

## CHEMISTRY

### CHAPTER- HYDROCARBONS (I PUC)

#### One mark questions

1. What type of structural isomerism is shown by alkanes?
2. Which metal is used in Wurtz reaction?
3. What happens when isopropyl bromide is subjected to Wurtz reaction?
4. What is the nature of mechanism of halogenation of alkanes?
5. Which conformation of ethane is most stable?
6. Can propane show chain isomerism?
7. Why are alkenes reactive in nature?
8. What is the state of hybridization of carbon atoms in ethene?
9. Which of the following show geometrical isomerism?  
 $\text{CHCl} = \text{CHCl}$ ;  $\text{CH}_2 = \text{CCl}_2$ ;  $\text{CCl}_2 = \text{CHCl}$
10. Name the halogen used to test unsaturation in a hydrocarbon?
11. Is peroxide effect applicable addition of HCl to propene? Give reason.
12. What is Bayer's reagent?
13. What is Lindlar's catalyst?
14. Name the reaction which locates the position of the double bond?
15. Give the tests to show that the given compound is an unsaturated compound.
16. Why alkynes does not show geometrical isomerism?
17. What happens when ethyne is hydrated with dilute solution of  $\text{HgSO}_4$  and  $\text{H}_2\text{SO}_4$ ?
18. Name the product formed when vapours of ethyne are passed through HCl solution?
19. Name the product when ethyne is reduced with Na in liquid ammonia?
20. What happens when vapours of ethyne are passed into red hot iron?
21. What is the nature of structure of benzene?
22. Why does benzene resist addition reactions?
23. Which catalyst is used in Friedel-Crafts reaction?
24. Name two ortho and two meta directing groups in benzene?
25. What is the nature of substitution in benzene?
26. Who gave the present cyclic structure of benzene?
27. Which electrophile is formed during nitration of benzene?
28. What does LNG stand for?
29. Which hydrocarbon is main constituent of CNG?

#### Two mark questions

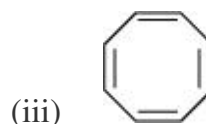
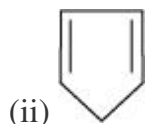
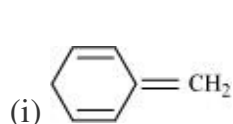
1. What is cracking / pyrolysis?
2. Write a short note on isomerization of alkanes?
3. Identify the products X and Y of the following reactions:  
$$\text{Y} \xleftarrow{\text{Na} + \text{NH}_3, \text{ heat}} \text{but-2-yne} \xrightarrow{\text{H}_2 / \text{Pd/BaSO}_4, \text{ Heat}} \text{X}$$

4. How will you prepare benzene from sodium benzoate?
5. What happens when benzene reacts with acetyl chloride in presence of  $\text{AlCl}_3$ .  
Represent in form of chemical reaction .
6. Write the conditions necessary for geometrical isomerism
7. Which one is more polar, cis-but-2-ene or trans-but-2-ene and why?
8. Write the name of ozonolysis products of but-1-ene.
9. What happens when alk. $\text{KMnO}_4$  is added to ethene? Write the reaction and the use of this reaction.
10. How is acetylene prepared on commercial scale?
11. Name the functional group of the compound prepared by reaction of propyne with water in presence of mercuric salt and sulphuric acid.
12. State Markovnikov's rule.
13. Name the acid whose sodium salt is required for the preparation of propane? Write chemical equation for the reaction.
14. Explain Wurtz reaction with an example. Where is it used?
15. Define decarboxylation with an example.
16. Name the type of reactions which alkanes undergo. Give one example also.
17. Define conformation.
18. What happens when ethanol is heated with conc. $\text{H}_2\text{SO}_4$ ?
19. Define hydrogenation.
20. Draw the Newman's projection of ethane.
21. Benzene despite having 3 double bonds is exceptionally stable. Explain.
22. Benzene undergoes electrophilic substitution reactions easily and nucleophilic substitutions with difficulty. Explain.
23. List the names of Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.
24. Define hydrocarbons.
25. What do you understand by torsional angle? Which of the conformations of ethane has the maximum and the minimum torsional strain?
26. What are the drawbacks of Kekulé's structure of benzene?
27. Draw the sawhorse projections of ethane
28. Which is more acidic among the following compounds, benzene, n-hexane and ethyne Arrange them in the decreasing order of acidic behaviour. Also give reason for this behaviour.

