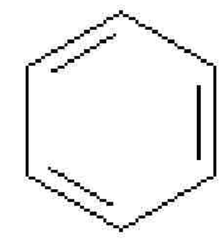
Chapter#9

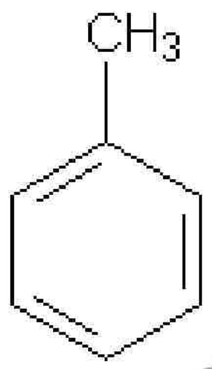
AromaticHydrocarbons

1. ***What are aromatic hydrocarbons? Give two examples.***

Ans: The aromatic hydrocarbons are closed-chain hydrocarbons containing a benzene ring or its derivatives. Examples are:



benzene



toluene

2. ***How are the aromatic hydrocarbons classified?***

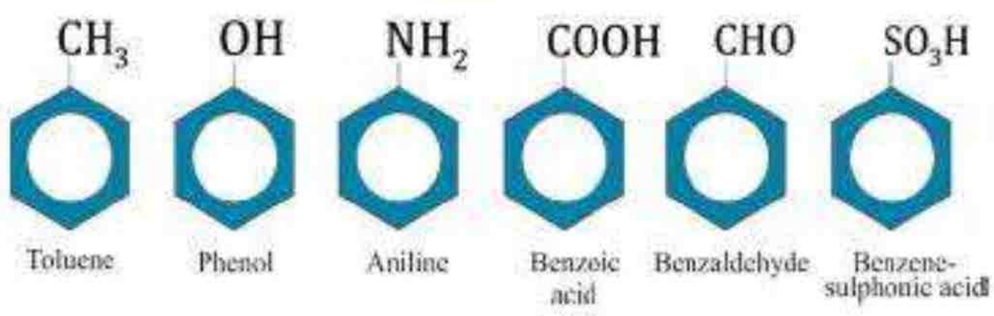
Ans: On the basis of the number of benzene rings aromatic hydrocarbons can be categorized into following classes:

a. Monocyclic Aromatic Hydrocarbons and their derivatives

b. Polycyclic Aromatic Hydrocarbons

3. ***What are Monocyclic Aromatic Hydrocarbons? Give examples.***

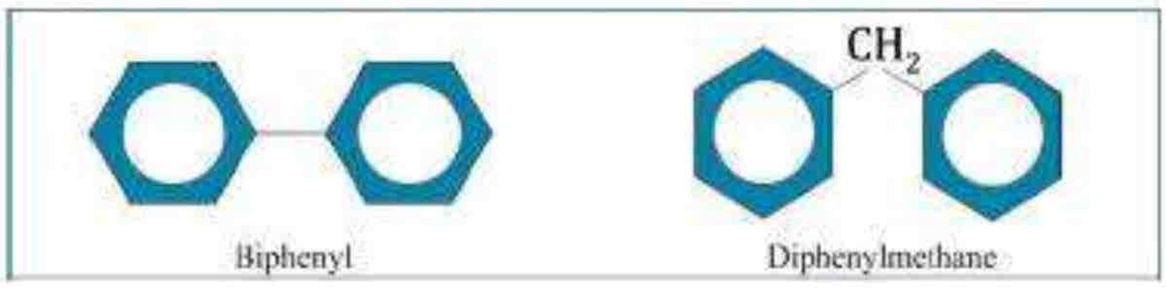
Ans: Aromatic hydrocarbons containing one benzene ring in their molecules are called Monocyclic Aromatic Hydrocarbons, e.g. benzene and its derivatives.



4. ***What are Polycyclic Aromatic Hydrocarbons? Give examples.***

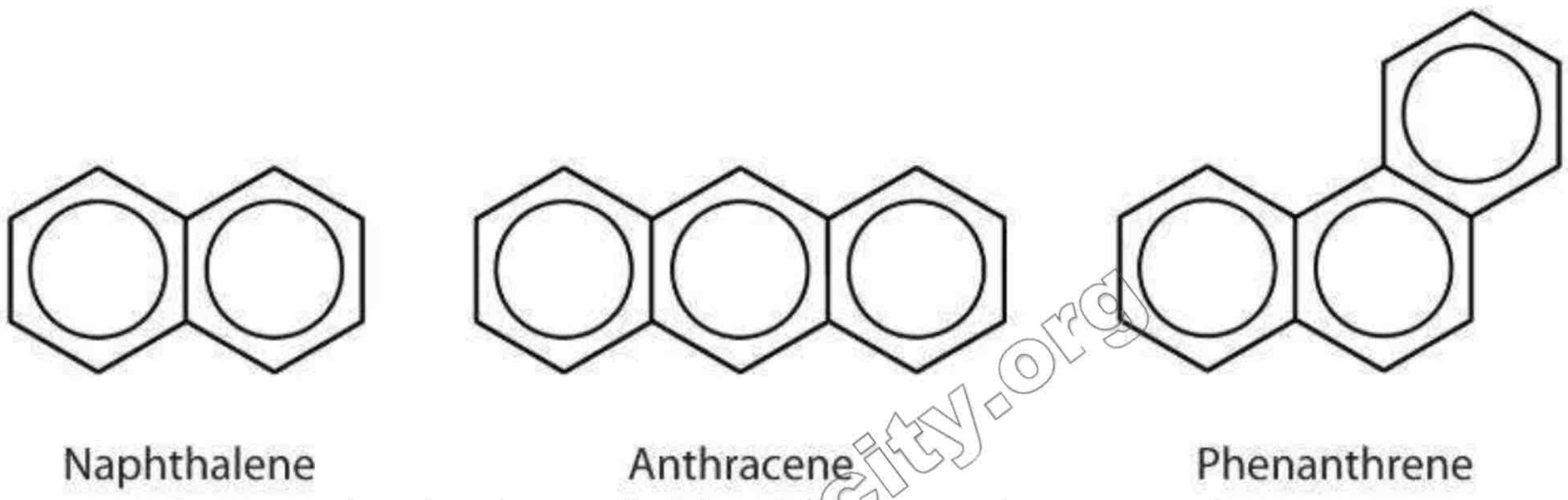
Ans: Aromatic hydrocarbons containing two or more benzene rings in their molecules are called

Polycyclic Aromatic Hydrocarbons. They may be divided into two main classes. (i) Those in which benzene rings are isolated, e.g. biphenyl, diphenylmethane, *etc.*



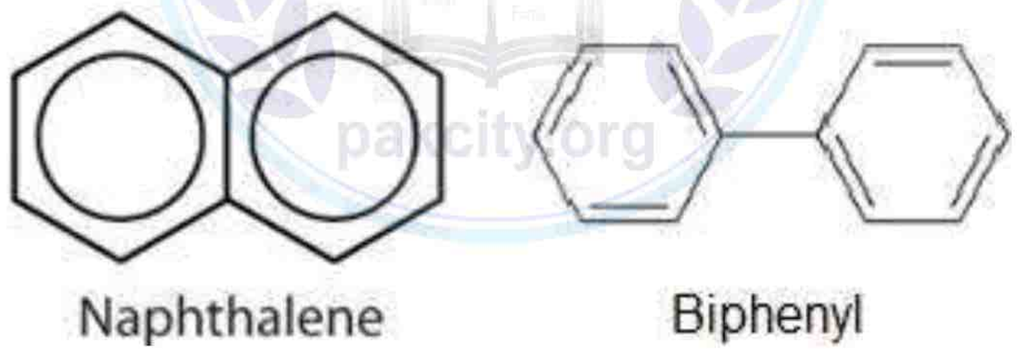
5. What are fused ring aromatic compounds? Give examples.

Ans: The compounds in which the benzene rings are fused together so that the adjacent rings have a common carbon to carbon bond are called fused ring aromatic compounds.



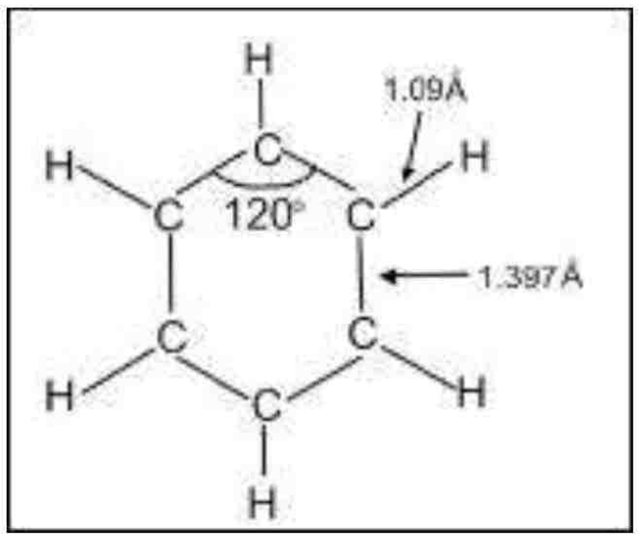
6. What are polycyclic aromatic hydrocarbons? Give examples.

