15. AROMATIC HYDROCARBONS

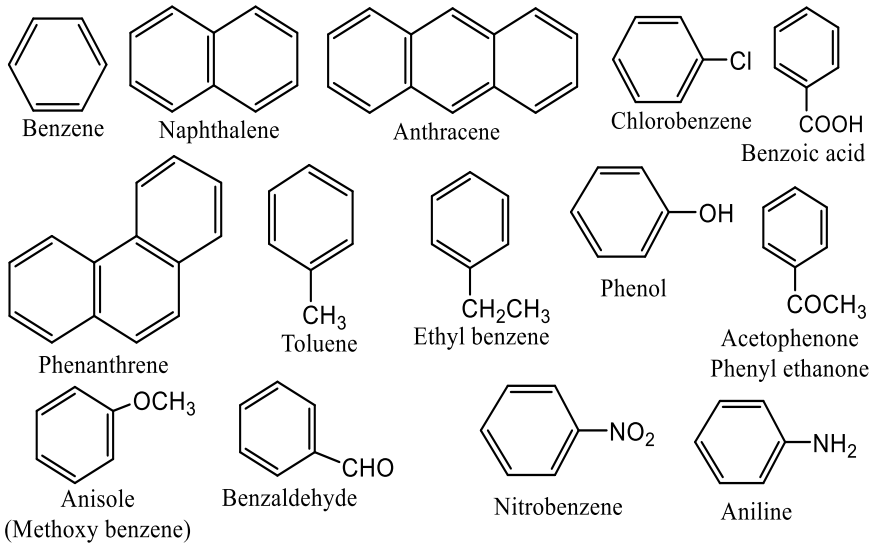
LEARNING OUTCOME

After the lesson, the students should be able to

- Introduction and characteristics of aromatic compounds
- Huckel's rule of aromaticity
- Kekule structure of benzene
- Resonance and isomerism
- Preparation of benzene from decarboxylation of Sodium
- benzoate, Phenol, and Ethyne only
- Physical properties of Benzene
- Chemical properties of benzene: Addition reaction: hydrogen,
- halogen, Electrophilic substitution reactions: orientation of benzene
- derivatives (o, m & p), nitration, sulphonation, halogenations,
- Friedel-Craft's reaction (alkylation and acylation), combustion of
- benzene (free combustion only) and uses

Aromaticity/ Huckel's rule

- Aromatic hydrocarbons are compounds containing one or more hexagonal benzene rings.
- The term aromatic comes from the Greek word 'aroma' meaning sweet fragrance.
- Hence, the term was originally used to designate the compounds having a sweet smell. In contrast to aliphatic compounds which were fatty or waxy (Greek: Aliphos = fat)
- Later, it was found that they contain one or more benzene rings. Aromatic compounds may be defined as compounds containing benzenoid rings or benzene. e.g.,



Characteristic of aromatic compounds

Later on, further study revealed that many other aromatic compounds do not resemble benzene. Now, the compounds having all the following characteristics are called aromatic compounds.

1. Aromatic compounds are cyclic (closed chain) or ring compounds with flat structures.
2. All the atoms in the ring are sp^2 hybridized, hence, making the ring planar.
3. They have a conjugated system i.e. have alternate single and double bonds in the ring.
4. They contain a delocalized system of (4n+2) π electrons. Where, n is an integer, n = 0, 1, 2, 3, 4…. This is known as **Huckel's rule.**

1. State Huckel's rule for aromaticity. 2
2. What are aromatic compounds according to Huckel's rule? 2
3. Why benzene is called an aromatic compound according to Huckel's rule? 1
4. What are aliphatic compounds? Give some examples. 2

