

## 13 ■ ■ ■

## Hydrocarbons

## I. MULTIPLE CHOICE QUESTIONS (TYPE-I)

1. Arrange the following in decreasing order of their boiling points.

- (A) *n*-butane (B) 2-methylbutane  
 (C) *n*-pentane (D) 2, 2-dimethylpropane  
 (i)  $A > B > C > D$  (ii)  $B > C > D > A$   
 (iii)  $D > C > B > A$  (iv)  $C > B > D > A$

Ans. (iv)

**Explanation:** Boiling point is directly proportional to molar mass and surface area. It decreases on branching because surface area decreases. Hence, *n*-pentane has the highest and *n*-butane has the lowest boiling points and in rest two branching is there, therefore, 2-methyl butane has higher boiling point than 2, 2-dimethylpropane.

2. Arrange the halogens  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ , in order of their increasing reactivity with alkanes.

- (i)  $I_2 < Br_2 < Cl_2 < F_2$  (ii)  $Br_2 < Cl_2 < F_2 < I_2$   
 (iii)  $F_2 < Cl_2 < Br_2 < I_2$  (iv)  $Br_2 < I_2 < Cl_2 < F_2$

Ans. (i)

**Explanation:** Fluorine is highly electronegative element. Electronegativity of halogens decreases down the group. As the electronegativity of halogens decreases, reactivity with alkanes, decreases. Therefore,  $F_2$  reacts vigorously and  $I_2$  reacts too slow.

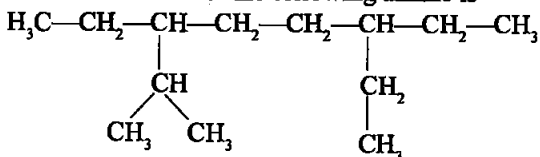
3. The increasing order of reduction of alkyl halides with zinc and dilute HCl is

- (i)  $R-Cl < R-I < R-Br$  (ii)  $R-Cl < R-Br < R-I$   
 (iii)  $R-I < R-Br < R-Cl$  (iv)  $R-Br < R-I < R-Cl$

Ans. (ii)

**Explanation:** The reactivity of halogens with alkane is  $F_2 > Cl_2 > Br_2 > I_2$ . Hence, reduction of alkyl halide with Zn / HCl follow reverse order. The reactivity of reduction increases as the bond strength of C—X decreases. It depends on the size of X. As the size of X increases, bond strength decreases and reactivity increases.

4. The correct IUPAC name of the following alkane is



- (i) 3, 6-Diethyl-2-methyloctane (ii) 5-Isopropyl-3-ethyloctane  
 (iii) 3-Ethyl-5-isopropyloctane (iv) 3-Isopropyl-6-ethyloctane

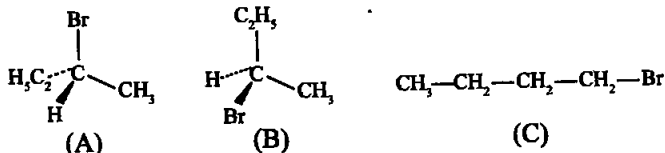
Ans. (i)

**Explanation:** The given alkane has the longest chain of 8 carbon atoms hence, it is Octane.

Side chain on carbon 2, 3 and 6 follow lowest sum rule.

On carbon 2-methyl, on carbon-3-and carbon-6-ethyl groups are present. Ethyl comes before methyl (alphabetically) and two ethyl groups are there. Hence the correct IUPAC name is 3, 6-Diethyl-2-methyloctane.

5. The addition of HBr to 1-butene gives a mixture of products A, B and C



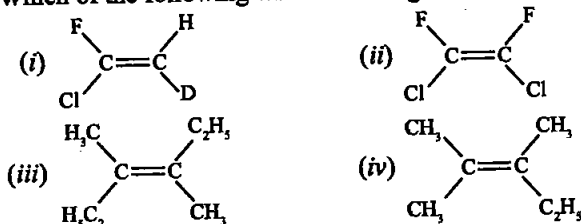
The mixture consists of

- A and B as major and C as minor products
- B as major, A and C as minor products
- B as minor, A and C as major products
- A and B as minor and C as major products

Ans. (i)

**Explanation:** Butene-1 is unsymmetrical, and according to Markovnikov's rule, 2-Bromobutane is major product and 1-Bromobutane is minor product. 2-Bromobutane has chiral carbon, hence it exists in two enantiomers which are mirror images of each other. Therefore, the mixture consists of A and B as major and C as minor product.