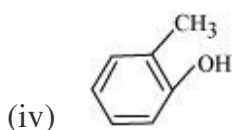
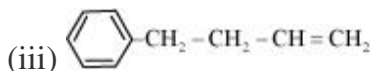
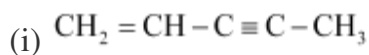
### Three or four mark questions

- 1) An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write the structure and IUPAC name of alkene 'A'.
- 2) Out of benzene, m-dinitrobenzene and toluene which will undergo nitration most easily and why?

- 3) Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.
- 4) State Huckel's rule. Draw the structure of Pyridine and Furan. Are these aromatic?
- 5) Explain the mechanism involved in the chlorination of methane.
- 6) Explain whether the following systems are aromatic or not?



- 7) Write IUPAC names of the following compounds:



- 8) Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.
- 9) Write chemical reactions for the following conversions:
  - (i) Phenol to benzene
  - (ii) Benzene to ethyl benzene
- 10) How do you convert the following?
  - (i) Benzene to p-nitrotoulene
  - (ii) Benzene to acetophenone
  - (iii) Benzene to m-chloronitrobenzene
- 11) Discuss the orbital structure of benzene.

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### CHAPTER- HYDROCARBONS (I PUC)

#### Answers : One mark questions:

- 1) Chain isomerism
- 2) Sodium
- 3) 2,3-dimethyl butane
- 4) Free radical mechanism
- 5) Staggered conformation
- 6) No
- 7) Due to the presence of pi bond in carbon to carbon double bond
- 8)  $sp^2$  hybridisation
- 9)  $CHCl = CHCl$
- 10) Bromine
- 11) No. Free radical is not formed due to high bond dissociation energy of HCl
- 12) Dilute alkaline potassium permanganate solution.
- 13) Pd supported over barium sulphate or calcium carbonate poisoned with quinoline or sulphur.
- 14) Ozonolysis
- 15)
  - a. Bayer's test
  - b. Bromination
- 16) As they are linear in nature.
- 17) Ethanal is formed.
- 18) 1,1-dichloroethane
- 19) Trans-2-butene
- 20) Benzene.
- 21) Planar
- 22) Due to delocalization of pi electron charge.
- 23) Anhydrous aluminium chloride
- 24) Ortho directing groups -- OH,  $NH_2$

Meta directing groups --- CHO, NO<sub>2</sub>

25) Electrophilic substitution

26) Kekule

27) Nitronium ion

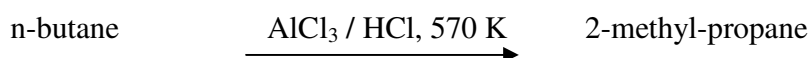
28) Liquefied natural gas

29) Methane.

**Answers: Two mark questions**

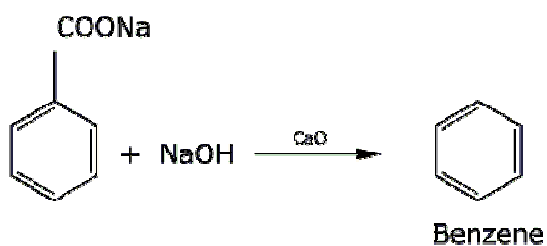
1) The decomposition of higher alkane into a mixture of lower alkanes , alkenes etc by the application of heat is called pyrolysis / cracking.