Ans: Aromatic compounds containing two or more benzene rings in their molecules are called polycyclic aromatic hydrocarbons. The benzene rings present in polycyclic aromatic hydrocarbons can be isolated (e.g.Biphenyl) or they may be fused together (e.g. Naphthalene).



7. Give X-ray studies of benzene.

Ans: The X-ray studies of benzene have confirmed the hexagonal structure for it. These studies have also revealed that all the carbon and hydrogen atoms are in the same plane. All the angles are of 120°. All C - C and C –H bond lengths are 1.397A and 1.09 A, respectively.



8. Compare reactivity of alkanes, alkenes and benzene.

Ans:

- Alkanes are unreactive class of compounds and their unreactivity is due to their non-polar nature and the inertness of ϭ-bond. However, they undergo substitution reactions relatively easily and these reactions involve free radicals.
- Alkenes are very reactive class of compounds and their reactivity is due to the inherent weakness of the π –bond and the availability of π electrons for the electrophilic reagents. They undergo electrophilic addition reactions easily. Being relatively unstable, alkenes undergo polymerization reactions and they are also readily oxidized.
- Benzene is unique in its behavior. It is highly unsaturated compound and at the same time, it is very stable molecule. The stability of benzene, is due to the extensive delocalization of π - electrons. It resembles alkenes when it gives addition reactions. The substitution of benzene does not involve free radicals. These are electrophilic substitution reactions and involve electrophiles. Its addition reactions require more drastic conditions than those for alkenes. Benzene does not undergo polymerization and it is resistant to oxidation.

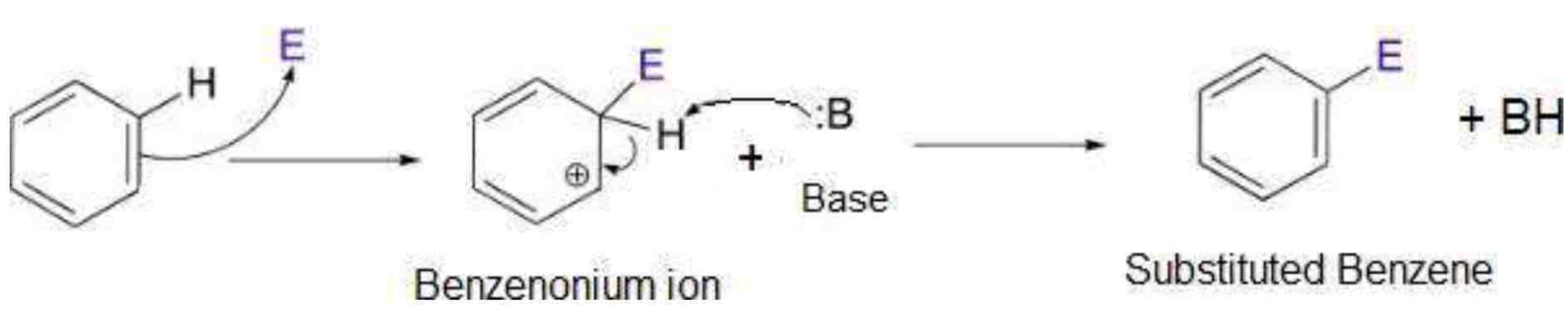
9. Write general mechanism of electrophilic substitution reactions in benzene OR Givegeneral pattern of reactivity of benzene towards electrophiles.

Ans: The general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows.

- Pi electrons of benzene ring are donated to the strong electrophile

(E^+) andbenzenonium ions are formed. Benzenonium ions are unstable.

- A proton is released with the help of strong base from benzenonium ion and stabilityof benzene is retained.

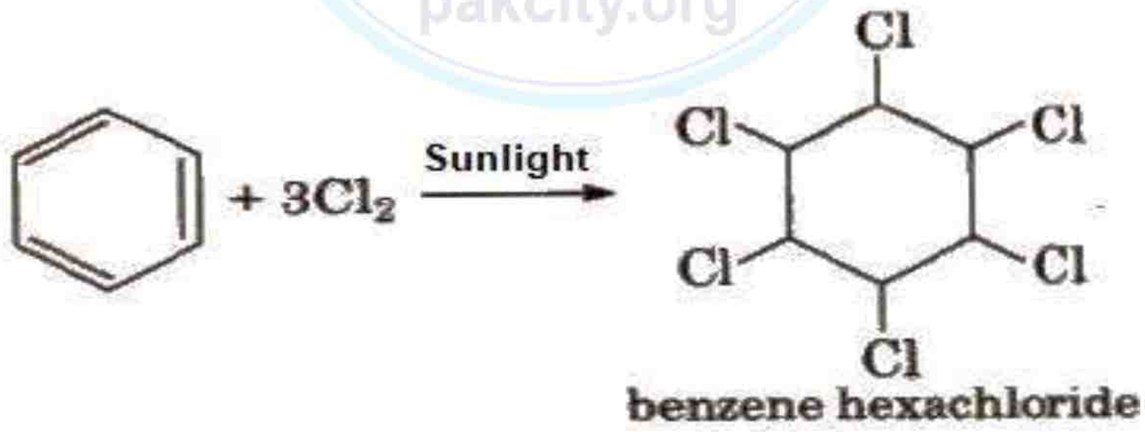


10. Benzene has three pi bonds. Prove it by two points.

Ans:

i. Benzene adds three hydrogen molecules in the presence of a catalyst. It indicates that it has three pi bonds in it.

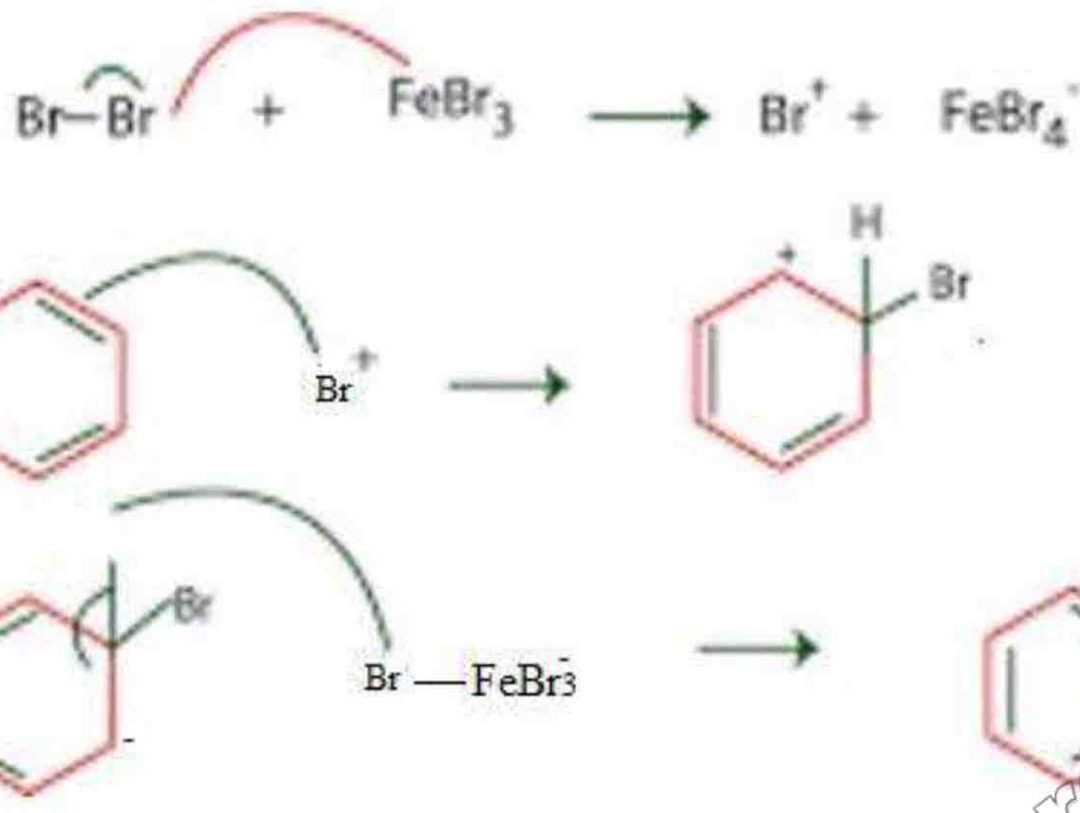
ii. Benzene adds three molecules of chlorine in the presence of sunlight, showing the presence of three pi bonds.



*11. **Predict major product of the bromination of benzene. Also give equation.***

Ans:

If hydrogen atom of benzene ring is substituted by bromine atom, it is called Bromination.