6. Which of the following will not show geometrical isomerism?



Ans. (iv)

**Explanation:** Geometrical isomerism is shown by the alkenes in which double bonded carbons must have different atoms or groups. In structure (iv), double bonded carbons have 3 groups same and one is different.

7. Arrange the following hydrogen halides in order of their decreasing reactivity with propene.

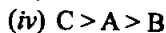
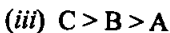
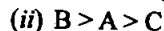
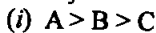
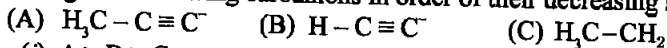
- $\text{HCl} > \text{HBr} > \text{HI}$
- $\text{HBr} > \text{HI} > \text{HCl}$
- $\text{HI} > \text{HBr} > \text{HCl}$
- $\text{HCl} > \text{HI} > \text{HBr}$

Ans. (iii)

**Explanation:** Reactivity of hydrogen halides depends upon bond dissociation energy and bond strength. As the size of halogen atom

increases in hydrogen halides, the bond strength decreases and bond dissociation energy also decreases. Therefore, the correct order of reactivity is  $\text{HI} > \text{HBr} > \text{HCl}$ .

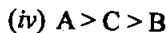
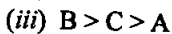
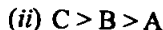
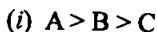
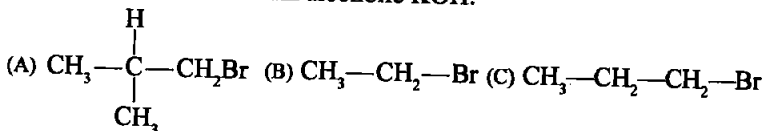
8. Arrange the following carbanions in order of their decreasing stability.



Ans. (ii)

**Explanation:** +I effect decreases the stability of carbon anion. Since  $\text{CH}_3$  group has +I effect. In B, there is no +I effect, in A, +I effect is there but distance is more from negatively charged carbon and in C, +I effect ( $\text{CH}_3$ ) direct to negatively charged carbon.

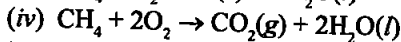
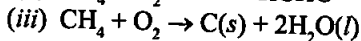
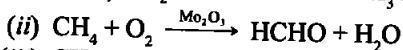
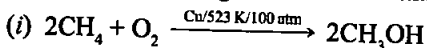
9. Arrange the following alkyl halides in decreasing order of the rate of  $\beta$ -elimination reaction with alcoholic KOH.



Ans. (iv)

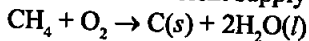
**Explanation:** Alkyl halides on heating with alc. KOH eliminates one molecule halogen acid and to form alkene. Hydrogen is eliminated from beta carbon atom. Nature of alkyl groups determines rate of reaction. Order of reactivity is  $3^\circ > 2^\circ > 1^\circ$  or  $\text{A} > \text{C} > \text{B}$ .

10. Which of the following reactions of methane is incomplete combustion?



Ans. (iii)

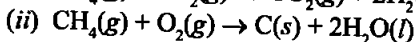
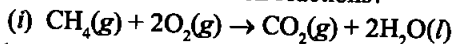
**Explanation:** During incomplete combustion carbon black is formed. It takes place when there is insufficient supply of air or oxygen.

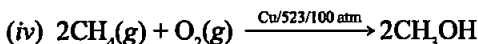
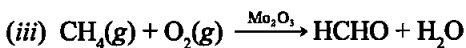


## II. MULTIPLE CHOICE QUESTIONS (TYPE-II)

In the following questions two or more options may be correct.