2) When unbranched alkanes are heated with anhydrous aluminium chloride and hydrogen chloride isomeric branched alkanes are formed. This process is called isomerization

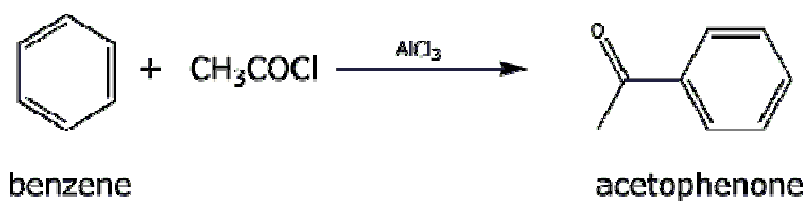


3) X is Cis-but-2-ene ; Y is trans-but-2-ene

4)



5)



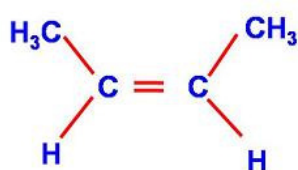
6) Conditions necessary for geometrical isomerism:

All compounds containing carbon-carbon double bonds do not show geometrical isomerism.

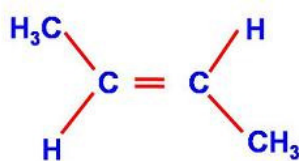
The molecules must contain a double bond.

Each of the two carbon atoms of the double bond must have different substituents which may be same or different.

7)



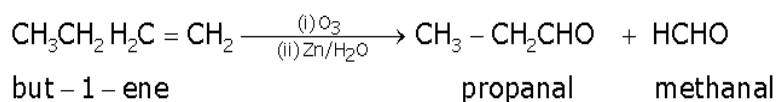
**cis but-2-ene**



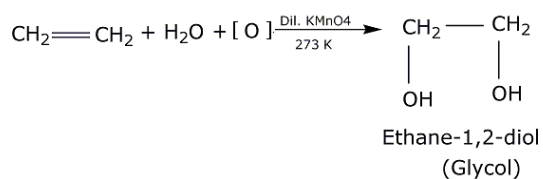
**trans but-2-ene**

Due to the occurrence of both methyl groups on the same side of the C=C bond, the combined effect of the two polar bonds makes cis-but-2-ene much more polar than trans-but-2-ene.

8)

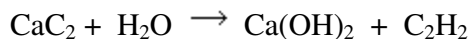


9)



It is used to test for unsaturation.

- 10) On commercial scale, acetylene is prepared by reaction of calcium carbide with water.

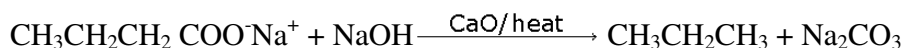


- 11) Ketone

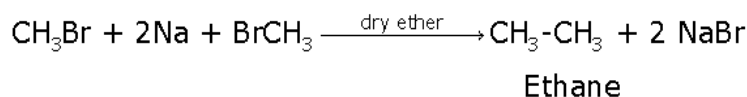


- 12) Markovnikov's rule states that, negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

- 13) Sodium salt of butanoic acid is required for the preparation of propane.

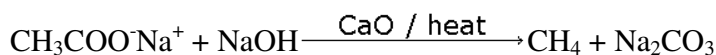


- 14) Alkyl halides on treatment with sodium metal in dry ether solution give higher alkanes. This reaction is known as Wurtz reaction.



This reaction is used for the preparation of higher alkanes containing even number of carbon atoms.

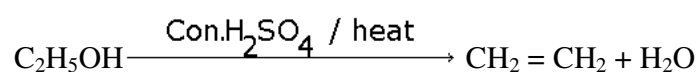
- 15) Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid. This elimination of carbon dioxide from a carboxylic acid is known as decarboxylation.



16) Alkanes undergo free radical substitution. The examples of this category are halogenation, nitration and sulphonation.