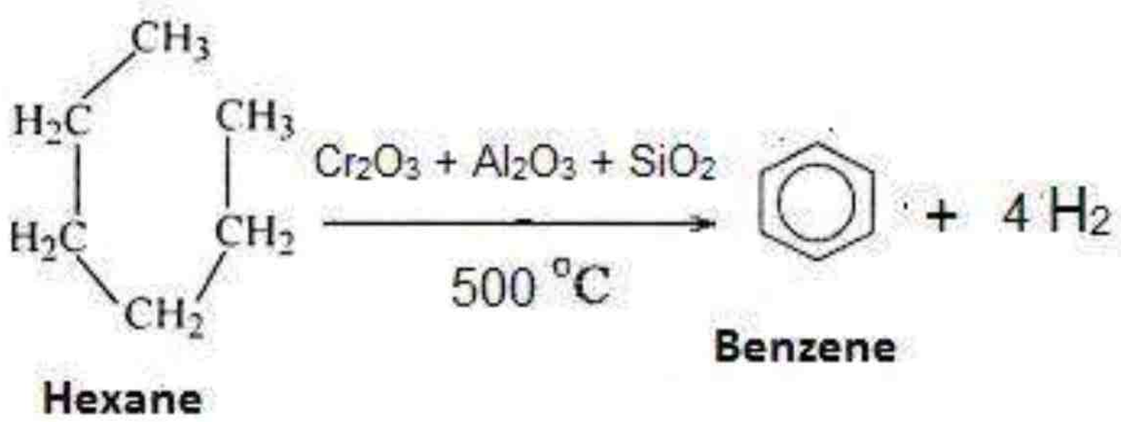
*12. **Benzene can be prepared commercially from acetylene. Give reaction with conditions.***

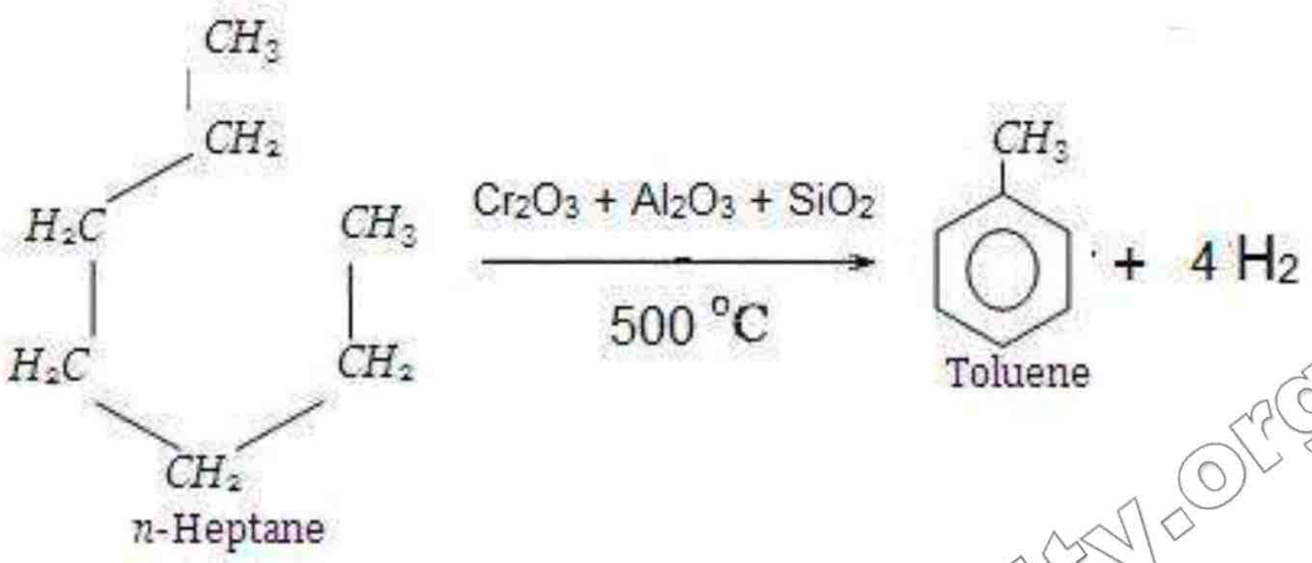
Ans:

Benzene is formed by passing acetylene under pressure over an organo-nickel catalyst at 70°C.

13. How Hexane and Heptane can give Benzene and Toluene respectively?

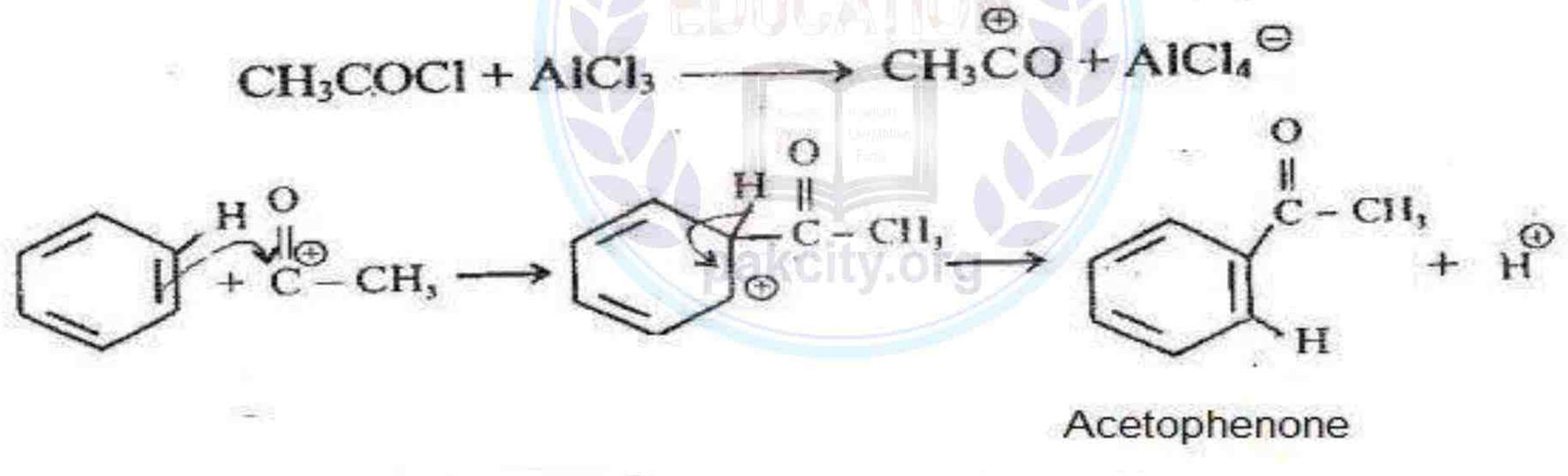
Ans:





14. How Benzene can be converted to Acetophenone? Give mechanism.

Ans: Benzene can be converted to Acetophenone by Friedel-Craft Acylation. The mechanism of reaction is given below.

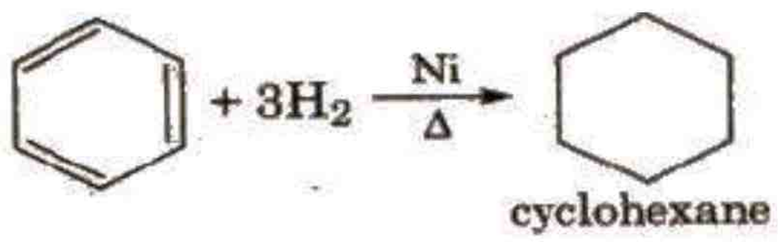


15. Convert benzene into:

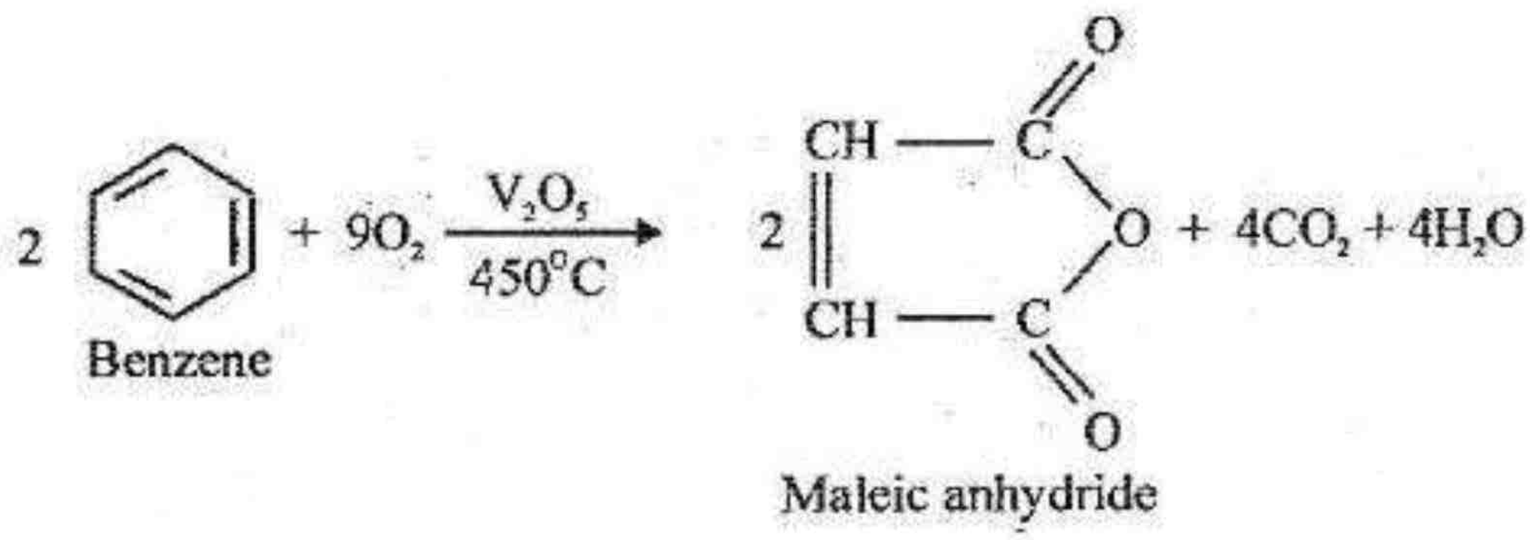
i. Cyclohexane ii. Maleic anhydride

Ans:

i.



ii.



