with ethanoyl chloride:

Esterification of phenol is not as easy as aliphatic alcohols. When phenol is shaken with NaOH in the presence of acid chloride in excess results the ester. NaOH is added in order to form sodium phenate which then reacts with the ethanoyl chloride.

4. Nitration of Phenol:

Phenol can be nitrated very easily due to its highly reactive nature. (The overlap of one of the lone pair of electrons on the oxygen with the benzene ring increases the electron density of the π ring. Phenol reacting with dilute nitric acid will result in a mixture of two products, 2-nitro phenol & 4-nitrophenol. Unlike benzene phenol does not need the nitrating mixture, in which H_2SO_4 acts as a catalyst & heat.

When conc. HNO_3 is added 2,4,6-tri nitro phenol (picric acid) is produced.

- Describe and explain the relative acidities of water, phenol and ethanol.

Phenol is acidic due to the stability of the phenate ion (phenoxide ion). Phenol is more acidic than water and ethanol due to the delocalization of the negative charge on the phenate ion over the π benzene ring which accounts for its stability. As a result, the H^+ ions are not strongly attracted to the phenate ion.

But such delocalization is not seen in water or in ethanol. Ethanol is a weaker acid than water due to the presence of the electron donating alkyl group attached to the oxygen in the ethoxide ion. Which increases the negative charge on the oxygen ion thus readily accepts the H^+ ion. Also, the heterolytic fission of the O-H bond is weaker due to the electron donating alkyl group.

Aromatic Amines

1. **Describe the structural characteristic of phenyl amine**

The lone pair on 'N' atom is in the same plane as the π electron cloud of benzene. This results 'N' atom being less –δ & so less effective as a base. Also, the benzene ring will increase its electron density thus become more susceptible to electrophilic attack.

2. **State the physical properties of phenyl amine**

- Liquid at room temperature & pressure, slightly denser than water.
- Slightly soluble in waters due to the formation of 'H' bonds. But the benzene ring inhibits solubility, dissolves readily in organic solvents.
- Toxic substance, can be absorbed through the skin.

3. **Preparation of aromatic amines:**

The interaction of the π electrons & the unshared pair on the halogen of halo benzene makes the halo benzene unreactive to nucleophiles such as OH^- & NH_3. Thus simple substitution of halo benzene by ammonia to form aromatic amines (phenyl amines) is not possible.

4. **Laboratory preparation of Phenyl amine:**

When nitro benzene is heated under reflux with tin & conc. HCl followed by NaOH produces phenyl amine. The 'Sn' & conc. HCl acts as a reducing agent to reduce nitrobenzene. NaOH prevents further reaction of phenyl amine with HCl.

Chemical Reactions.

5. **Reaction of phenyl amines with acids:**

Phenyl amine is a weak base, it reacts with strong acids to form phenyl ammonium salts.

6. **Reaction of amines with nitrous acid to form diazonium ions. (Diazotisation)**

Nitric (III) acid also known as Nitrous acid (HNO_2) is an unstable pale blue solution which is made by adding sodium nitrite & dilute HCl acid. When nitrous acid is added to phenyl amine at 0^0C- 5^0C diazonium ion will be produced.

The temperature must be maintained at 0^0C- 5^0C as the intermediate phenyl diazonium ion is kinetically stable at this low temperature. If the temperature is raised it reacts with water to form phenol.

The initial formation of the diazonium ion is called the diazotization.

Nitrous acid (HNO_2) with primary amines produces alcohols. This is a simple test for primary amines.

7. Coupling Reactions of Benzene diazonium ion

The diazonium ion acts as an electrophile & reacts with phenol to produce highly coloured compounds. The reaction of diazonium ion with phenol is called coupling.

- Reaction with phenol:

Phenol in NaOH results in phenate ion in which the diazonium ion attacks this by electrophilic substitution.

- Reaction with 2-naphthol:

The above reactions are used as tests for primary aromatic amines. The main use of the reaction is to produce synthetic dyes & acid-alkali indicators.