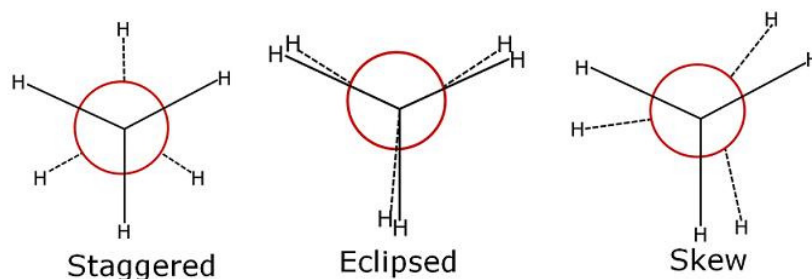
17) The spatial arrangements, which are obtained by free rotation around sigma bonds, are called conformation or conformational isomers.

18) Ethene is obtained.



19) Hydrogenation is a process of adding hydrogen to unsaturated compounds, e.g., vegetable oils are unsaturated compounds which are converted into ghee by hydrogenation.

20)



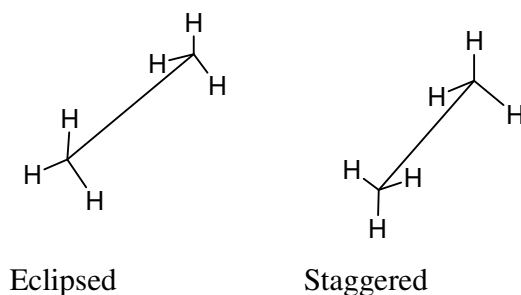
21) Benzene is exceptionally stable due to resonance. The delocalised electrons cause resonance which in turn makes it stable.

22) Benzene is a planar molecule having delocalized electrons above and below the plane of ring. Hence, it is electron-rich. As a result, it is highly attractive to electron deficient species i.e., electrophiles. Therefore, it undergoes electrophilic substitution reactions very easily. Nucleophiles are electron-rich. Hence, they are repelled by benzene. Hence, benzene undergoes nucleophilic substitutions with difficulty.

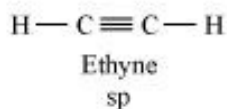
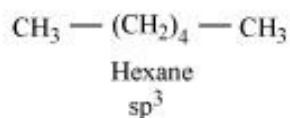
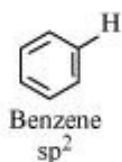


- 23) Any Lewis acid like anhydrous  $\text{FeCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{BF}_3$  etc. can be used during the ethylation of benzene.
- 24) Organic compounds containing only hydrogen and carbons are called hydrocarbons.
- 25) The repulsive interaction between the electron clouds, which affects stability of a conformation, is called torsional strain. Magnitude of torsional strain depends upon the angle of rotation about C-C bond. This angle is called dihedral angle or torsional angle. Of all the conformations of ethane, the staggered form has the least torsional strain and the eclipsed form has the maximum torsional strain.
- 26)
- Unusual stability of benzene.
  - According to Kekule, two ortho disubstituted products are possible. But in practice only one ortho disubstituted product is known.
  - Heat of hydrogenation of benzene is 49.8 kcal/mole, whereas theoretical value of heat of hydrogenation of benzene is 85.8 kcal/mole. It means resonance energy is 36 kcal/mole.
  - C - C bond length in benzene are equal, (although it contains 3 double bonds and 3 single bonds) and are 1.39 Å.

27)



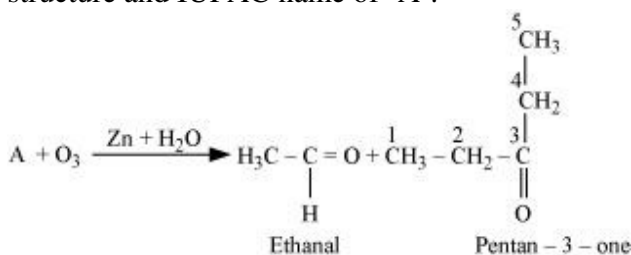
28)



