

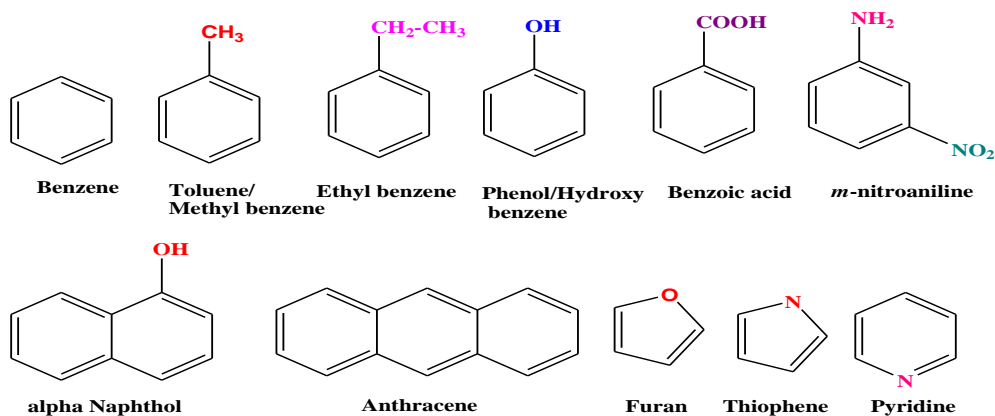
Chapter –VI **Arenes and aromaticity**

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Chapter -VI Arenes and aromaticity

- Introduction:** Hydrocarbons that consist of only aromatic ring or both aliphatic and aromatic groups are known as Arenes. Examples are,

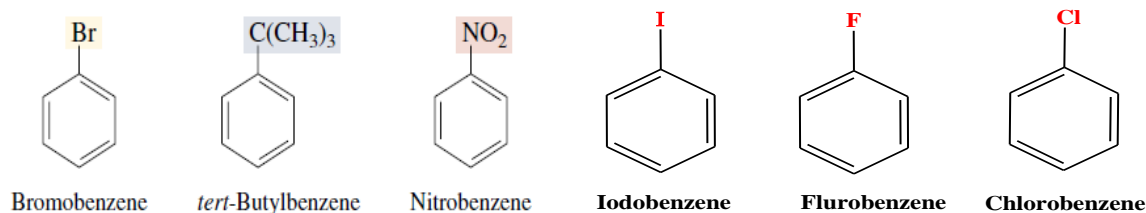


Aryl group: An aryl group is one derived from an arene by removal of hydrogen atom and is represented as **Ar-**

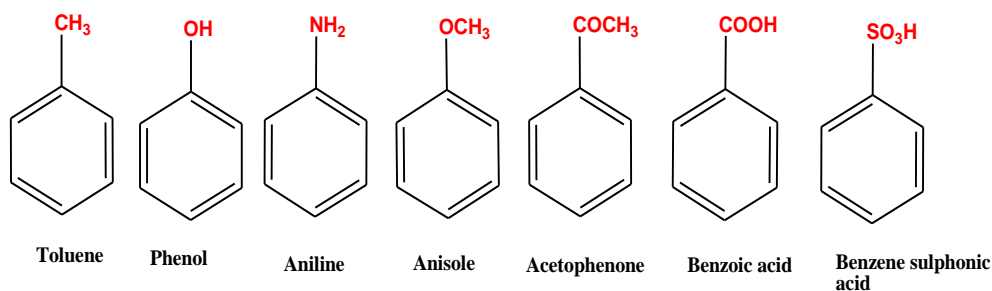
Thus Arenes designated as **Ar-H**, just as alkanes are designated as R-H

Nomenclature of benzene derivatives:

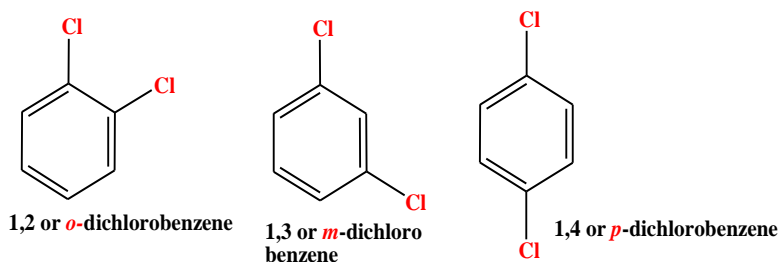
A) Benzene as parent name and the substituent is indicated by a prefix



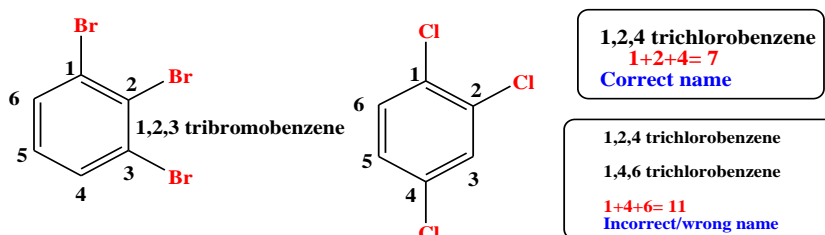
B) Substituent along with the benzene ring is given a new name.



C) When substituent are present, their relative positions are indicated by the prefix **ortho, meta and Para** (abbreviated as, *o*-, *m*-, *p*-) or by the use of numbers.

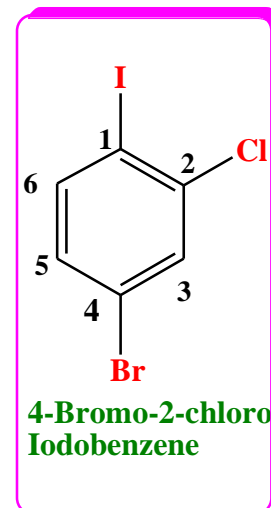
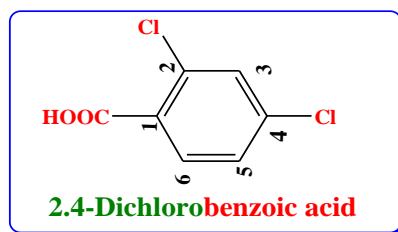
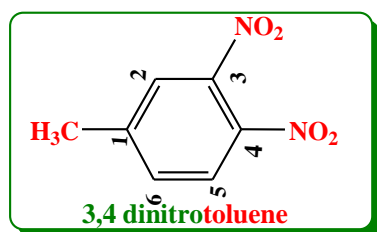


D) If more than two substituents are present, their relative positions are not indicated by *-o*, *m* and *-p* terms. Their positions are indicated by the use of numbers only. Benzene ring is numbered so as to get the lowest possible sum of the numbers.