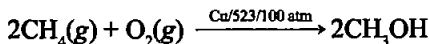
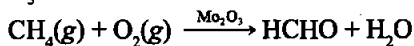
11. Some oxidation reactions of methane are given below. Which of them is/are controlled oxidation reactions?



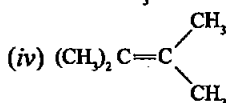
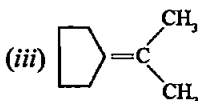
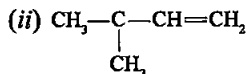
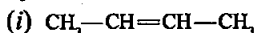


Ans. (iii) and (iv)

**Explanation:** Alkanes on combustion give  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Combustion in insufficient supply of air or  $\text{O}_2$  give carbon black and water. Alkanes, on heating with regular supply of oxygen or in controlled way give  $\text{HCHO}$  and  $\text{CH}_3\text{OH}$ .



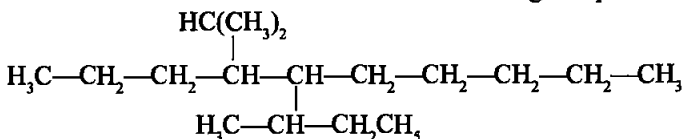
12. Which of the following alkenes on ozonolysis give a mixture of ketones only?



Ans. (iii) and (iv)

**Explanation:** Alkenes on ozonolysis give two molecules of carbonyl compounds depending upon groups or atoms attached to double bonded carbon atoms. If double bonded carbon atoms have alkyl groups then ketones are formed.

13. Which are the correct IUPAC names of the following compound?



(i) 5-Butyl-4-isopropyldecane

(ii) 5-Ethyl-4-propyldecane

(iii) 5-sec-Butyl-4-iso-propyldecane

(iv) 4-(1-methylethyl)-5-(1-methylpropyl)-decane

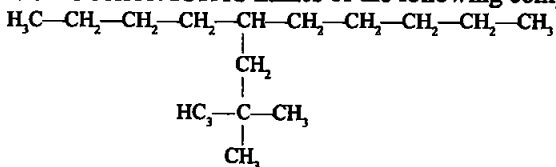
Ans. (iii) and (iv)

**Explanation:** The compound has the longest chain of 10 carbon atoms. Side chains are on 4th and 5th carbon atoms according to lowest sum rule. On C 4, there is isopropyl group, and on C 5, sec-Butyl group. In IUPAC system, isopropyl is named as 1-Methylethyl group, sec-Butyl group is named as 1-Methylpropyl group. Hence, the names of organic compound are—

(iii) 5-sec-Butyl-4-iso-propyldecane

(iv) 4-(1-methylethyl)-5-(1-methylpropyl)-decane

14. Which are the correct IUPAC names of the following compound?



- (i) 5-(2', 2'-Dimethylpropyl)-decane  
 (ii) 4-Butyl-2, 2-dimethylnonane  
 (iii) 2,2-Dimethyl-4-pentyl-octane  
 (iv) 5-*neo*-Pentyldecane

Ans. (i) and (iv)

**Explanation:** The given compound has the longest chain of ten carbon atoms and side chain is present on 5th carbon atom. Side chain of 5 carbon atoms is *neo*-Pentyl and in IUPAC system it is 2', 2'-Dimethylpropyl. Hence, the names of the compound are

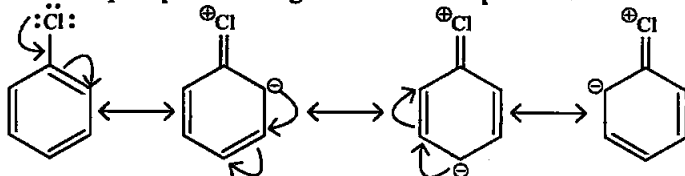
- (i) 5-(2', 2'-Dimethylpropyl)-decane  
 (iv) 5-*neo*-Pentyldecane

15. For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring \_\_\_\_\_.

- (i) deactivates the ring by inductive effect  
 (ii) deactivates the ring by resonance  
 (iii) increases the charge density at ortho and para position relative to meta position by resonance  
 (iv) directs the incoming electrophile to meta position by increasing the charge density relative to ortho and para position.