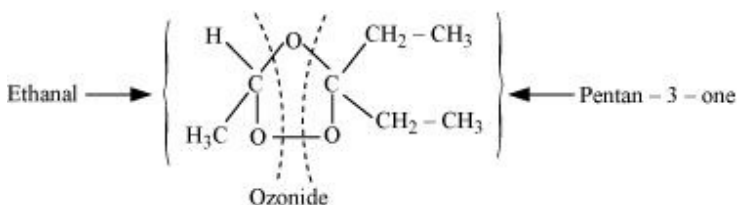
As the  $s$ -character increases, the electronegativity of carbon increases and the electrons of C–H bond pair lie closer to the carbon atom. As a result, partial positive charge of H-atom increases and  $H^+$  ions are set free. The  $s$ -character increases in the order:  $sp^3 < sp^2 < sp$ . Hence, the decreasing order of acidic behaviour is Ethyne > Benzene > Hexane.

**Answers: Three marks / four marks questions**

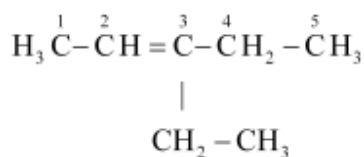
1) An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.



During ozonolysis, an ozonide having a cyclic structure is formed as an intermediate which undergoes cleavage to give the final products. Ethanal and pentan-3-one are obtained from the intermediate ozonide. Hence, the expected structure of the ozonide is:



This ozonide is formed as an addition of ozone to 'A'. The desired structure of 'A' can be obtained by the removal of ozone from the ozonide. Hence, the structural formula of 'A' is:

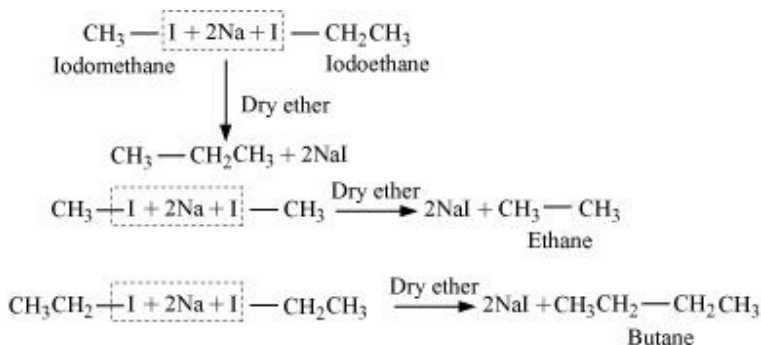


The IUPAC name of 'A' is 3-Ethylpent-2-ene.

2) Nitration reactions are examples of electrophilic substitution reactions

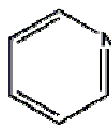
where an electron-rich species is attacked by a nitronium ion ( $\text{NO}_2^+$ ). Now,  $\text{CH}_3-$  group is electron donating and  $\text{NO}_2-$  is electron withdrawing. Therefore, toluene will have the maximum electron density among the three compounds followed by benzene. On the other hand, m- dinitrobenzene will have the least electron density. Hence, it will undergo nitration with difficulty.

3) Wurtz reaction cannot be used for the preparation of unsymmetrical alkanes because if two dissimilar alkyl halides are taken as the reactants, then a mixture of alkanes is obtained as the products. Since the reaction involves free radical species, a side reaction also occurs to produce an alkene. For example, the reaction of bromomethane and iodoethane gives a mixture of alkanes.

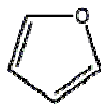


The boiling points of alkanes (obtained in the mixture) are very close. Hence, it becomes difficult to separate them.

4) Huckel's rule states that, compounds that have  $(4n + 2)\pi$  -electrons, are said to be Aromatic compounds, where  $n = 1, 2, 3, 4, \dots$  etc.



**Pyridine**



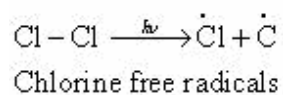
**Furan**

Pyridine is aromatic because it follows Huckel's rule and has 6 pi electrons where  $n=1$ . Furan is also aromatic compound because one of the lone pair of electrons at the oxygen delocalise towards benzene ring and then it follows Huckel's rule where  $n=1$ .