5. Benzene is an aromatic organic compound. Discuss the rule that this molecule follows to be an aromatic compound. 1

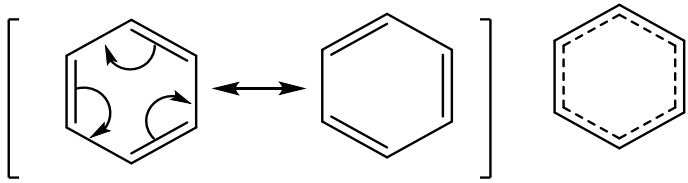
1. Organic cyclic compounds having the properties of aliphatic compounds are
   a. Aromatic c. Cyclic b. Alicyclic d. Homocyclic
2. When the –OH group is linked in benzene, the compound formed is:
   a. Phenol c. Benzaldehyde
   b. Benzyl alcohol d. Acetophenone
3. The C-C hybridization in benzene is of the type
   a. sp^3 c. sp^2
   b. sp and sp^2 d. sp
4. The structure of benzene is
   a. Planar c. Chair form
   b. Trigonal bipyramidal d. Tetrahedral
5. Aromaticity is given by
   a. Kekule's rule c. Huckel's rule
   b. 4n+2 π electrons rule d. Both b and c
6. The statement of Huckel's rule is:
   a. The aromatic compound should be cyclic.
   b. The aromatic compound should contain an alternate single and double bond.
   c. The aromatic compound should contain (4n+2) delocalised pi-electrons, where n = 0, 1, 2, ...
   d. All
7. In the chemistry lab we have four organic compounds (A, B, C and D) which are cyclic, planar and have a fully conjugated system. Which among these may represent an aromatic compound?

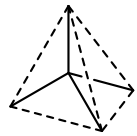
   A (2 π e^-s) **B** (4 π e^-s) **C** (6 π e^-s) **D** (8 π e^-s)

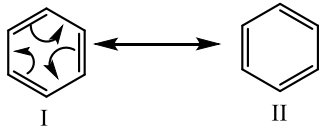
   a. Both A and C c. Only C
   b. Both A and D d. Only D

Structure of Benzene

Kekule's structure







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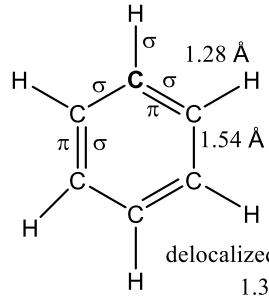
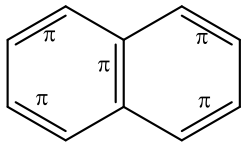
Kekule's structure of benzene



delocalized system of 6 π electrons

1.37Å



4n+ 2 π electrons

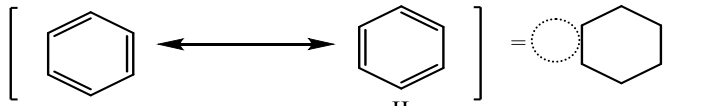
4 x 0+ 2= 2

4 x 1 + 2= 6

4 x 2 + 2 = 10

4 x 3 +2 =14

Resonance theory



Resonating structures

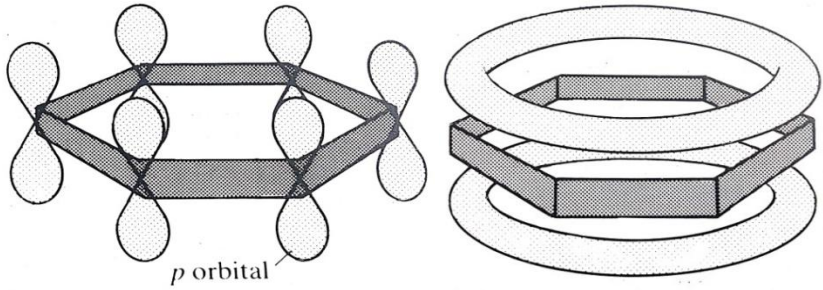
Resonance Hybrid

Electron Delocalization in Benzene

The extra stability of benzene and the fact that its C-C bonds are all of equal length can be explained using the following model, which is currently accepted by most chemists.