16. Give two reasons that rule out straight chain structures of benzene.

Ans:

ii. Considering a straight chain structure for benzene and further assuming that each carbon carries one H-atom, it should be capable of forming three mono substitution products. But benzene only gives one mono substituted product. Which shows it does not have straight chain structure.

iii. The molecular formula of benzene is C_6H_6. This formula does not correspond toany aliphatic hydrocarbon like Alkane C_nH_{2n+2}, Alkene C_nH_{2n} or Alkyne C_nH_{2n-2}.

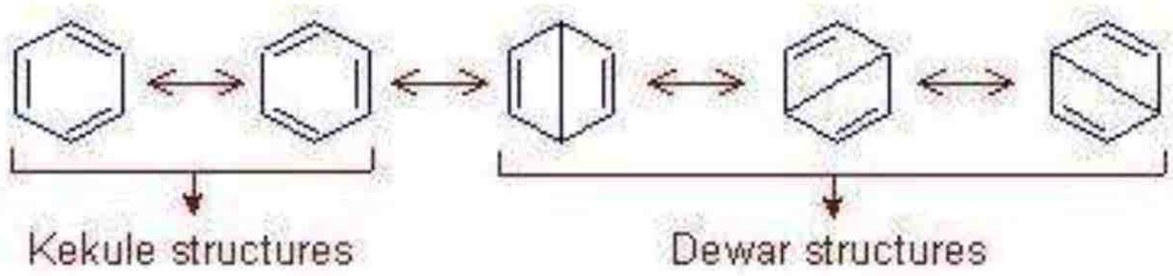
All above points indicate that benzene does not belong to open chain hydrocarbons and has cyclic structure.

17. Define Resonance and write down resonance structures of benzene.

Ans:

The possibility of different pairing schemes of valence electrons of atoms in a molecule is called resonance, and the different structures thus arranged are called resonance structures.

Resonance structures of benzene:



18. Prove that Benzene has cyclic structure.

Ans:

i. Benzene gives only one mono substituted product.

ii. Benzene gives only three di substituted products.

These points confirm the regular hexagonal structure for benzene in which all the carbon atoms are occupying identical positions in the molecule. So, we can say that benzene has a cyclic structure, therefore benzene forms only one toluene, one phenol and one nitrobenzene.

19. What is Wurtz-Fittig reaction? Give an example.

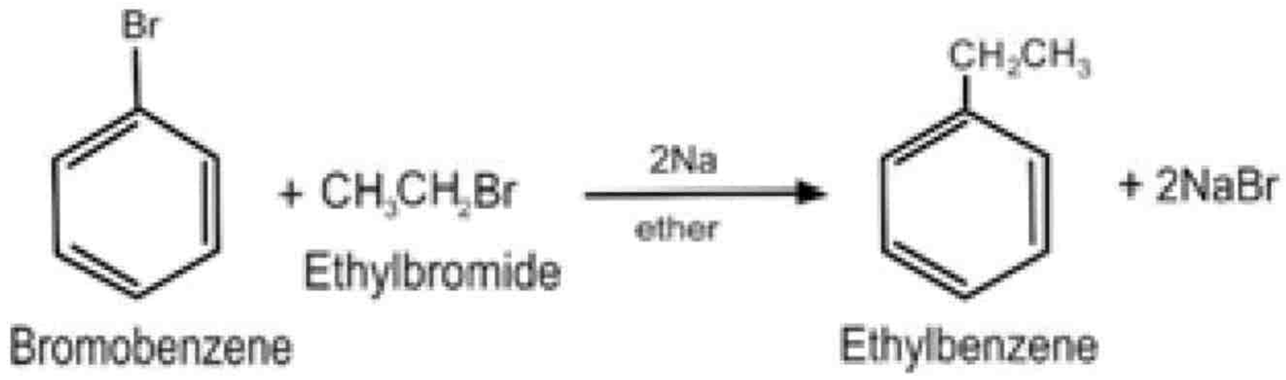
Ans:

The Wurtz reaction for the synthesis of alkanes was extended by Fittig in 1864 to thesynthesis of alkyl aromatic hydrocarbons.

When a mixture of alkyl halide and an aryl halide is treated with sodium metal in dry ether, the sodium preferentially attack the alkyl halide to form alkylated aromatic compound. Thus

mixed Wurtz reaction is called Wurtz –Fittig reaction.

Example:



---

20. Define resonance energy. Give resonance energy of benzene.

Ans:

The difference in energy between hypothetical structure (1,3,5-cyclohexatriene) and actual structure (benzene) is called resonance energy.

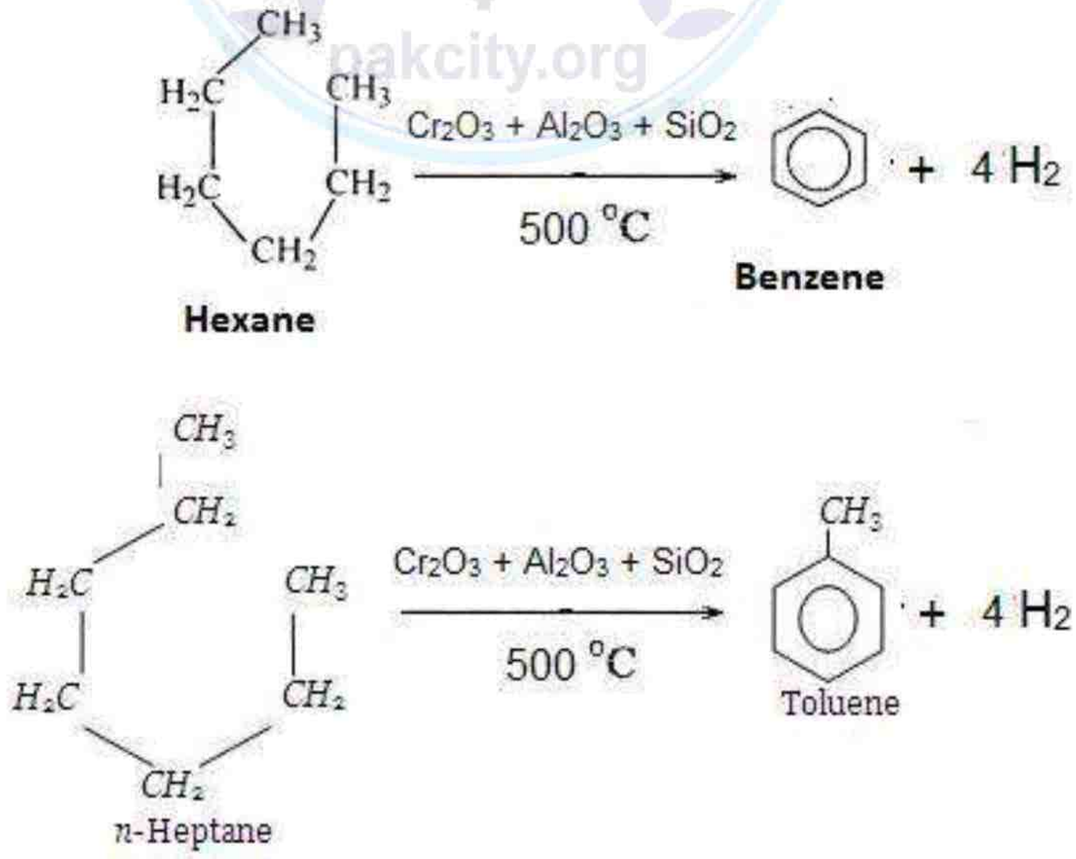
Resonance energy of benzene:

The resonance energy of benzene is 150.5 kJ/mol, which shows that it is more stable than 1,3,5-cyclohexatriene by 150.5kJ/mol.