Mechanisms of Benzene

1. Describe the general mechanism for heterolytic electrophilic aromatic substitution of benzene

Benzene undergoes heterolytic electrophilic substitution due to the electron rich π system in benzene, it attracts electrophiles. Hence it undergoes substitution, NOT addition, as the delocalized π system is stable.

The electrophile has to be a powerful one as the π system of benzene is stable. Therefore, catalyst or UV light is necessary.

All electrophilic aromatic substitution reactions take place by two-step mechanism. In the 1st step benzene reacts with the electrophile (E^+), forming a carbocation intermediate. The structure of the carbocation can be represented by three resonance structures. In the second step a base in the reaction mixture pulls off a proton from the carbocation and the electron held by the proton, moves into the ring to form the benzene ring. Note that the proton is always removed from the 'C' that has the new electrophile. The loss of H^+ from the carbonium ion is energetically favourable than the addition of an anion unlike in alkene, because the aromatic π system is more energetically favoured due to its high stability.

2. Mechanism for Bromination:

3. Mechanism for nitration:

4. Mechanism for the reaction of benzene with chloroalkanes (Friedel-crafts Alkylation)

5. Mechanism for the reaction of benzene with acid chlorides (Friedel-crafts Acylation)

Reactions of Methyl Benzene

1. **Reaction with Halogens:**

In the presence of diffused sunlight (U.V light) methyl benzene reacts with Cl_2 or Br_2 vapour & substitutes the 'H' of the side chain. The reaction is similar to the reaction of aliphatic compounds with halogens. The reaction is initiated by the halogen free radicals.

Free radicals do not attack the benzene ring if a side chain is available.

If kept exposed to Cl_2 & U.V light trichloro methyl benzene will be produced stepwise.

But in the presence of the $AlCl_3$ / $FeCl_3$ catalyst ortho / para halogeno product will be produced.

2. **Nitration :**

Methyl benzene in the presence of the nitrating mixture introduce a nitro substituent at ortho /para positions when heated to 50 ^0C.

Positions of Electrophilic Substitution

1. Explain how does a group attached to the benzene ring influences the position of the electrophilic substitution

When the benzene ring undergoes substitution for the second time, the first substituted group influences the position of the second group on the benzene ring. The presence of the first group has 2 main effects.

a) The Rate : How fast/ slow the ring is attacked. Some group make the ring react faster, some slower.

b) Orientation effect : The position of the benzene ring where the second group is attached.

2. Describe the activating & deactivating effects on the benzene ring, thus give examples for activating & deactivating groups.

Activate group donates electrons to the benzene ring & makes it richer in electrons. Therefore, electrophiles will attack rapidly.

The delocalized groups decrease the electron density of the benzene ring by withdrawing delocalized electron cloud of benzene to itself. Therefore, the electrophiles feel less attractive towards the ring.

Activating Groups	**Deactivating Groups**

3. State the names given for the different positions of the benzene ring based on the first substituent group

4. State whether activating & deactivating groups are ortho, para or meta directors.

All the activating groups are groups that direct ortho & para positions. All the deactivating groups are meta directors, apart from halogens which are ortho, para directors.

Ortho, Para directors	Meta directors

5. Describe how the activating & deactivating groups donate & withdraw electrons respectively

When the substituent is attached to a highly electronegative atom then the electronegative atom attracts electrons to itself making the benzene ring deactive.

When the substituent is attached to an atom which contains lone pairs of electrons it will activate even though it is highly electro negative. The reason is that the lone pair can interact with the π cloud of electrons of benzene, making it richer in electrons.

6. Explain why compounds like phenol & methoxybenzene activate the benzene ring even though they have an electronegative atom directly attached to the ring?

The lone pair on the oxygen atom in phenol & methoxy benzene interact with the π cloud electron ring of benzene thus makes it richer in electrons. Hence activate the benzene ring as a result the incoming electrophile will attack ortho, para positions.

7. Explain why halogens are ortho-para directors even though it's a ring deactivating group

Halogens are electron withdrawing hence deactivate the benzene ring. As a result, the incoming electrophile will find halobenzene less attractive than benzene itself. The reaction of halobenzene with halogen will show a slow reaction rate.

Chembase - School of Chemistry I All Rights Reserved I www.chembase.lk