The carbon atoms in the ring are bonded to one another and their hydrogen atoms by σ-bonds. This leaves one unused p orbital on each carbon, each containing a single electron. The p orbitals are perpendicular to the plane of the ring, with one lobe above and one below this plane (Figure -1). Each p orbital overlaps sideways with the two neighbouring orbitals to form a

single π-bond that extends as a ring of the charge above and below the plane of the molecule (Fig.-2)



a: σ-bonded skeleton (C & H Atoms omitted for clarity)

b: σ- skeleton with π- bonds

Fig 1: Bonding in benzene (Plane of the molecules is Perpendicular to the paper)

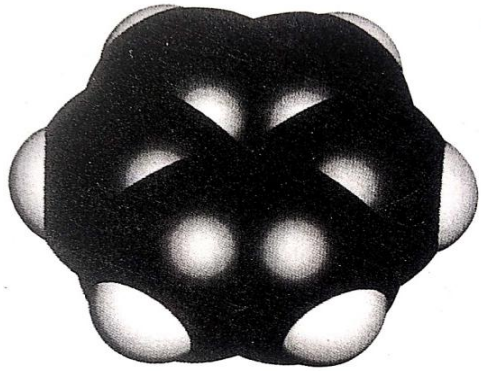


Fig 2: Computer-generated model of the benzene molecule (Planar symmetrical shape)

The electrons in the π-bond cannot be said to 'belong to' any particular carbon atom. Each electron is free to move throughout the entire π-system, so the electrons are said to be ***delocalized.*** *It is this delocalization that gives benzene its extra stability; any system in which electron delocalization can occur is stabilized. The reason for this is not hard to see. Electrons tend to repel one another, so a system in which they are as far*

apart as possible will involve minimum repulsion and will therefore be stabilized.

To conform with this model, the structural formula of benzene is nowadays often written as  *rather than*  *. The delocalization of π-electrons has a profound effect on the chemical properties of benzene.*

The word aromatic is used to describe any system that is stabilized by a ring of delocalized π- electrons. Non-aromatic compounds (such as alkanes and alkenes) are called aliphatic.

The structure described above means that the benzene molecule is planar, symmetrical, and nonpolar. Its lack of polarity results in benzene being a liquid at room temperature and makes it immiscible in water. Its boiling point is 80 °C and its melting point 6^{0}C. The surprisingly high melting point is due to the ease with which highly symmetrical benzene rings can pack into a crystal lattice. Compare it with that of the structurally similar but less symmetrical compound methyl benzene $C_6H_5CH_3$, which melts at -95^{0}C.

(From the book- Chemistry in Context- by Graham Hill and John Holman)

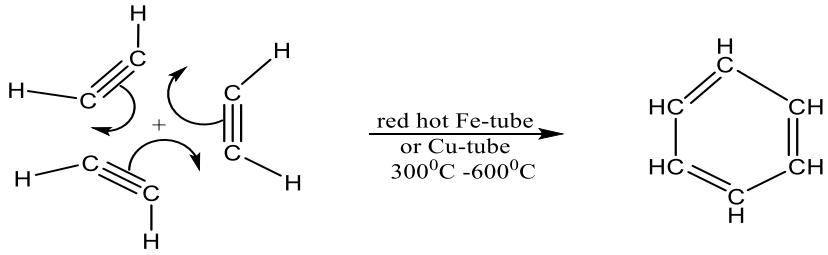
Resonance in Chemistry Explained in Simple Words with Examples

8. Benzene is more stable than alkenes due to
   a. Electron losing tendency of ring
   b. Electron gaining tendency of ring
   c. Resonance of the ring
   d. Electromeric effect
9. Resonance (Mesomeric effect) occurs due to:
   a. Delocalization of σ e^{-s}
   b. Migration of H-atoms
   c. Delocalization of π electrons
   d. Migration of protons

Preparation of Benzene

1. From Ethyne (by polymerization)

Benzene can be prepared by polymerization of Ethyne (acetylene) in a red hot copper tube. This is addition polymerization. It can also be called trimerisation as three molecules form a benzene molecule.



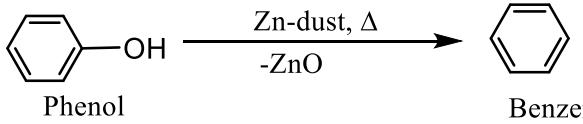
Or $3\ C_2H_2$ (Ethyne) $\xrightarrow{\text{red hot Cu-tube}}$ C_6H_6 (Benzene)

6. Name the monomer which on polymerization can give benzene. What type of polymerization is this? 2

7. *How would you prepare benzene from: i. Ethyne* 1

2. From Phenol (by heating with zinc dust)

Phenol gives benzene when heated with Zn-dust.