21. What is aromatization?

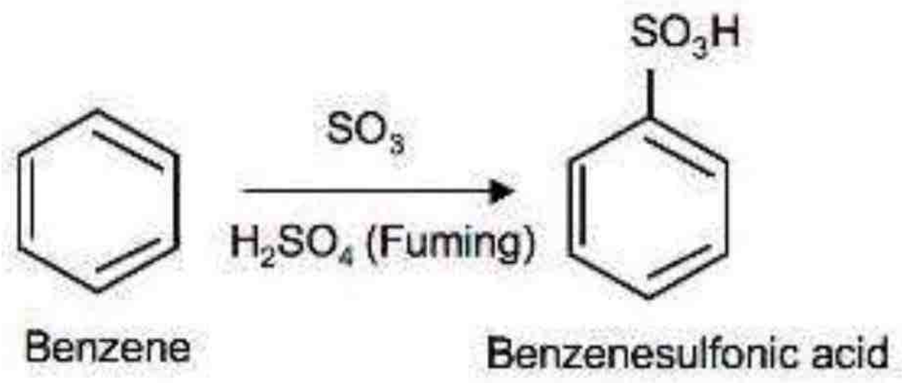
Ans:

Aromatization is the conversion of a nonaromatic hydrocarbon to an aromatic hydrocarbon. Benzene and toluene can be formed by aromatization of n-hexane and n-heptane as follows.



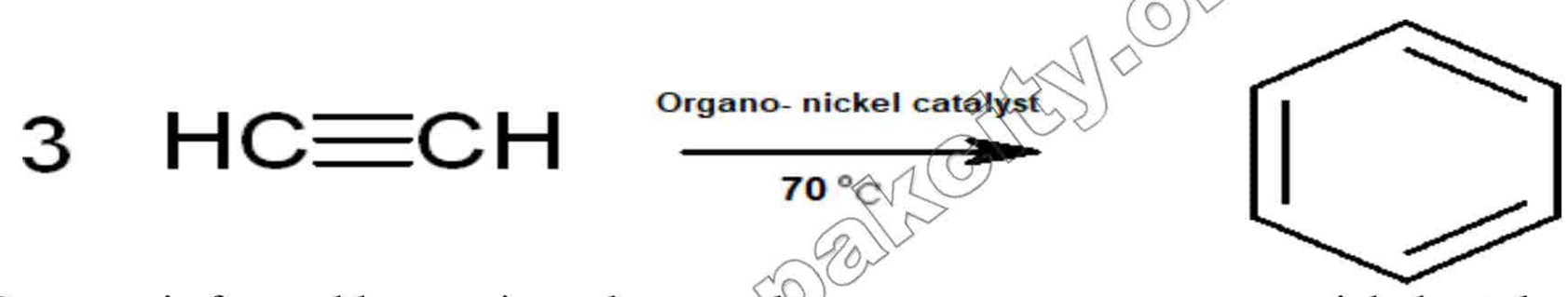
22. Give reaction of benzene with SO_3.

Ans: Benzene reacts with sulphur trioxide in the presence of concentrated sulphuric acid toproduce Benzene sulfonic acid.



23. How will you synthesize benzene from Ethyne?

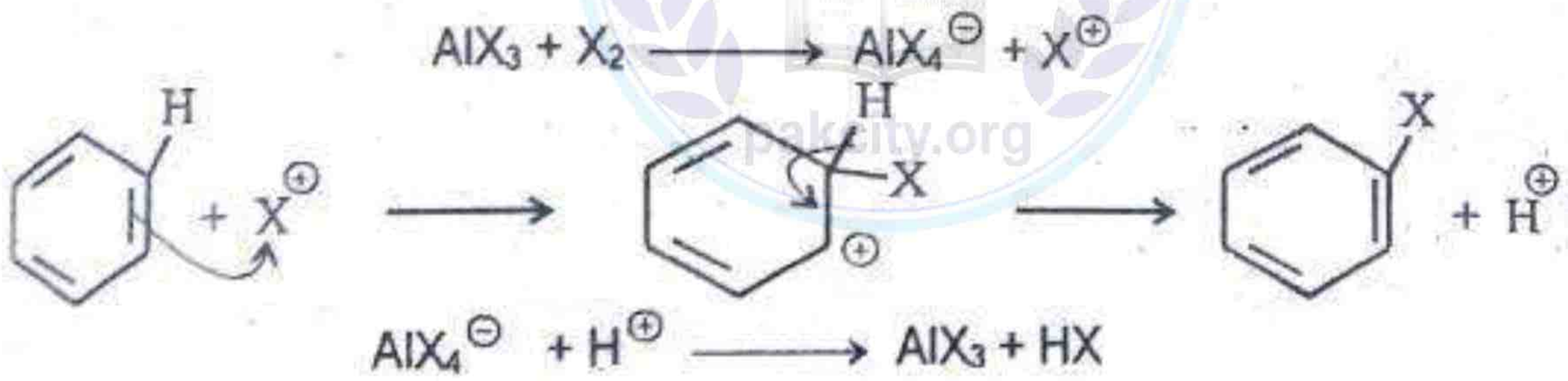
Ans:



Benzene is formed by passing ethyne under pressure over an organo-nickel catalystat 70°C.

24. Write down mechanism for Halogenation of benzene.

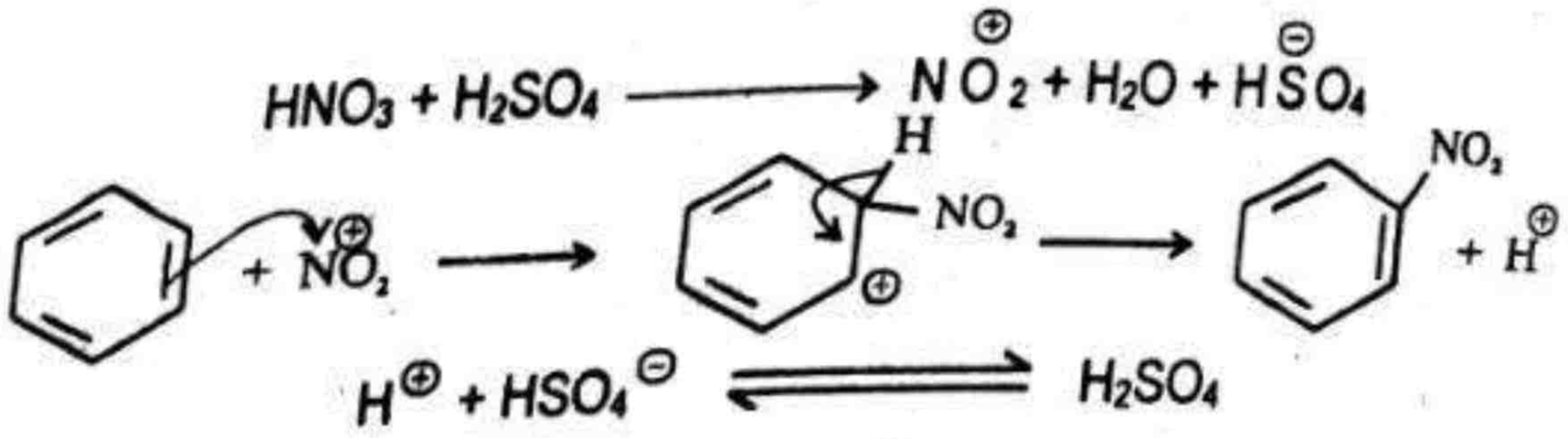
Ans:



25. Give mechanism for nitration of benzene. OR What is meant by nitration of benzene?

Ans: Introduction of nitro group in the benzene ring is called nitration of benzene. It takes placewhen benzene is heated with conc. HNO_3 and conc. H_2SO_4 at 50°C.

Mechanism:

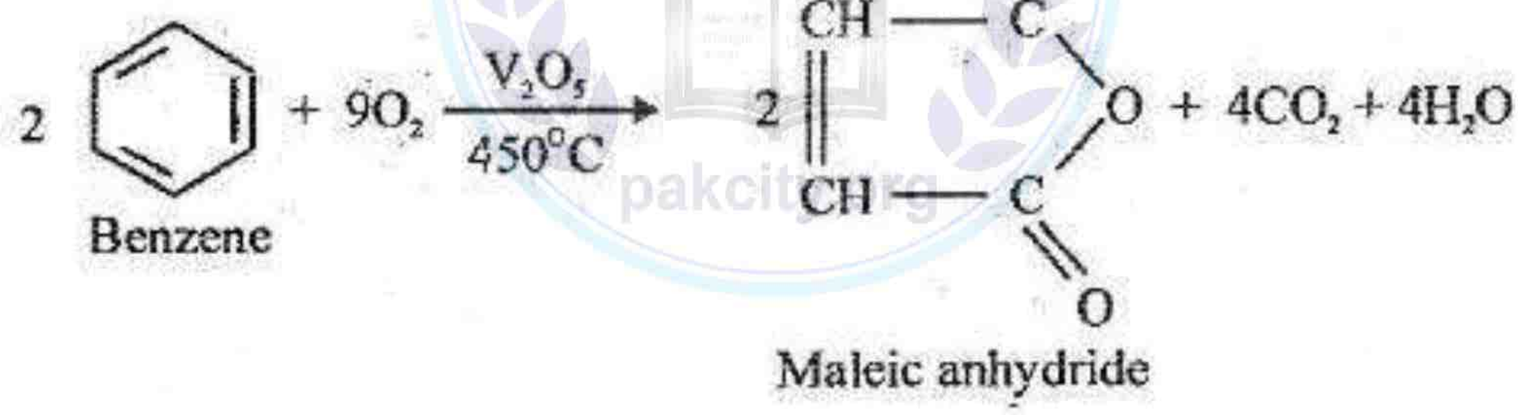


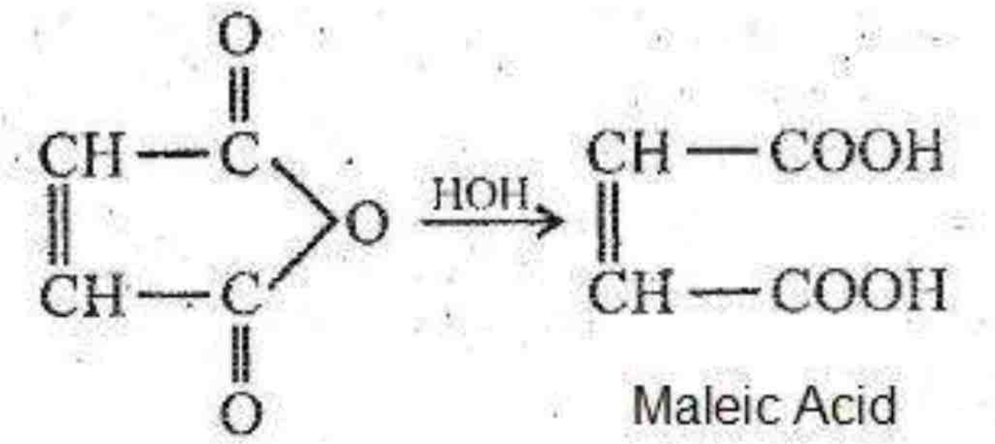
26. Give reaction of benzene with ozone.

Ans:

27. How benzene is converted into Maleic acid by catalytic oxidation?

Ans:





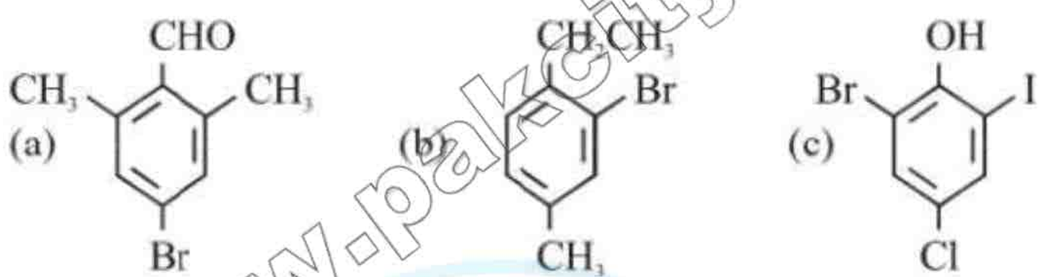
Maleic Acid

28. What happens when benzene is burnt in free supply air? Give equation.

Ans: When benzene is burnt in free supply of air, it is completely oxidized to CO_2 and H_20.

$$2C_6H_6 + 15O_2 \text{ -------> } 12CO_2 + 6H_2O$$

29. Write IUPAC names of the following molecules:



Ans:

(a) 4-bromo-2, 6-dimethyl benzaldehyde

(b) 3-bromo-4-ethyl toluene

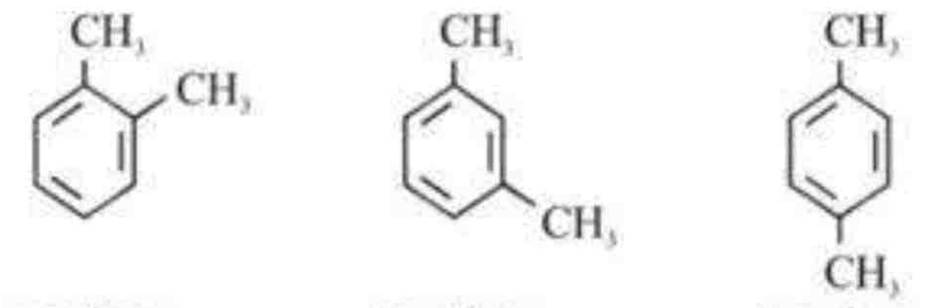
(c) 6-bromo-4-chloro-2-iodophenol

30. Give names and possible isomeric structures of the following:

(i) Xylenes ***(ii) Trimethylbenzene*** ***(iii) Bromonitrotoluene***

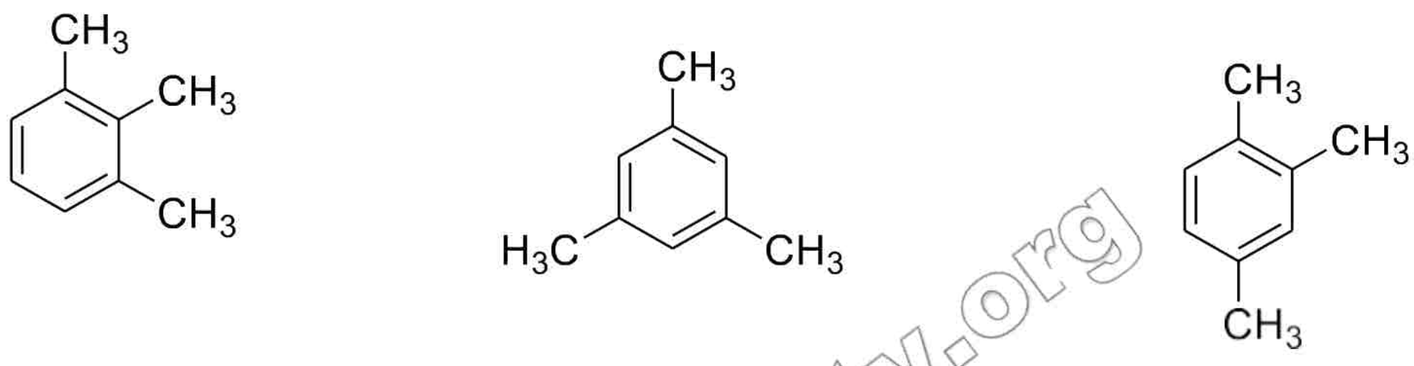
Ans:

(i) Xylenes



o-xylene m-xylene p-xylene

(ii) Trimethylbenzene



(iii) Bromonitrotoluene

31. Draw structural formulas for the following compounds:

(i) m-chlorobenzoic acid **(ii) p-hydroxybenzoic acid**

(iii) o-bromonitrobenzene **(iv) o-ethyltoluene**

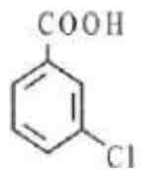
(v) p-nitroaniline **(vi) 2, 4, 6 trinitrotoluene**

(vii) m-nitrophenol **(viii) p-dibenzylbenzene**

(ix) 2-amino-5-bromo-3 nitrobenzenesulphonic acid

Ans:

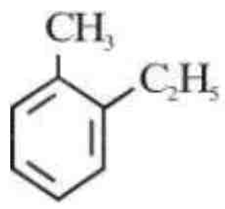
(i)



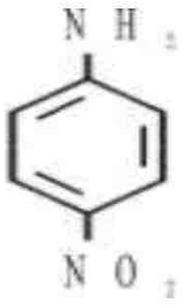
(ii)

(iii)

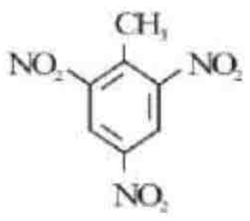
(iv)



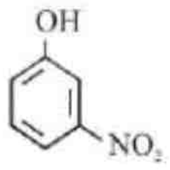
(v)



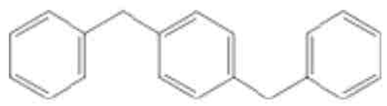
(vi)



(vii)



(viii)



(ix)

32. What is meant by the terms:

(i) Aromatic (ii) Oxidation (iii) Sulphonation (iv) Nitration

(v) Halogenation

Ans:

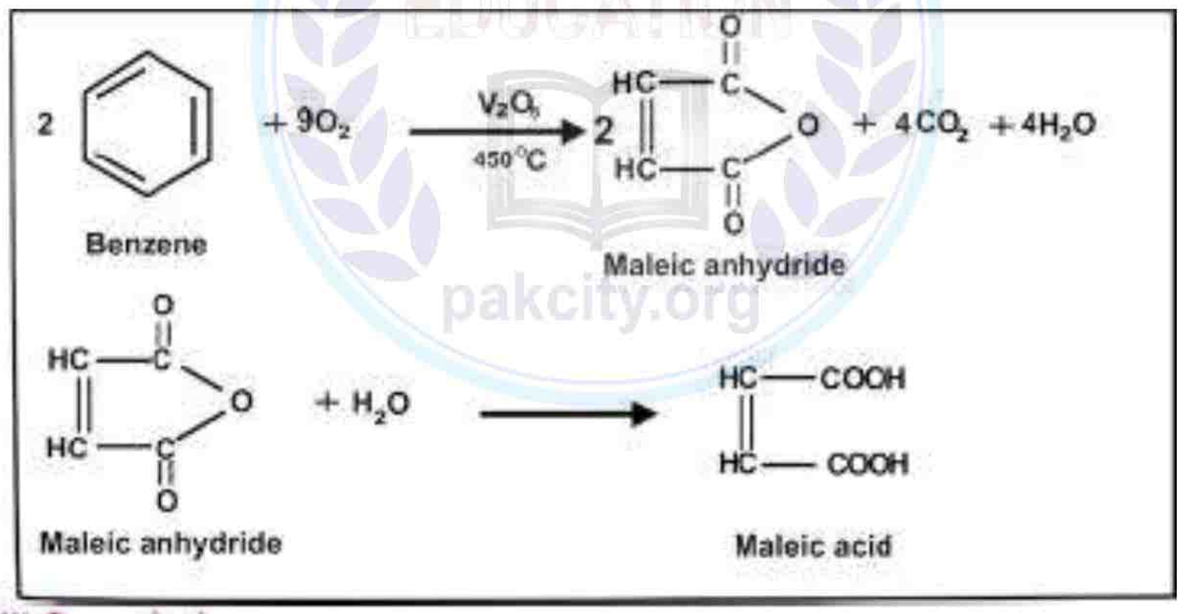
(i) Aromatic

The term aromatic was derived from the Greek word 'aroma' meaning "fragrant" and was used in Organic Chemistry for a special class of compounds which contain benzene ring in their structure. Example

Toluene

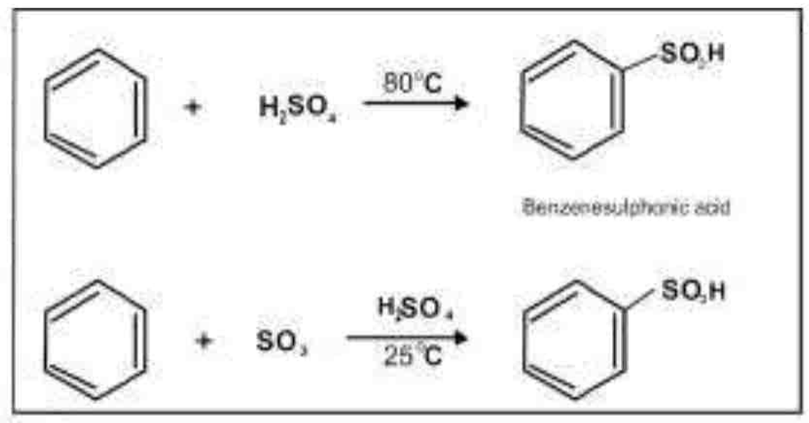
(ii) Oxidation

Oxidation is a process by which a carbon atom gains bonds to more electronegative elements, most commonly oxygen. Benzene is not oxidized by $KMnO_4$ or $K_2Cr_2O_7$ at room temperature. The ring is destroyed when benzene is strongly heated with air in the presence of V_2O_5 as a catalyst.



(iii) Sulphonation

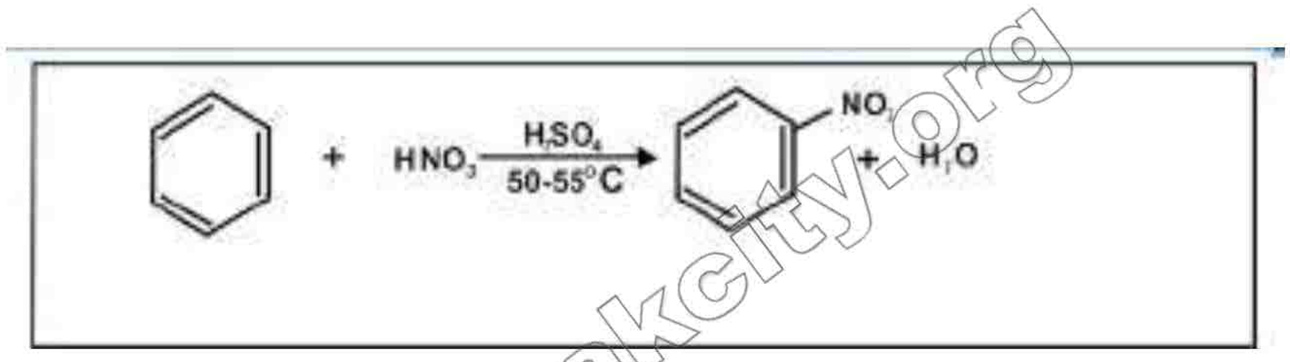
The introduction of sulphonic acid group in benzene ring is called Sulphonation. When benzene is heated with fuming H_2SO_4 or conc. H_2SO_4 it yields benzene sulphonic acid.



Formation of benzenesulphonic acid

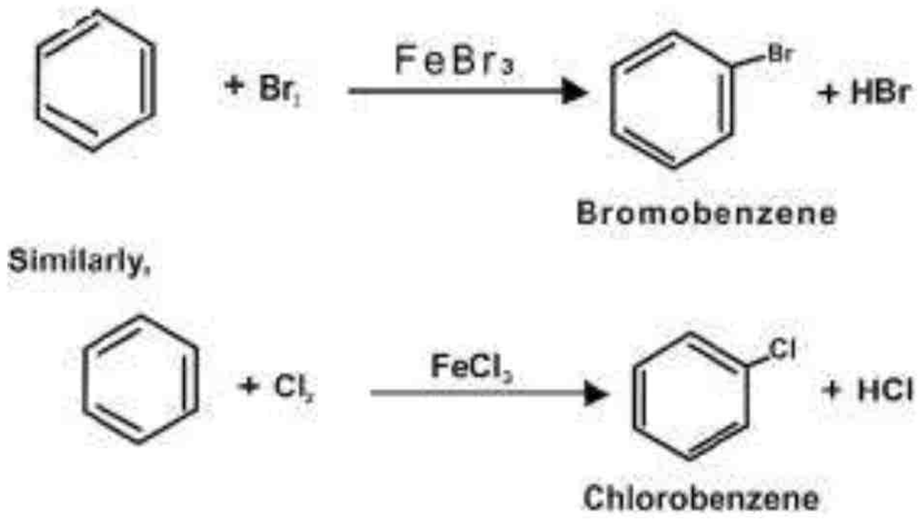
(iv) Nitration

The introduction of NO_2 group in benzene ring is called "Nitration". The nitration of benzene takes place when it is heated with a 1:1 mixture of con. HNO_3 and conc.H_2SO_4 at 50- 55°C. Sulphuric acid reacts with nitric acid to generate nitronium ion, (NO_2^+).



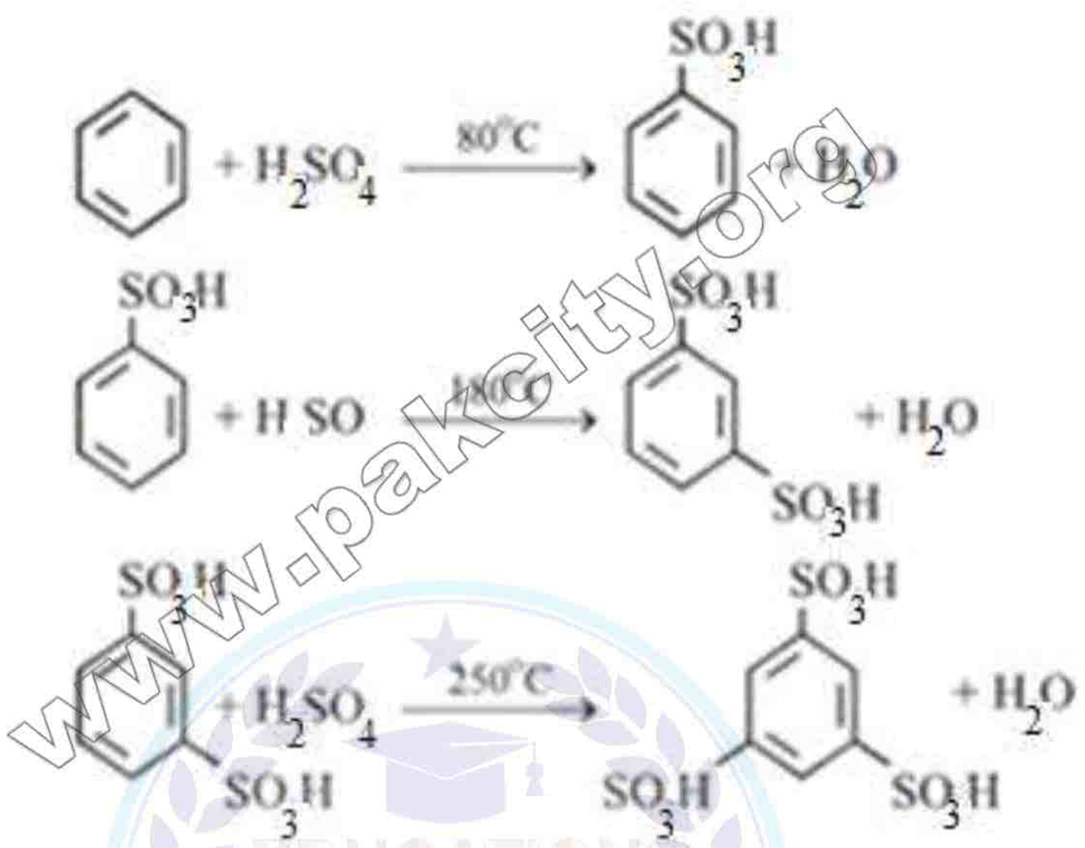
(v) Halogenation

The introduction of halogen group in benzene ring is called "Halogenation" Benzene reacts with halogen in the presence of a catalyst like $FeBr_3$, $AlCl_3$, etc. Chlorination and bromination are normal reactions but fluorination is too vigorous to control. Iodination gives poor yield.