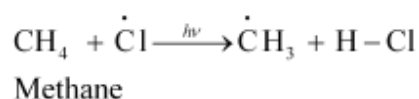
5) Chlorination of methane proceeds via a free radical chain mechanism. The whole reaction takes place in the given three steps.

**Step 1: Initiation:**

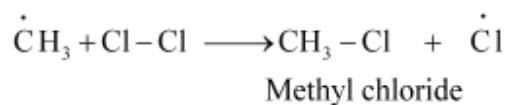
The reaction begins with the homolytic cleavage of Cl – Cl bond as:

**Step 2: Propagation:**

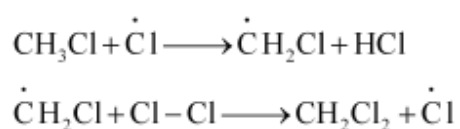
In the second step, chlorine free radicals attack methane molecules and break down the C–H bond to generate methyl radicals as:



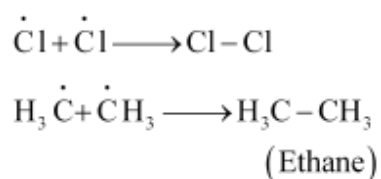
These methyl radicals react with other chlorine free radicals to form methyl chloride along with the liberation of a chlorine free radical.



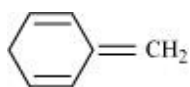
Hence, methyl free radicals and chlorine free radicals set up a chain reaction. While HCl and CH<sub>3</sub>Cl are the major products formed, other higher halogenated compounds are also formed as:

**Step 3: Termination:**

Formation of ethane is a result of the termination of chain reactions taking place as a result of the consumption of reactants as:



6) (i)



For the given compound, the number of  $\pi$ -electrons is 6. By Huckel's rule,

$$4n + 2 = 6; 4n = 4; n = 1$$

For a compound to be aromatic, the value of  $n$  must be an integer ( $n = 0, 1, 2, \dots$ ). Since the value of  $n$  is an integer, the given compound is aromatic in nature.

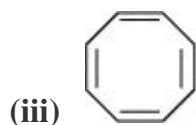
(ii)



For the given compound, the number of  $\pi$ -electrons is 4.

By Huckel's rule,  $4n + 2 = 4; 4n = 2;$  
$$n = \frac{1}{2}$$

For a compound to be aromatic, the value of  $n$  must be an integer ( $n = 0, 1, 2, \dots$ ), which is not true for the given compound. Hence, it is not aromatic in nature.



For the given compound, the number of  $\pi$ -electrons is 8.

By Huckel's rule,  $4n + 2 = 8; 4n = 6;$  
$$n = \frac{3}{2}$$

For a compound to be aromatic, the value of  $n$  must be an integer ( $n = 0, 1, 2, \dots$ ). Since the value of  $n$  is not an integer, the given compound is not aromatic in nature.