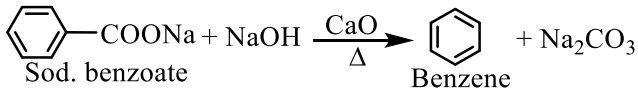


***8.* What happens when Phenol is heated with zinc dust? 1**

9. How would you obtain benzene from Phenol? 1

3. From Sodium benzoate (by soda lime decarboxylation)

Another general method of preparation of benzene is soda lime decarboxylation of sodium benzoate.



10. **What1 happens when sodium benzoate is heated with soda lime?1**

11. Give an example of a decarboxylation reaction. 1

12. How would you prepare benzene from Sodium benzoate?

1

10. The product formed by heating Phenol with zinc dust is

a. Diphenyl b. Benzene c. Toluene d. Alcohol

11. Ethyne on polymerization gives
    a. Mesityline c. Propyline
    b. Propylbenzene d. Benzene
12. Which reagent is used to change **Acetylene** into Benzene?
    a. Zinc dust c. Anhydrous $AlCl_3$
    b. $LiAlH_4$ d. Red hot Iron tube

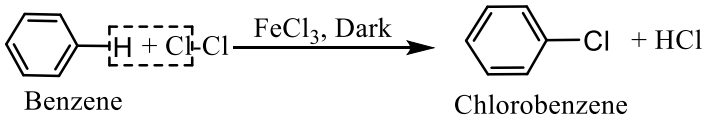
Chemical Properties

1. Electrophilic Aromatic Substitution reactions

Though benzene or aromatic compounds are highly unsaturated compounds these do not undergo addition reactions commonly instead undergo electrophilic substitution reactions. This is because of **resonance stabilization** in aromatic compounds, these do not try to lose the aromaticity. Hence undergo electrophilic aromatic substitution. One more factor that supports electrophilic substitution is that the aromatic ring is electron-rich, so prone to attack by an electrophile.

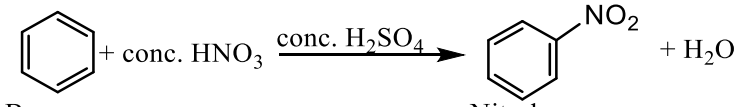
a. Halogenation

Chlorination:



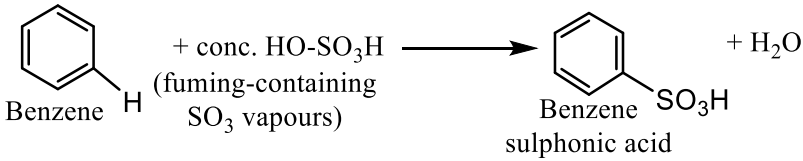
Benzene Chlorobenzene

b. Nitration

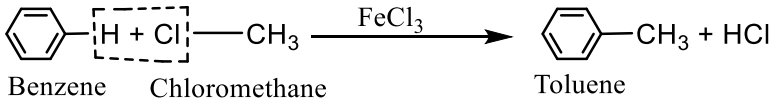


Benzene Nitrobenzene

c. Sulphonation



d. Friedel-Craft's alkylation



13. Give an example of Friedel Craft's alkylation. **1**

e. Friedel-Crafts acylation

14. **<u>Explain</u> with example of electrophilic substitution in aromatic compounds.** **4**

15. Give an example of Friedel Craft's acylation. *2*

16. Show your acquaintance with Friedel Craft's acylation. *5*

17. What happens when benzene is heated with acetic anhydride in the presence of anhydrous $AlCl_3$? *1*

18. Write short notes on Friedel Craft's reaction. *5*

13. The typical reaction of aromatic compounds is:

a. Electrophilic addition
b. Free radical addition
c. Nucleophilic addition
d. Electrophilic substitution

14. Which one of the following is not an electrophilic substitution reaction?

a. $C_6H_5CH_3 + \text{conc. } HNO_3/H_2SO_4(\text{fuming}) \longrightarrow \text{TNT}$

b. $C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$

c. $C_6H_6 + 3Cl_2 \xrightarrow{\text{sunlight}} C_6H_6Cl_6$

d. $C_6H_6 + \text{conc. } H_2SO_4 \longrightarrow C_6H_5HSO_3$ (MOE 2053)