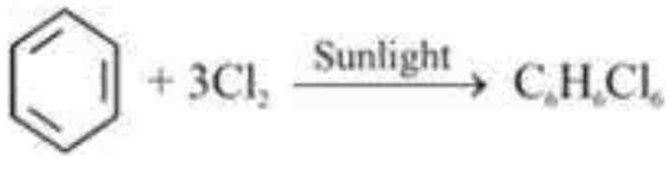
33. What happens when benzene is heated with conc. H_2SO_4 at 250 ^oC?

Ans:



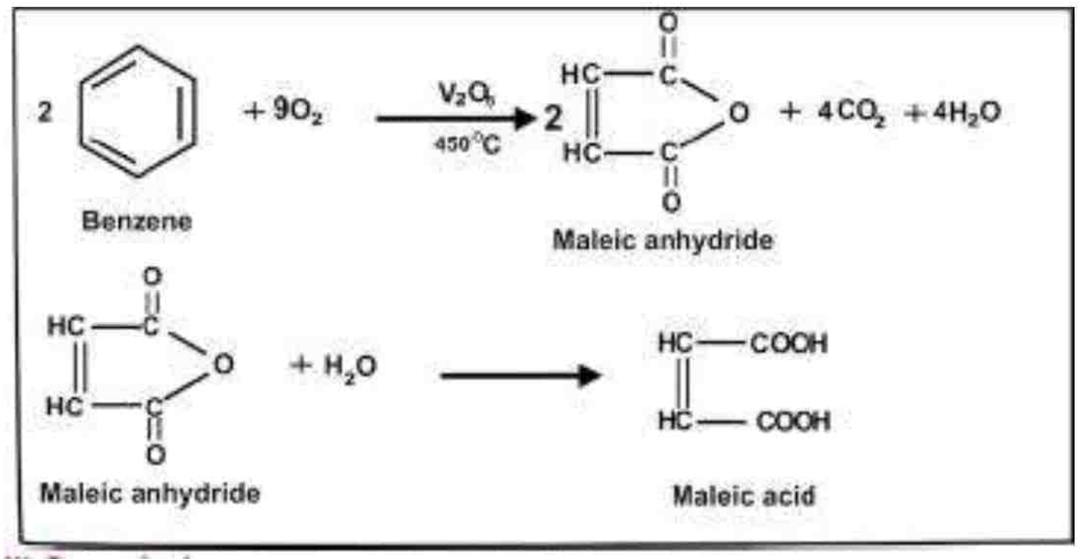
34. What happens when chlorine is passed through benzene in sunlight?

Ans:



35. What happens when a mixture of benzene vapours and air are passed over heated vanadium pentaoxide?

Ans:



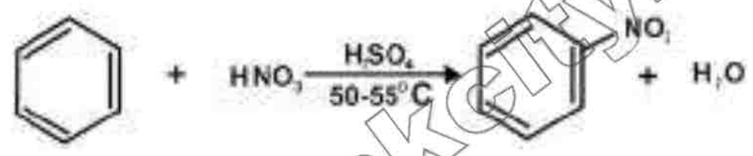
36. What happens when benzene is burnt in free supply of air?

Ans:

$$2C_6H_6 + 15\ O_2 \longrightarrow 12\ CO_2 + 6H_2O$$

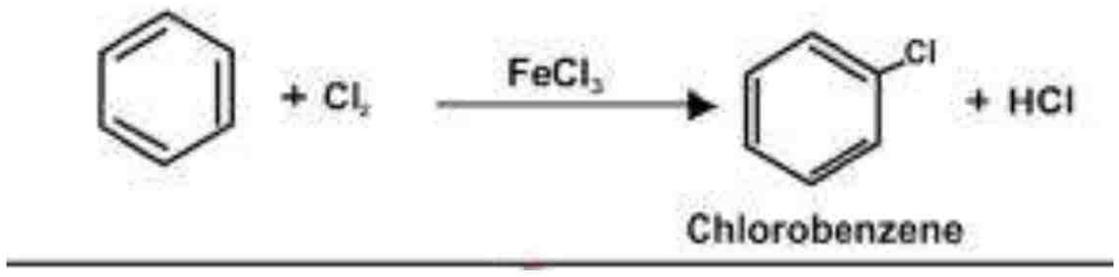
37. How will you prepare m-chloronitrobenzene from benzene in two steps?

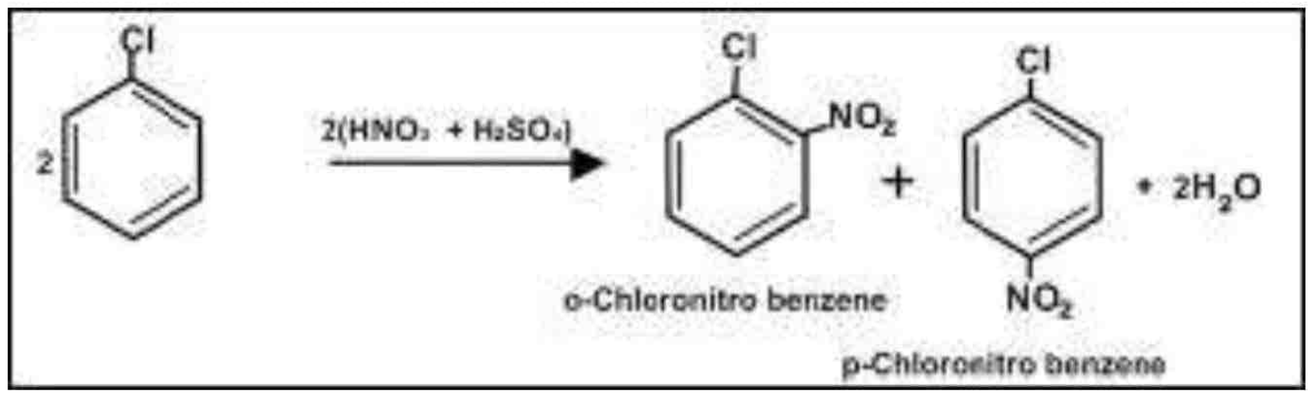
Ans:



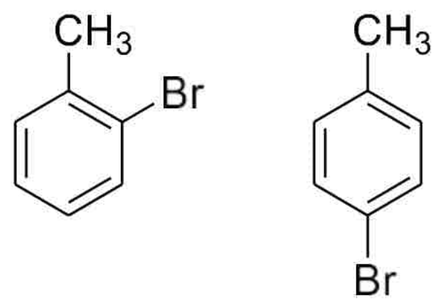
38. How will you prepare p-chloronitrobenzene from benzene in two steps?

Ans:





39. ***Predict the major products of bromination of toluene***



Ans:

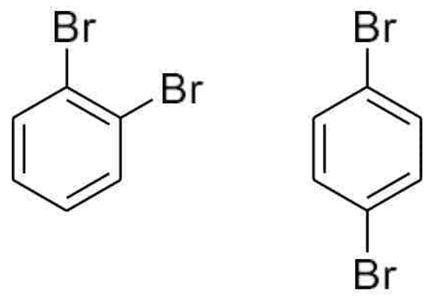
Write complete equation

40. ***Predict the major products of bromination of nitrobenzene***

Ans:

Write complete equation

41. ***Predict the major products of bromination of bromobenzene***



Ans:

Write complete equation

42. ***Predict the major products of bromination of benzoic acid***

Ans:

Write complete equation

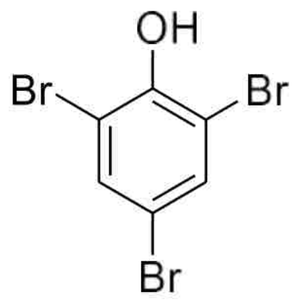
43. Predict the major products of bromination of benzaldehyde

Ans:

Write complete equation

44. Predict the major products of bromination of phenol

Ans:



Write complete equation