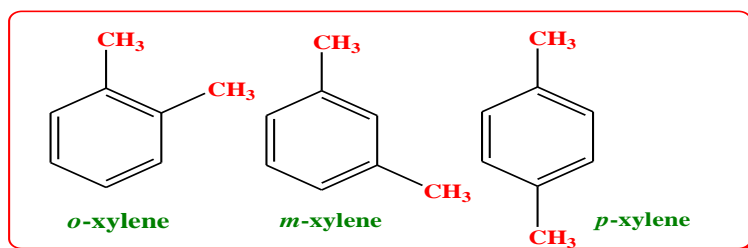


E) When more than two substituents are present and the substituents are different, they are listed in alphabetical order.

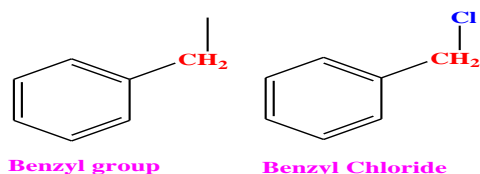
F) When a substituent is one that when taken together with the Benzene ring gives a new base name that substituent is assumed to be in position '1' and the new parent name is used.



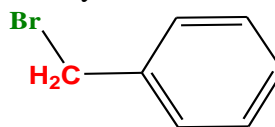
G) Dimethyl benzenes are called as Xylenes.



H) When $-C_6H_5$ group is present as substituent. It is called as phenyl group and denoted by $(-C_6H_5$ or $Ph-)$. $C_6H_5-CH_2-$ Phenyl methyl is given special name –benzyl

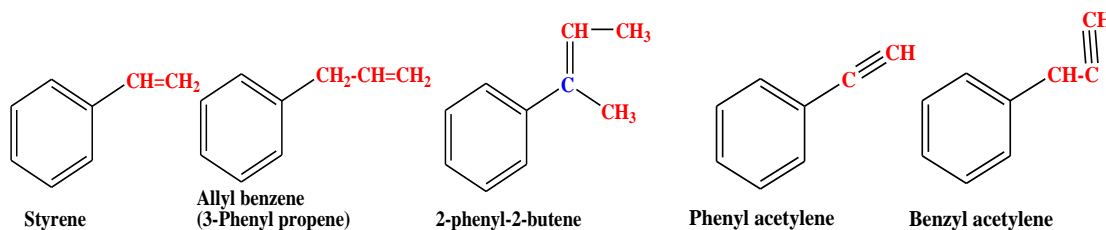


I) Organic halides in which halogen atom is directly attached to benzene ring and present in the side chain are called aralkyl halides.



Benzyl bromide

J) Alkenyl benzene has special name styrene



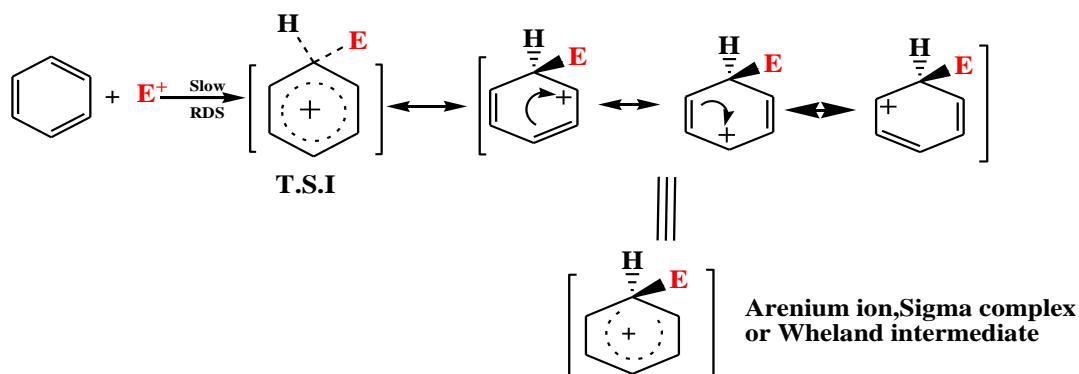
Molecular formula and Kekule structure of Benzene (1865):

Benzene has pi electron cloud above and below its sigma bond framework. Hence benzene is susceptible to Electrophilic attack, thus undergoes substitution reactions.

Mechanism of aromatic Electrophilic substitution reaction involves following two steps.

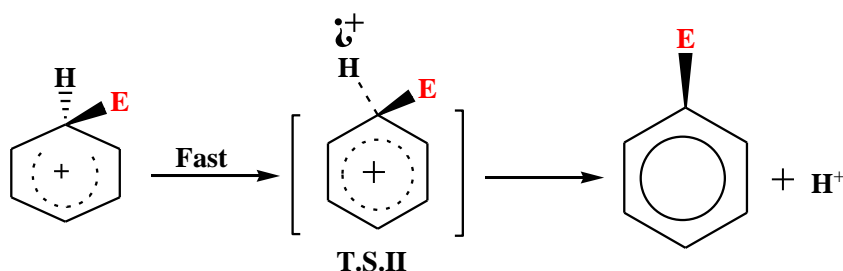
- **Step-I : a)** Electrophile (E^+) approaches one of the carbon atom of benzene to form initially partial bonding which represents Transition state-I (T.S.)
- **b)** Then two electrons of the six electrons ' π ' (pi) system form a ' σ ' (sigma) bond to one carbon atom of benzene ring.
- **c)** Resulting +vely charged species is called as ' σ ' (**sigma**) **complex** or **Wheland intermediate** or **Arenium ion**.
- **d)** The carbon of benzene that forms an ' σ ' bond to the Electrophile becomes SP^3 hybridized and remaining five carbon atoms remain still SP^2 hybridized with p orbital.
- **e)** The four ' π ' electrons of the arenium ion are delocalized through these five p-orbital.
- **f)** The arenium ion gets stabilized due to delocalization of positive charge over the ring forming corresponding resonating structure.

- g) The formation of arenium ion is slow step hence it is rate determining step.