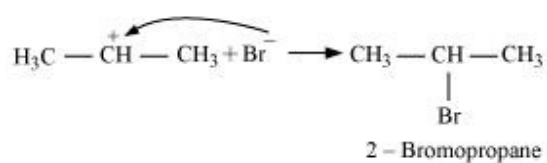
7) (i) Pen-1-ene-3-yne

(ii) Buta-1,3-diene

(iii) 4-Phenyl but-1-ene

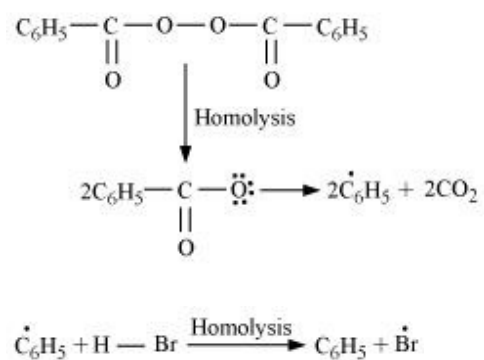
(iv) 2-Methyl phenol

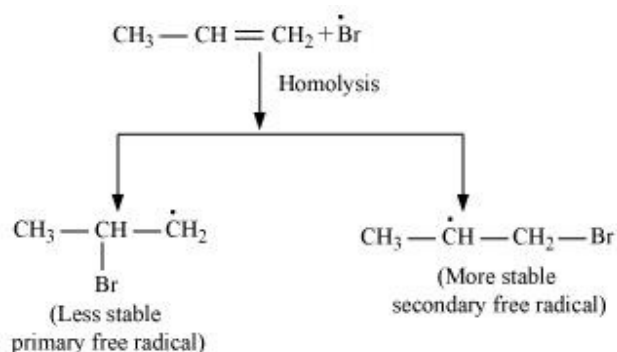
8)



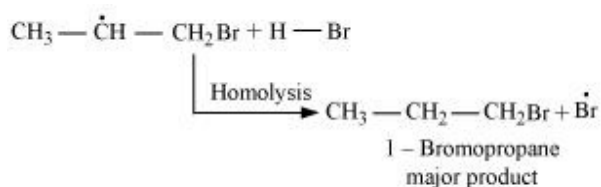
This reaction follows Markovnikov's rule where the negative part of the addendum is attached to the carbon atom having a lesser number of hydrogen atoms.

In the presence of benzoyl peroxide, an addition reaction takes place anti to Markovnikov's rule. The reaction follows a free radical chain mechanism as:



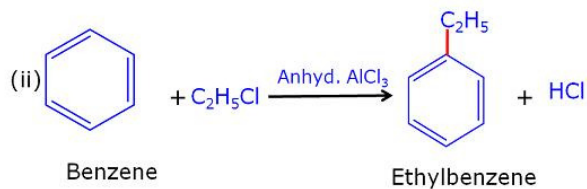
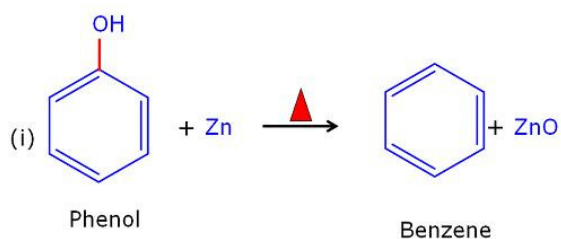


Secondary free radicals are more stable than primary radicals. Hence, the former predominates since it forms at a faster rate. Thus, 1 – bromopropane is obtained as the major product.

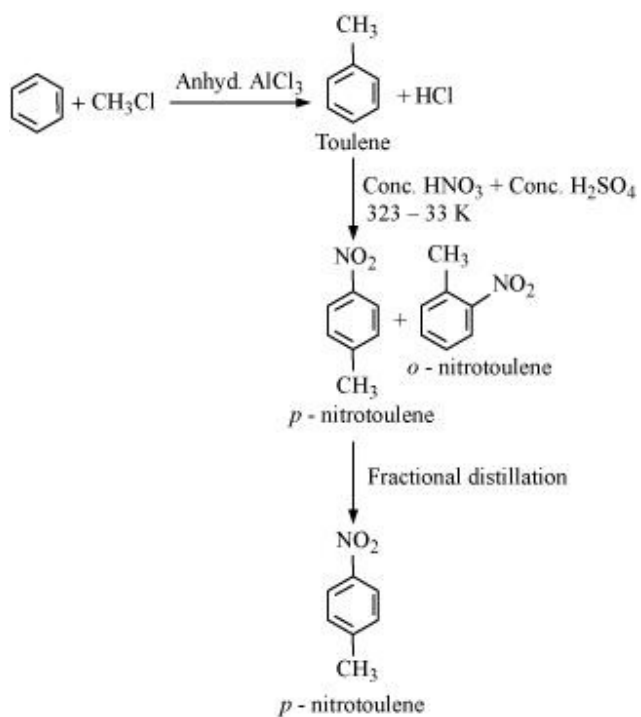


In the presence of peroxide, Br free radical acts as an electrophile. Hence, two different products are obtained on addition of HBr to propene in the absence and presence of peroxide.