Ans. (i) and (iii)

**Explanation:** Halogen atom present on benzene ring shows +R effect and increases electron density on ortho and para position and direct electrophile on ortho and para positions. Halogen being more electronegative pulls the electron from benzene due to -I effect and decreases electron density but due to resonance the electron density on ortho and para positions is greater than meta position.



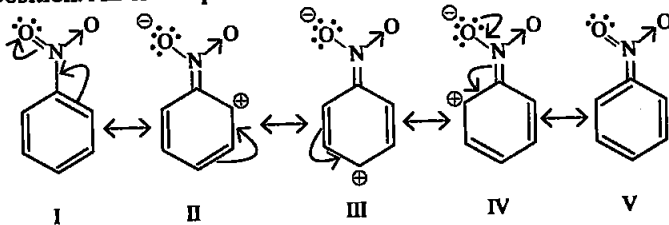
16. In an electrophilic substitution reaction of nitrobenzene, the presence of nitro group \_\_\_\_\_.

- (i) deactivates the ring by inductive effect.  
 (ii) activates the ring by inductive effect.

- (iii) decreases the charge density at ortho and para position of the ring relative to meta position by resonance.  
 (iv) increases the charge density at meta position relative to the ortho and para positions of the ring by resonance.

Ans. (i) and (iii)

**Explanation:** Nitro group deactivates the benzene ring due to  $-I$  effect and decreases electron density at ortho and para positions than meta position. An electrophile attacks on meta position.



17. Which of the following are correct?

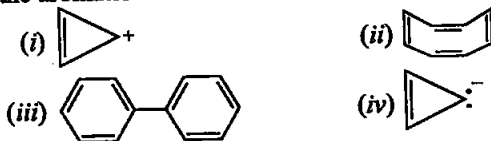
- (i)  $\text{CH}_3\text{—O—CH}_2^\oplus$  is more stable than  $\text{CH}_3\text{—CH}_2^\oplus$   
 (ii)  $(\text{CH}_3)_2\text{CH}^\oplus$  is less stable than  $\text{CH}_3\text{—CH}_2\text{—CH}_2^\oplus$   
 (iii)  $\text{CH}_2=\text{CH—CH}_2^\oplus$  is more stable than  $\text{CH}_3\text{—CH}_2\text{—CH}_2^\oplus$   
 (iv)  $\text{CH}_2=\text{CH}^\oplus$  is more stable than  $\text{CH}_3\text{—CH}_2^\oplus$

Ans. (i) and (iii)

**Explanation:**  $+I$  effect increases stability of carbocation. In (i),  $+I$  effect of  $\text{CH}_3\text{—O}$  is greater than  $\text{—CH}_3$ . Hence,  $\text{CH}_3\text{—O—CH}_2^\oplus$  is more stable than  $\text{CH}_3\text{—CH}_2^\oplus$ .

In (iii),  $\text{CH}_2=\text{CH—CH}_2^\oplus \leftrightarrow \text{}^+\text{CH}_2\text{—CH=CH}_2$  is stabilized by resonance effect. While  $\text{CH}_3\text{—CH}_2\text{—CH}_2^\oplus$  is stabilized by  $+I$  effect of  $\text{—C}_2\text{H}_5$  group. Resonance effect is stronger than  $+I$  effect. Hence,  $\text{CH}_2=\text{CH—CH}_2^\oplus$  is more stable than  $\text{CH}_3\text{—CH}_2\text{—CH}_2^\oplus$ .

18. Four structures are given in options (i) to (iv). Examine them and select the aromatic structures.



Ans. (i) and (iii)

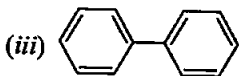
**Explanation:** Aromaticity requires following conditions:

- (a) Planarity  
 (b) Complete delocalisation of the  $\pi$  electrons in the ring  
 (c) Presence of  $(4n + 2)$   $\pi$  electrons in the ring where  $n$  is an integer ( $n = 0, 1, 2, \dots$ ). This is often referred to as **Hückel Rule**.