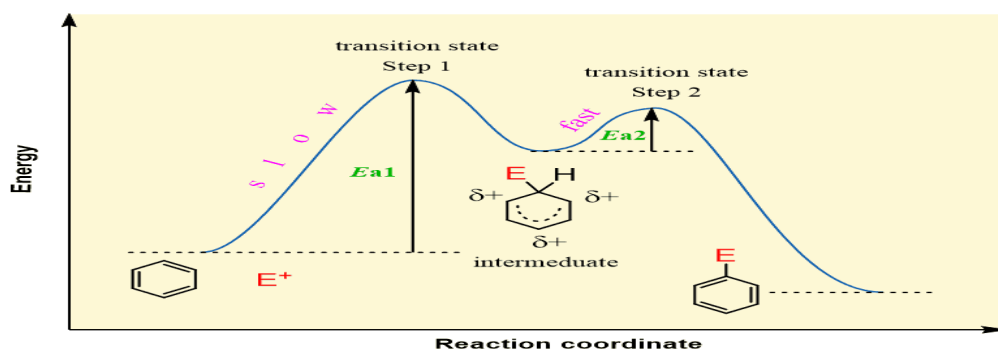


Step-I :

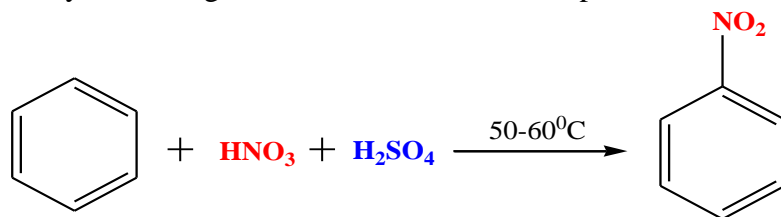
- a) Bonding between carbon and hydrogen becomes weak forming partial bonding, It represents T.S.-II.
- b) Arenium ion loses a proton from the carbon atom that bears the Electrophile. Benzene ring regains its two electrons.
- c) The carbon atom that bears the electrophile becomes sp^2 hybridized again and benzene with six fully delocalized ' π ' electrons is formed.
- d) In step-II, the loss of a proton takes place rapidly relative to step-I. Hence it is a fast step and has no effect on the overall rate of reaction.



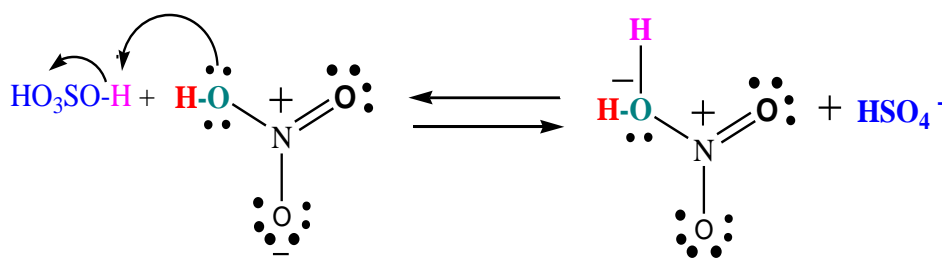
Energy profile diagram for aromatic electrophilic substitution reaction.



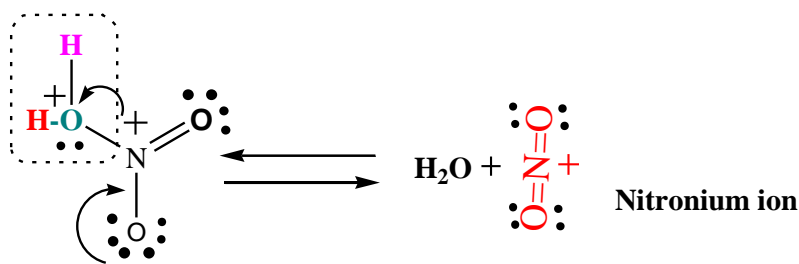
Nitration reaction: Benzene on heating with a mixture of conc. nitric acid and conc. sulphuric acid at 50-60 °C forms nitrobenzene. Conc. sulphuric acid increases the rate of reaction by increasing the concentration of electrophile NO_2^+ .



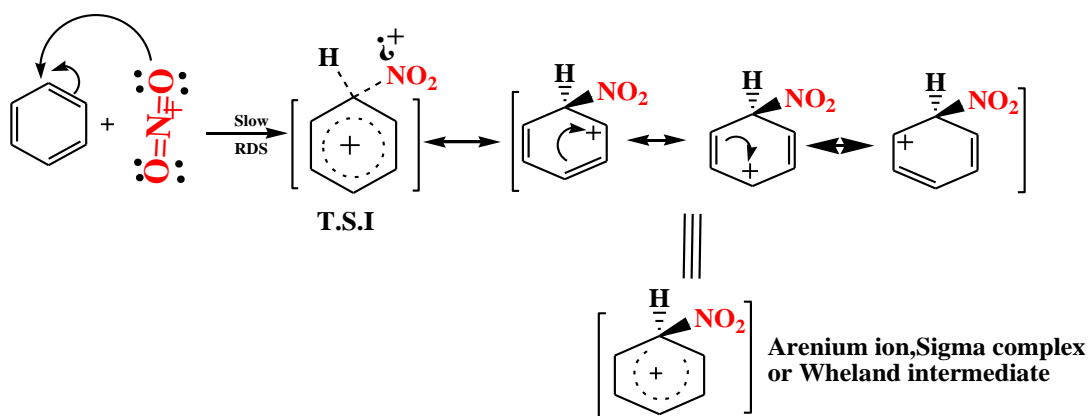
Step-I : Nitric acid accepts proton from the stronger Sulphuric acid.



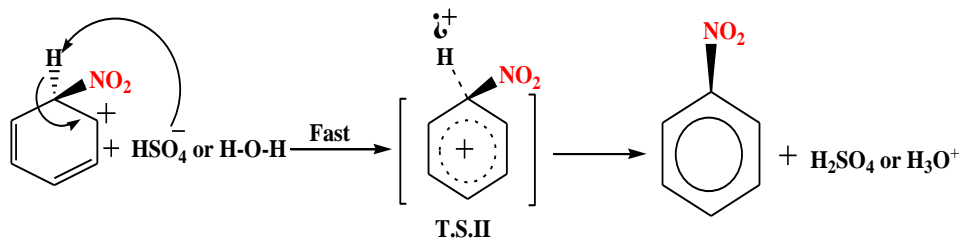
Step-II: Protonated Nitric acid dissociates to form a Nitronium ion.



Step-III: Nitronium ion acts as an electrophile and attacks one of the carbon atoms of benzene to form a resonance stabilized arenium.



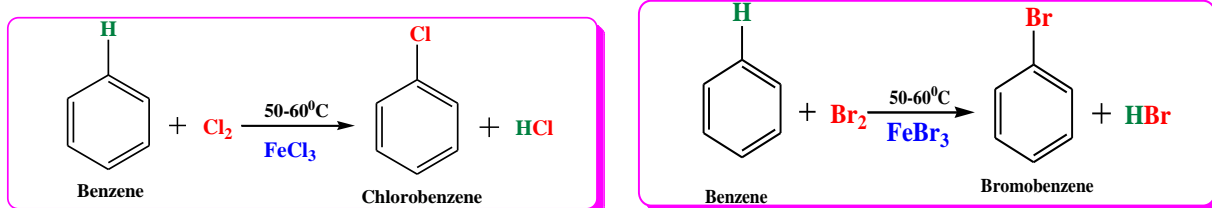
Step-IV: Proton from arenium ion is abstracted by base HSO_4 or H_2O to form nitrobenzene.