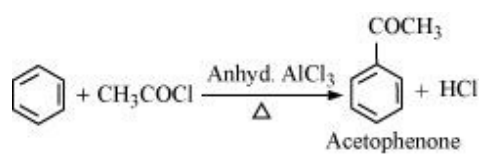
- 9) (i) Phenol into benzene.  
 (ii) Benzene into ethyl benzene.



- 10) (i) Benzene to p-nitro toluene

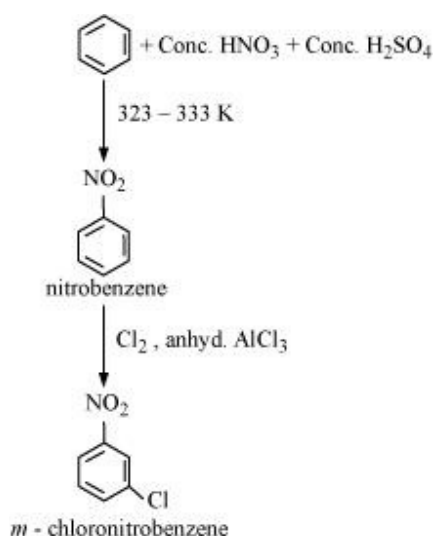


(ii) Benzene to acetophenone

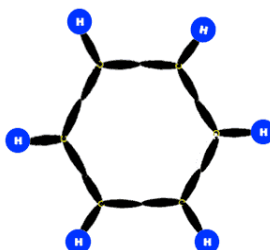


(iii) Benzene to m-chloronitrobenzene

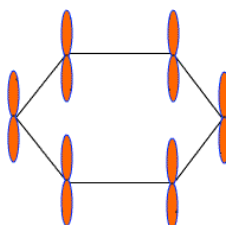




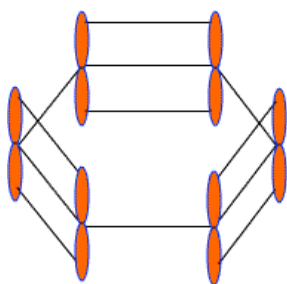
11) The structure of benzene molecule is best described in terms of molecular orbital treatment theory. According to this theory, all the C-atoms in benzene are  $\text{sp}^2$ -hybridized. Two  $\text{sp}^2$ -hybrid orbitals of each C-atom overlap with two  $\text{sp}^2$ -hybrid orbital of two other C-atoms to form sigma bonds. In this way there are six sigma bonds are formed between six C-atoms which are  $120^\circ$  apart. Remaining six  $\text{sp}^2$ -orbital of six C-atoms overlap with 1s orbital of six H-atoms individually to form six sigma bonds. Since sigma bond results from the overlap of above said planar orbital, all H and C atoms are in the same plane and their generate a hexagonal ring of C-atoms.



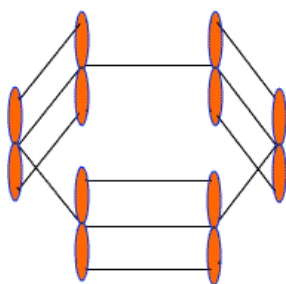
Each C-atom in benzene also has an unhybrid 2p<sub>z</sub>-orbital containing one electron. These 2p<sub>z</sub>-orbital are perpendicular to the plane of sigma bonds.



These 2p<sub>z</sub>-orbitals by lateral overlapping form three alternate pi-bonds in benzene ring. There are two possibilities of pi-bond formation in benzene.



OR



Actually these 2pz-orbital produce a pi-molecular orbital containing six electrons. One half of this pi- molecular orbital lies above the plane of hexagonal ring and remaining half below the ring like a sandwich.