15. The most common reaction of benzene and its derivatives are

a. Electrophilic addition reactions c. Electrophilic substitution reactions
b. Nucleophilic addition reactions d. Nucleophilic substitution reactions

16. Nitration of benzene is
    a. Electrophilic substitution c. Electrophilic addition
    b. Nucleophilic substitution d. Nucleophilic addition
17. The nitration of benzene by nitric acid and sulphuric acid is
    a. Electrophilic substitution c. Nucleophilic substitution
    b. Free radical substitution d. Electrophilic addition
18. The radical which attracts in electrophilic substitution of benzene is
    a. HSO_4^- c. SO_3^+
    b. HSO_3^+ d. SO_2^+
19. The chemical composition of fuming sulphuric acid is
    a. H_2SO_4 c. $H_2SO_4 + SO_2$
    b. $H_2SO_4 + H_2O$ d. $H_2SO_4 + SO_3$ (IOM 2016)
20. The electrophile in the sulphonation of benzene is
    a. HSO_4^- c. SO_3^+
    b. HSO_3 d. SO_3
21. The following reaction is

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$$

    a. Fittig reaction c. Friedel Craft's reaction
    b. Coupling reaction d. Diazotization reaction
22. What is the name of the following reaction?

$$\text{Benzene} + CH_3Cl \xrightarrow{\text{anhy. } AlCl_3} \text{Toluene}$$

    a. Friedel Craft's alkylation c. Wurtz reaction
    b. Fittig reaction d. Cannizaro's reaction
23. Friedel Craft's reaction is given by
    a. Aliphatic compounds d. aromatic compounds
    b. Alicyclic compounds c. benzene only
24. Friedel-Craft's reaction is given by
    a. Nitrobenzene c. Aniline
    b. Benzene d. All of above
25. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form
    a. Chlorobenzene c. Benzylchloride
    b. xylene d. toluene
26. For the formation of toluene by Friedel Craft's reaction, the reactants used are
    a. C_2H_2 & CCl_4 c. CH_4 & $CaCN_2$

b. C_6H_6 & CH_3Cl d. C_2H_5OH & Zn

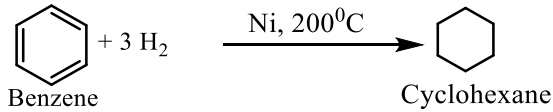
27. Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ in the presence of zinc dust to give
    a. n-propyl benzene c. Isopropyl benzene
    b. Xylene d. Mesitylene
28. The function of $FeCl_3$ in Friedel Craft's reaction is to produce
    a. Electrophile c. Nucleophile
    b. Free radical d. Carbocation

c. In Friedel Craft's alkylation besides $AlCl_3$, other reactants are
    a. $C_6H_6 + NH_3$
    b. $C_6H_6 + CH_4$
    c. $C_6H_6 + CH_3COCl$
    d. $C_6H_6 + CH_3Cl$

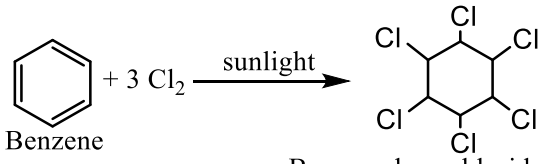
d. Which of the following is used for the preparation of aromatic ketones?
    a. Aldol condensation c. Friedel Craft's acylation
    b. Polymerization of Ethyne d. Friedel Craft's alkylation

2. Addition Reactions

a. Addition of H_2



b. Addition of Cl_2



Benzene hexachloride (BHC)
1,2,3,4,5,6-hexachlorocyclohexane
(*An important insecticide*)

3. Combustion reaction

$C_6H_6 + O_2 \longrightarrow CO_2 + H_2O + heat$

29. Benzene reacts with H_2 in the presence of metal catalyst to form cyclohexane. This is an example of

a. Addition reaction
b. Substitution reaction
c. Reduction reaction
d. Oxidation reaction