Halogenations reaction:

Benzene reacts with Cl_2 and Br_2 in the presence of Lewis acids like FeCl_3 , FeBr_3 and AlCl_3 to form chlorobenzene and bromobenzene respectively.

Reaction:

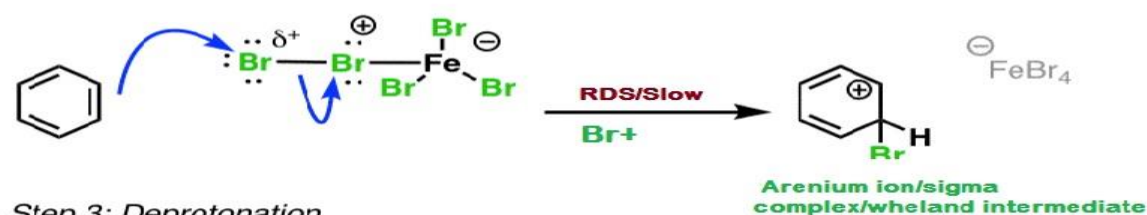


Bromination of Benzene: The Mechanism

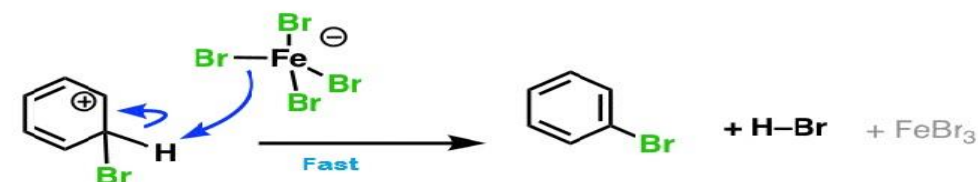
Step 1: Activation of Lewis acid



Step 2: Attack of electrophile by the benzene ring



Step 3: Deprotonation



Iodination of benzene: Iodine is very unreactive. The reaction of iodine with aromatic compound is highly reversible. Loss of iodine occurs more often from arenium ion than loss of hydrogen (last step).

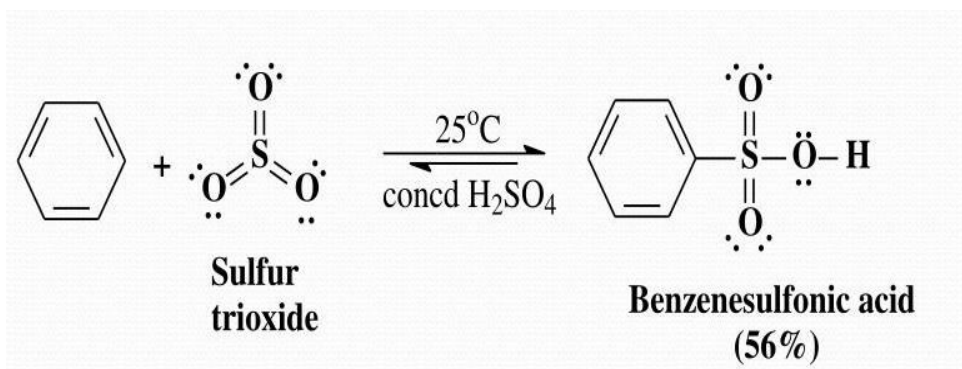
Fluorination of benzene: Benzene reacts with fluorine vigorously; hence direct fluorination of benzene is not possible.

✚ Sulphonation of Benzene:

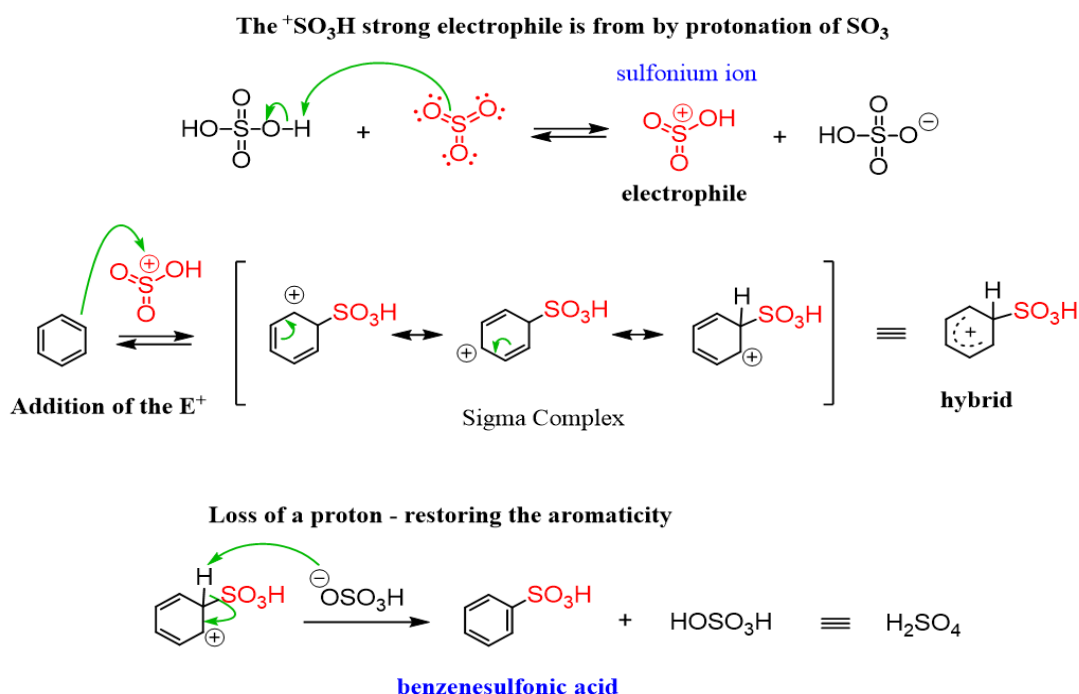
1) Benzene reacts with fuming sulfuric acid (Conc.H₂SO₄ saturated with SO₃) at room temp. to produce benzene sulphonic acid.

2) Sulphonation also takes place in **Conc.H₂SO₄** alone but the **reaction is very slow**. In both cases **SO₃ acts as electrophile**.