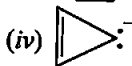
(i)  $n = 0$ , planar,  $\pi$  electrons = 2



$\pi$  electrons = 8, not planar,  $n$  = not integer



planar,  $\pi$  electrons =  $(4n + 2) = 6$  in each ring



planar,  $n$  = not integer

Therefore, (i) and (iii) are aromatic structures.

19. The molecules having dipole moment are \_\_\_\_\_.

(i) 2, 2-Dimethylpropane      (ii) *trans*-Pent-2-ene

(iii) *cis*-Hex-3-ene      (iv) 2, 2, 3, 3 - Tetramethylbutane.

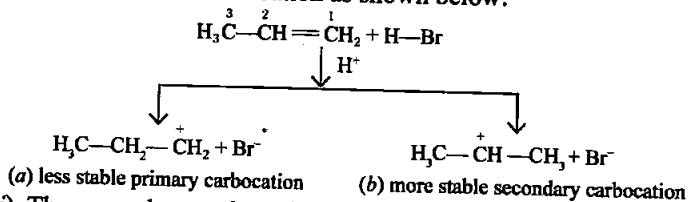
Ans. (ii) and (iii)

**Explanation:** *trans*-Pent-2-ene shows net dipole moment because of different groups attached and *cis*-Hex-3-ene shows dipole moment because both  $C_2H_5$  groups are inclined to each other at an angle of  $60^\circ$  so, has resultant dipole moment.

### III. SHORT ANSWER TYPE

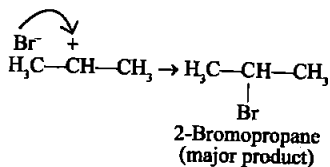
20. Why do alkenes prefer to undergo electrophilic addition reaction while arenes prefer electrophilic substitution reactions? Explain.

Ans. Alkenes have  $\pi(\pi)$  electrons, due to which they show electrophilic addition reaction. HBr provides an electrophile  $H^+$  which attacks the double bond to form carbocation as shown below:

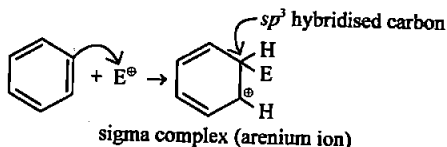


(i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.

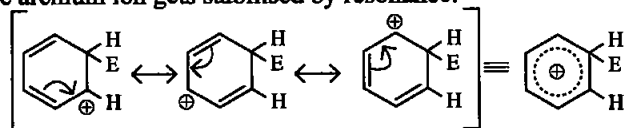
(ii) The carbocation (b) is attacked by  $Br^-$  ion to form the product as follows.



In arenes, due to delocalized  $(4n + 2)$   $\pi$  electrons, electrophilic substitution takes place.

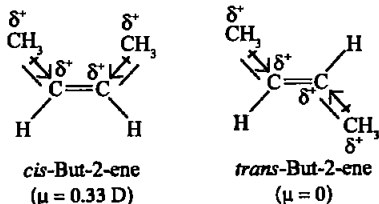


The arenium ion gets stabilised by resonance:



21. Alkynes on reduction with sodium in liquid ammonia form trans alkenes. Will the butene thus formed on reduction of 2-butyne show the geometrical isomerism?

Ans. On reduction of butyn-2, Butene-2 is formed in which either both the methyl groups are in the same side or opposite side to show geometrical isomers.

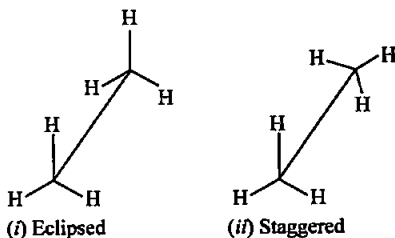


22. Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

Ans. Alkanes contain carbon-carbon sigma ( $\sigma$ ) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C-C bond which is not disturbed due to rotation about its axis. This permits free rotation about C-C single bond. This rotation results into different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called **conformations** or **conformers** or **rotamers**. Alkanes can have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of  $1\text{-}20 \text{ kJ mol}^{-1}$  due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called **torsional strain**.