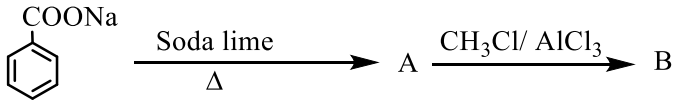
30. Benzene when reacts with hydrogen in the presence of Nickel at high temperatures to give cyclohexane, the reaction is

a. Addition
b. Oxidation
c. Reduction
d. Substitution

Conversions

19. How would you convert Ethyne into Toluene? **2**

***20.* Identify A and B in:**



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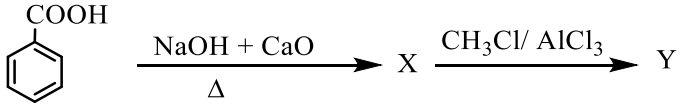
21. Identify X and Y in:



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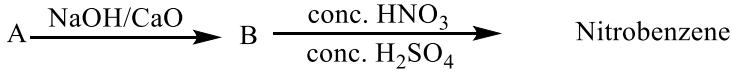
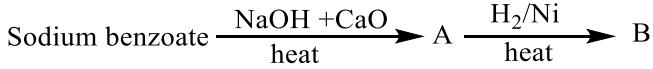
22. How is Sodium benzoate converted into Acetophenone? 2

23. How could you synthesize Toluene from Phenol? 2.5

24. Identify A and B in the following reaction sequence



25. Identify the major products A and B in the following reaction sequence



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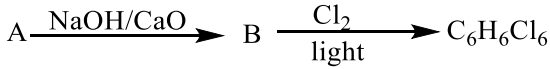
26. Identify A and B in the following reaction sequence:



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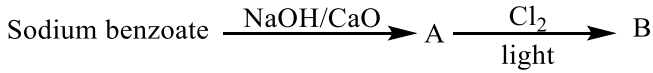
27. Identify A and B in the following reaction sequence:



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28. Write down the correct reactions for the conversions of Ethyne into BHC. 2

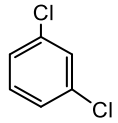
29. Benzene is an aromatic organic compound having a molecular formula C_6H_6. Write the requisite examples (chemical reactions) with their IUPAC names for the following;
    A) One method for preparation of benzene.
    B) Mono-nitration of benzene.
    C) Friedel Crafts alkylation reaction

Uses of Benzene

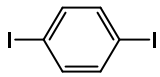
1. To produce polystyrene via Ethylbenzene and styrene.
2. To produce Cumene which is converted into phenols for the production of resins & adhesives.
3. To prepare cyclohexane used for the manufacture of nylon.
4. To prepare aniline (for dyes) and dodecylbenzene (for detergents).

Substitution in substituted benzenes

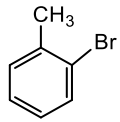
- Naming the di-substituted Benzenes



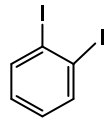
1,3-dichlorobenzene
m-dichlorobenzene



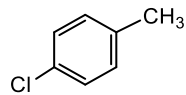
1,4-diiodobenzene
p-chlorobenzene



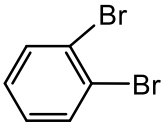
2-bromotoluene
o-bromotoluene



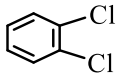
1,2-diiodobenzene
o-diiodobenzene



4-chlorotoluene
p-chlorotoluene



1,2-dibromobenzene
(o-dibromobenzene)

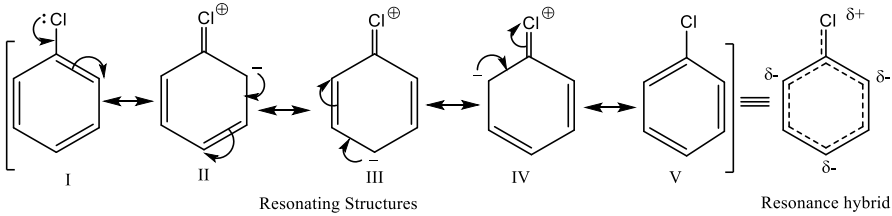
30. Write the name of the following compound according to the IUPAC rule. 