Reaction:



Mechanism:



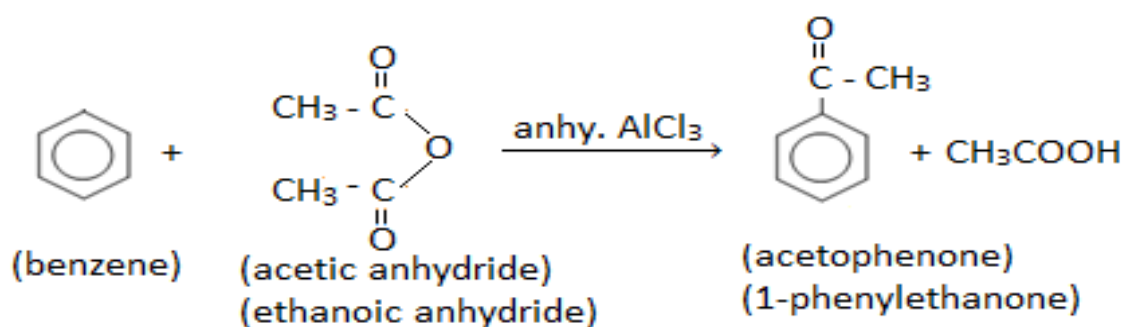
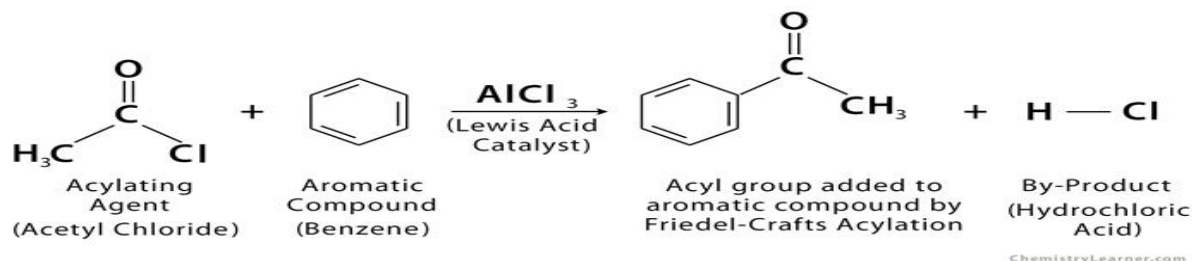
❖ Friedel-Crafts reaction:

This reaction divides into two types:

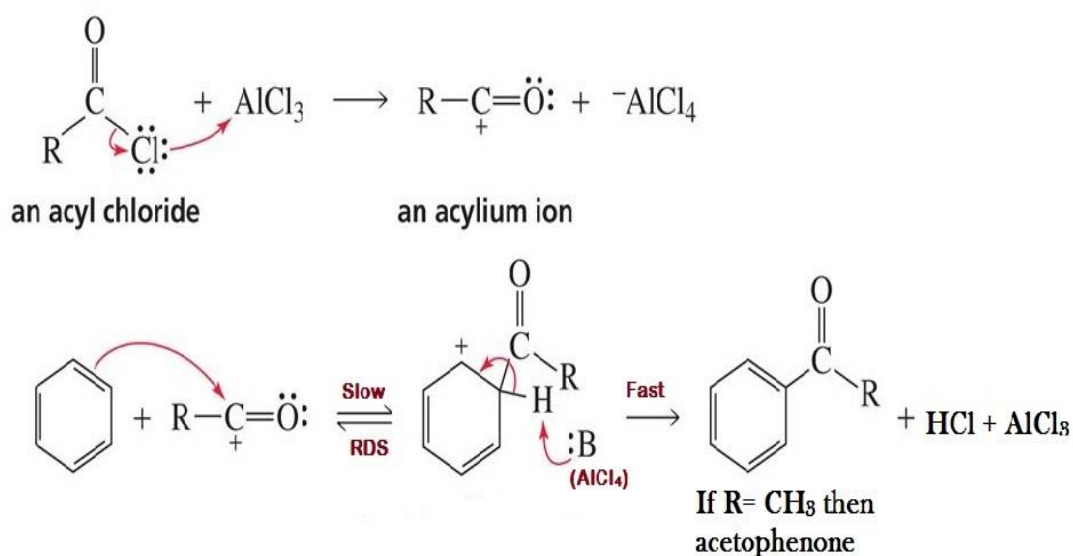
- 1) Friedel-Crafts Acylation
- 2) Friedel-Crafts Alkylation

Friedel-Crafts Acylation: Acylation of Benzene: Benzene in the presence of Lewis acid like anhydrous aluminum chloride reacts with acetyl chloride or acetic anhydride at 80 C using benzene as solvent to form acyl chloride that is acetophenone.

Friedel-Crafts Acylation

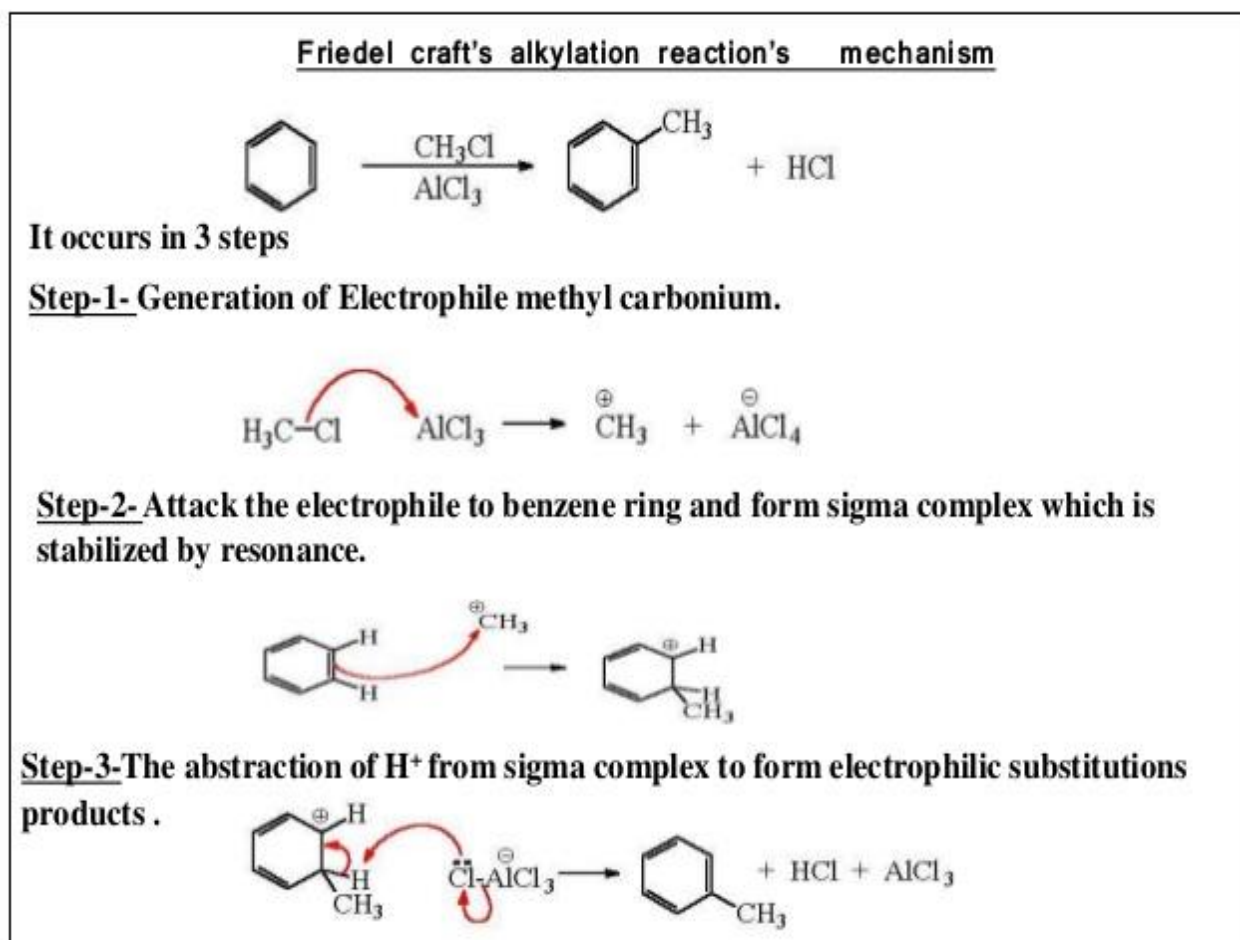


Mechanism:



Alkylation of Benzene: Benzene in the presence of **anhydrous** AlCl_3 reacts with alkyl halide to form alkyl benzene. Lewis acid AlCl_3 enhances electrophilicity of alkylating agents.

Example: Benzene in presence of **anhydrous** AlCl_3 reacts with **methyl chloride** to form methyl benzene (Toluene).





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DEPARTMENT OF CHEMISTRY

Question Bank

Class: B.Sc. Semester -I

Name of Paper: Organic Chemistry (Paper -II) CHE-102

Title of Chapter: Arenes and aromaticity.

Questions:

1. What are arenes? Discuss in detail structure of benzene with respect to stability and orbital picture of benzene?
2. What is meant by aromaticity? State Huckel rule and explain the stability of cycloproenyl cation and cyclopentadienyl anion?
3. Explain why benzene prefers to undergo electrophilic substitution reactions. Give its general mechanism with energy profile diagram.
4. Offer the mechanism of nitration, Sulphonation and halogenation of benzene?
5. Discuss the mechanism of Friedel-Crafts reaction to prepare acetophenone and toluene from benzene?
6. Offer explanations for the following.
 - A) Benzene is more stable than cyclohexadiene and cyclohexatriene.
 - B) Benzene prefers to undergo electrophilic substitution reactions rather than nucleophilic substitution reactions.
 - C) Benzene reacts with fuming H_2SO_4 to give benzene sulphonic acid.
 - D) Benzene reacts with mixture of nitric acid and sulphuric acid produces nitrobenzene.
 - E) Benzene reacts with bromine in presence of Ferric bromide gives bromobenzene.
 - F) Benzene generally not gives iodination reaction with Iodine.

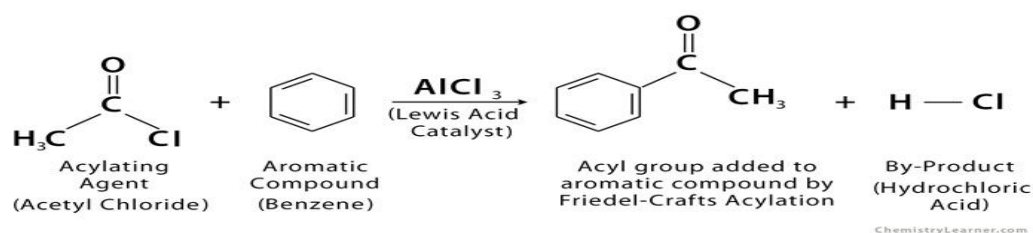
7. Write short notes on following:

- Nitration of benzene
- Sulphonation of benzene
- Halogenation (Chlorination) of benzene
- Friedel-Crafts acylation reaction of benzene
- Friedel-Crafts alkylation reaction of benzene

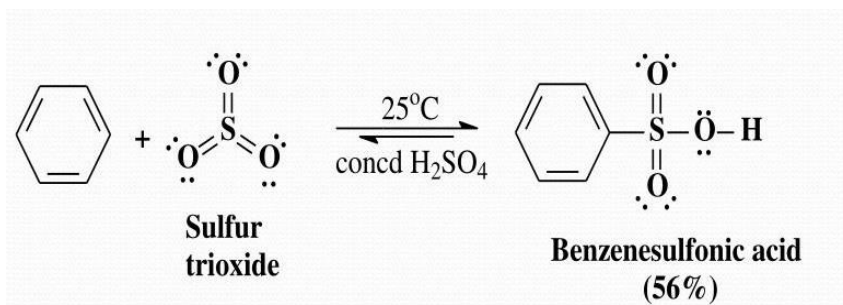
8. Offer the **mechanism** for the following reactions.

A)

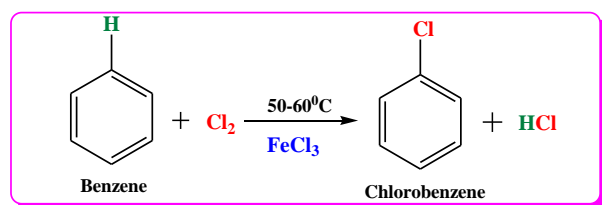
Friedel-Crafts Acylation



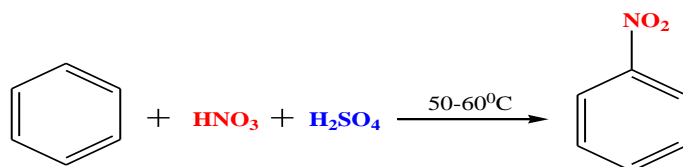
B)



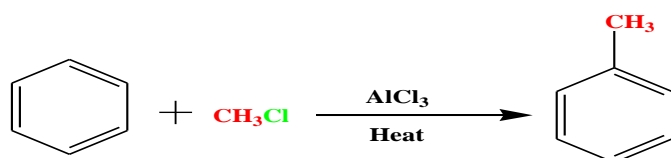
C)



D)



E)



Multiple choice questions:**1. Find the true statement about benzene**

- (a) It possesses two types of C-C bonds
- (b) Three isomeric forms are possible in monosubstituted benzene
- (c) It readily undergoes addition due to unsaturation
- (d) pi-electrons are delocalised in the ring

2. Nitration of benzene is carried out by which of the following reactive species?

- (a) NO_2^+
- (b) NO_2^-
- (c) HNO_3
- (d) NO_3

In Chlorination of benzene, which of the following acts as an electrophile?