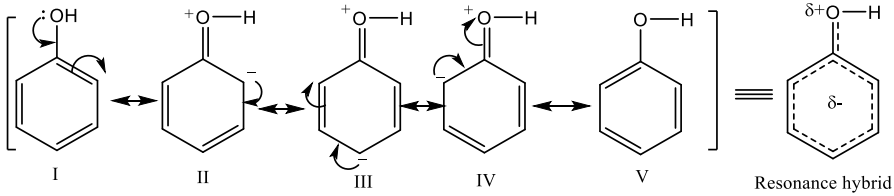
1

- **Effect on reactivity**
    - Activating groups:
    - Deactivating groups:

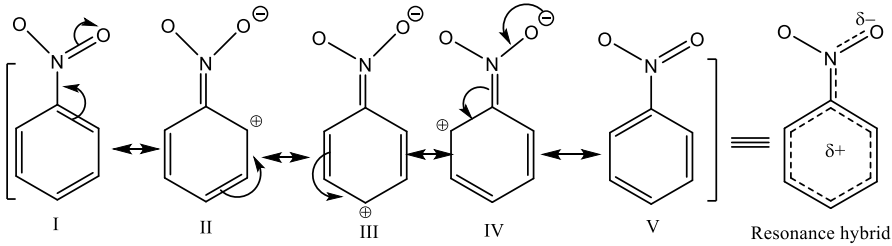
31. Why is Chlorobenzene less reactive than benzene in electrophilic substitution reactions? 2

- Effect on orientation
  - -o,-p directing groups





  - m- directing groups



Resonating structures of Nitrobenzene

32. Write resonance hybrid structure of arene containing meta director and ortho-para director substituent each. 2

33. Why does Chlorobenzene give ortho and para products during electrophilic substitution? 2

34. How do you explain that the –OH group of phenol is ortho/para directing? 2

35. Explain why the amino group of aniline is ortho para directing. 1

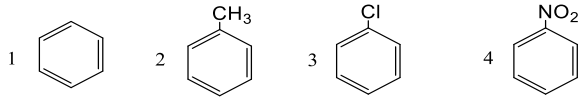
36. Write the resonating structure of nitrobenzene and explain why does it give meta-substituted product during electrophilic substitution? 2

37. *Why is the $-NO_2$ group a meta-directing towards electrophilic aromatic substitution?* *2*
38. *Electrophilic substitution reaction in nitrobenzene occurs at the meta position. Give reason.* *2*
39. *Electrophilic substitution reaction in nitroarene occurs at the meta position. Give reason.* *2*
40. *Account for the fact that $-NO_2$ is a meta-directing group towards electrophilic aromatic substitution.* *2*
41. *Why halogenation of Nitrobenzene occurs at the meta position?* *2*
42. *How would you predict that the nitro group in Nitrobenzene is an electron-withdrawing group?* *2*
43. Consider the functional groups given below;

    CHO NO_2 OH OCH_3 NO_2 $COCH_3$

    Put any of the above functional group on the benzene ring. Name the resulting organic compound. Making an assumption that this compound further undergoes an electrophilic substitution, show with the help all possible resonating structures at what position incoming electrophile will attack on the ring. *3*

31. Identify the correct order of reactivity towards electrophilic substitution reaction of the following compounds



a. 1 >2 > 3 > 4 c. 4 > 3 > 2 > 1
b. 2> 1 > 3 > 4 d. 2 > 3 > 1 > 4

32. Nitration takes place faster in
a. Toluene c. Phenol
b. Benzene d. Nitrobenzene

33. The compound that is most reactive towards electrophilic aromatic substitution is
a. Toluene c. Benzene
b. Benzoic acid d. Nitrobenzene

34. Which of the following shows electrophilic aromatic substitution most strongly
a. Benzene c. Phenol
b. Nitrobenzene d. Dinitrobenzene

35. Phenol is ortho para directing due to
a. Mesomeric effect c. Electromeric effect

b. +Inductive effect d. – Inductive effect (IOM 2017)

36. -CHO group is
    a. Para directing
    b. Meta directing
    c. Ortho directing
    d. Ortho and para directing
37. According to orientation rules in aromatic compounds, ortho and para-directing groups generally
    a. Positive atoms or groups
    b. Unsaturated groups
    c. Molecules which are deactivated
    d. Groups which decrease the electron density around the m-position
38. Which of the following groups is not a meta-directing group
    a. –COOH b. $-NO_2$ c. –CHO d. $-NH_2$

(This is incomplete note- study missing topics from class notes and books in detail)