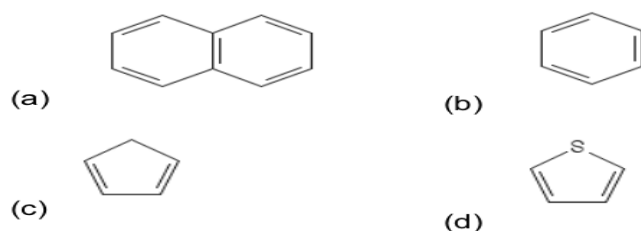
- (a) Cl^+
- (b) Cl^-
- (c) Cl
- (d) FeCl_3

3. Arenes do not show

- (a) Delocalisation of pi-electrons
- (b) Greater stability
- (c) Resonance
- (d) Electrophilic additions

4. The product formed, when benzene reacts with CH_3COCl in the presence of AlCl_3 is

- (a) $\text{C}_6\text{H}_5\text{CH}_3$
- (b) $\text{C}_6\text{H}_5\text{Cl}$
- (c) $\text{C}_6\text{H}_5\text{COCH}_3$
- (d) $\text{C}_6\text{H}_5\text{COCl}$

5. Which of the following compounds is not aromatic?**6. Which of the following is not a characteristic property of arenes?**

- (a) Delocalisation of π -electrons
- (b) Resonance
- (c) Greater stability
- (d) Electrophilic additions

7. Which of the following statements is true for benzene?

- (a) Benzene easily undergoes addition due to unsaturation
- (b) π -electrons are delocalised in the benzene ring
- (c) Three isomeric forms are formed on monosubstitution of benzene
- (d) Two types of C-C bonds are present in benzene.

8. Which of the following is the correct representation to relate the two resonating Kekule structures of benzene?

- (a) \rightarrow (b) \equiv (c) \leftrightarrow (d) \rightleftharpoons

9. The bond length of C-C bonds in benzene is

- (a) 110 pm (1.10 Å) (b) 156 pm (1.56 Å) (c) 121 pm (1.21 Å) (d) 139 pm (1.39 Å)

10. Which of the following is a characteristic of an aromatic compound?

- (a) Cyclic (b) Planar (c) $(4n+2)$ electrons (d) All of the above

11. Which of the following is incorrect for benzene?

- (a) Planar C_6 ring (b) Localised π bonding
- (c) sp^2 hybridised C atoms (d) It shows reactions characteristics of C=C double bonds

11. The number of delocalised π electrons in the benzene ring are

- (a) 6 (b) 8 (c) 2 (d) 4

12. Which of the following is the reactive species in the nitration of benzene?

- (a) NO_2^+ (b) NO_2^- (c) NO_3 (d) HNO_3

13. With respect to the electrophilic aromatic substitution of benzene which of the following is **not** true?

- (a) A non-aromatic intermediate is formed
- (b) Benzene acts as an electrophile
- (c) A proton is lost in the final step
- (d) Resonance forms are important

14. Which of the following statements is **incorrect**: aromatic compounds...

- (a) Are planar (b) Have $4n \pi$ -electrons
(c) Are cyclic (d) Are generally less reactive than similarly substituted alkene

15. With respect to the electrophilic aromatic substitution of benzene which of the following is **not** true:

- a) A non-aromatic intermediate is formed
b) Benzene acts as an electrophile
c) A proton is lost in the final step
b) Benzene acts as an electrophile

16. Which of the following is not associated with electrophilic aromatic substitution?

- a) The formation of nitrobenzene b) The formation of benzyne
c) The formation of bromobenzene d) the formation of benzene sulfonic acid.

17. Which of the following statements regarding Friedel-Crafts reactions is wrong?

- a) Alkylation of benzene with an alkyl chloride requires only a catalytic amount of a Lewis acid such as aluminum chloride.
b) Alkylation of benzene with an alcohol requires only a catalytic amount of a Brønsted acid such as phosphoric acid.
c) Acetylation of benzene with acetyl chloride requires only a catalytic amount of a Lewis acid.
d) Acetylation of benzene with acetic anhydride requires more than one equivalent of a Lewis acid.

18. Aromatic hydrocarbons are also known as ?

- a) Acetaldehyde b) Butyne c) Arenes d) Arines

19. Which statement about benzene is incorrect?

- a) Each Carbon atom is SP² hybridized.
b) The C-C π bonding is delocalized.
c) The reactivity of the benzene reflects the presence of carbon-carbon double bonds.
d) The C₆ ring is planar.

20. Which statement about the reaction of benzene with Cl_2 in the presence of AlCl_3 is incorrect?
- a) The mechanism goes via an intermediate cation
 - b) The mechanism is electrophilic addition.
 - c) AlCl_3 is a catalyst.
 - d) Chlorobenzene is formed.
21. The reaction of benzene with MeCl under Friedel-Crafts conditions leads to which of the following?
- a) Methylbenzene (toluene) as the only product.
 - b) 1,2-Dimethylbenzene and 1,4-dimethylbenzene as the only products.
 - c) Methylbenzene and 1,2-dimethylbenzene as the only products
 - d) A mixture of methylbenzene, 1,2-dimethylbenzene and 1,4-dimethylbenzene
22. Which of the following is a not a Hückel ($4n + 2$) aromatic system?
- a) Cyclopentadienyl anion (C_5H_5^-)
 - b) Cyclooctatetraene (C_8H_8)
 - c) [18]-Annulene ($\text{C}_{18}\text{H}_{18}$)
 - d) Benzene (C_6H_6)
23. Halogenation is banned to it's...
- a) Degradation
 - b) Unreactiveness
 - c) Non-toxicity
 - d) None of the above.
24. Nitration of benzene molecule shows the reaction of
- a) Electrophilic substitution reaction
 - b) Addition reaction
 - c) Nucleophilic substitution reaction
 - d) None of the above

25. Benzene reacts with bromine in presence of anhydrous Iron bromide (III) catalyst to give..

- a) Electrophilic substitution reaction
- b) Addition reaction
- c) Nucleophilic substitution reaction
- d) None of the above

26. To make nitrobenzene, the nitrating mixture is refluxed at...

- a) 55°C
- b) 15 °C
- c) 25 °C
- d) 43°C

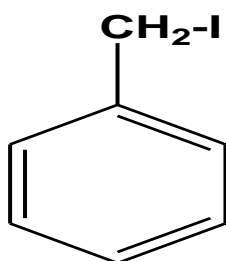
27. An aromatic molecule will:

- a) Have $4n\pi$ electrons
- b) have $(4n+2)\pi$ electrons
- c) Be planar
- d) be cyclic

28. Identify the correct statement which is related to aromatic hydrocarbon

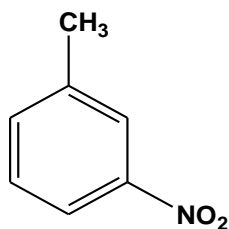
- a) It has a sigma and delocalized pi bond
- b) It has a sigma bond
- c) It has a two delocalized pi bond
- d) All of them

29. Suggest the correct name for the following compound...



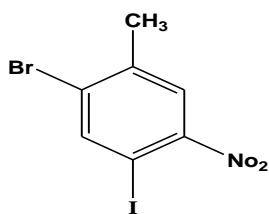
- a) Benzoyl bromide
- 2) Benzyl bromide
- 3) Phenyl bromide
- 4) 1- Iodo-benzyl benzene

30. Suggest the correct name for the following compound...



- a) M-nitro toluene
b) Toluene nitrobenzene
- b) m-nitro phenyl nitrobenzene
d) none of the above.

31. Suggest the correct name for the following compound...



- a) 2-bromo-4 iodo-5-nitro toluene
b) 5-bromo-4 iodo-3-nitro toluene
- b) 5-nitro -4 iodo -2-bromo toluene
d) 5-bromo-2- iodo-6-nitro toluene

32. Benzene on hydrogenation evolves.....kcal/mole less energy than expected diene or triene compound.

- a) 56 kcal/mole b) 36 kcal/mole c) 63 kcal/mole d) 55.4 kcal/mole

33. During aromatic electrophilic substitution reaction which of the following intermediate is formed...

- a) Carbanion b) nitrenes c) Arenium ion/wheland complex d) free radicals

34. How many transition state is formed during aromatic electrophilic substitution reaction..

- a) Three b) One c) Four d) Two

35. In Nitration reaction Conc.H₂SO₄ is used to...

- a) To increase the concentration of electrophile NO₂⁺.
b) To increase the concentration of benzene

c) To decrease the concentration of NO_2^+ .

d) To attack sulphonium ion on benzene fastly.

36. In Sulphonation reaction of benzene which of the following reagent is used..

a) Nitric acid and sulphuric acid

b) Phosphoric acid and acetic acid

c) Benzoic acid and sulphur

d) Sulphuric acid and sulphur trioxide.

37. In case of aromatic electrophilic substitution reaction which one of the following is correct..

a) Attack of benzene to electrophile and formation of wheland complex is slow step and rate determining while abstraction of aromatic proton is slow step.

b) Attack of benzene to electrophile and formation of wheland complex is fast step and not rate determining while abstraction of aromatic proton is slow step and rate determining.

c) Attack of benzene to electrophile and formation of sigma complex is fast step and not rate determining while abstraction of aromatic proton is also fast step.

d) All are correct.

38. Which of the following is suitable catalyst for halogenation of benzene..

a) FeCl_3 , AlCl_3 or FeBr_3

b) $\text{Fe}(\text{NO}_3)_3$

c) CdCl_2

d) MgCl_2

39. Which of the following is catalyst used for Friedel-Crafts acylation and alkylation of benzene..

a) Anhy. AlCl_3

b) Anhy. $\text{Ca}(\text{OH})_2$

c) Moist Ag_2O

d) iodine.

40. Which of the following is acylating agent used for Friedel-Crafts acylation of benzene..

a) Acetyl chloride or acetic anhydride

b) Ferric chloride and acetic acid

c) Sulphuryl chloride or thionyl chloride

d) NBS and Benzoyl peroxide.

41. Which type of hybridization is involved in benzene molecule.

a) SP^2

b) SP^3

c) SP

d) SP^2d^2

42. During the Sulphonation reaction of benzene the product formed is.
- a) Benzene nitric acid b) benzene sulphonic acid c) benzene sulphuric acid d) benzil
43. Nitrobenzene is the main product during the reaction of
- a) F.C. acylation of benzene b) halogenation of benzene
c) Nitration of benzene d) None of above
44. When benzene reacts with acetyl chloride in presence of anhydrous AlCl_3 give the product
- a) Acetophenone or 1-phenyl ethanone b) Benzophenone c) acetone d) Propyl methanone
45. When benzene reacts with methylchloride in presence of anhydrous AlCl_3 give the product
- a) Ethyl benzene b) butyl benzene c) Toluene d) Nitrobenzene
46. Benzene not undergoes iodination reaction because....
- a) Iodine is unreactive, reaction is highly reversible and loss of iodine occurs more often from arenium ion than loss of hydrogen.
b) Iodine is expensive, reaction is highly irreversible and loss of iodine not occurs more often from arenium ion.
c) Iodine is highly reactive, reaction is highly vigorous and product is unstable.
d) Iodine is large in size, not dissolves in reactant and thus reaction is very slow.
47. Structure of benzene is explained in details by....
- a) Boyle b) Charle c) Sir Cahn and Ingold d) Friedrich A.Kekule
48. $4n+2$ rule is explained by
- a) Markovnikov b) Kharasch c) Erich Huckel d) Curie.

49. The stability of benzene is explained by ...
- a) Heat of neutralization and heat of Combustion
 - b) Heat of formation and heat of solution
 - c) Heat of hydrogenation and heat of Combustion
 - d) Heat of addition and heat of ring formation
50. Which of the following is true for benzene...
- a) Benzene is cyclic, planar with delocalization of 6 pi electrons obeys $4n+2$ rule.
 - b) Benzene is noncyclic, nonplanar with nodelocalization of 6 pi electrons not obeys $4n+2$ rule.
 - c) Benzene is open chain, ring compound with delocalization of 2 pi electrons obeys $4n+2$ rule.
 - d) All are correct.
51. During the acylation of benzene the first step is formation of
- a) Nitronium ion.
 - b) Acylium ion
 - c) Bromonium ion
 - d) Methyl carbocation.