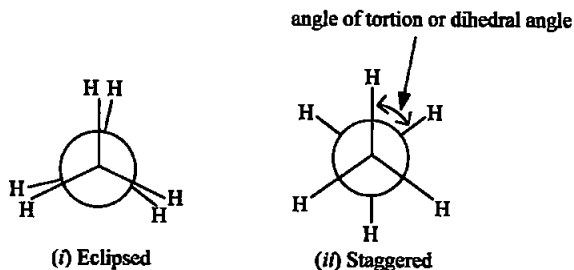
23. Draw Newman and Sawhorse projections for the eclipsed and staggered conformations of ethane. Which of these conformations is more stable and why?

Ans.



**Sawhorse projections of ethane**



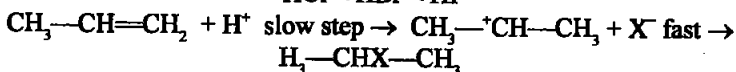


### Newman's projection of ethane

**Stability of conformation:** In staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon-hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. Staggered form is more stable.

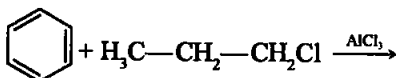
24. The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is  $430.5 \text{ kJ mol}^{-1}$ ,  $363.7 \text{ kJ mol}^{-1}$  and  $296.8 \text{ kJ mol}^{-1}$  respectively. What will be the order of reactivity of these halogen acids?

**Ans.** Hydrogen halides (HCl, HBr, HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is  $\text{HI} > \text{HBr} > \text{HCl}$ . Reactivity of HX depends on bond dissociation enthalpy of HX. Bond enthalpy of HI ( $296.8 \text{ kJ mol}^{-1}$ )  $<$  HBr ( $363.7 \text{ kJ mol}^{-1}$ )  $<$  HCl ( $430.5 \text{ kJ mol}^{-1}$ ) is in this order hence the reactivity is in reverse order:

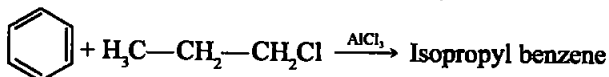
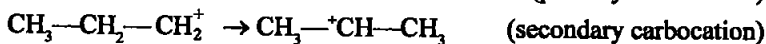


Slow step is rate determining step and it depends on the availability of  $\text{H}^+$ . Availability of  $\text{H}^+$  depends on bond dissociation enthalpy of HX.

25. What will be the product obtained as a result of the following reaction and why?



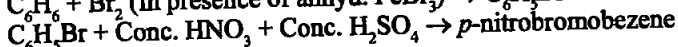
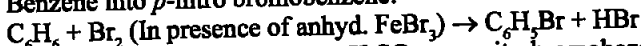
**Ans.**  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{Cl} + \text{AlCl}_3 \rightarrow \text{AlCl}_4^- + \text{CH}_3\text{—CH}_2\text{—CH}_2^+$   
(primary carbocation)



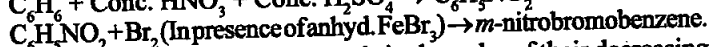
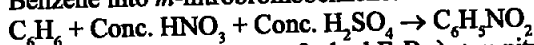
When Friedel-Crafts alkylation takes place with higher alkyl halide in which primary carbocation is formed first and convert into secondary carbocation which is more stable and formed by rearrangement therefore product is isopropylbenzene.

26. How will you convert benzene into (i) *p*-nitrobromobenzene  
(ii) *m*-nitrobromobenzene?

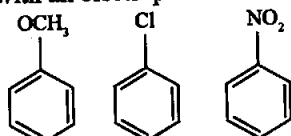
Ans. (i) Benzene into *p*-nitro bromobenzene:



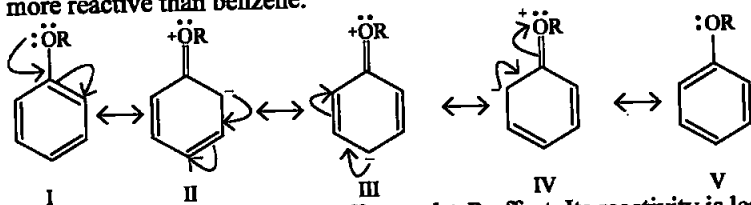
(ii) Benzene into *m*-nitrobromobenzene:



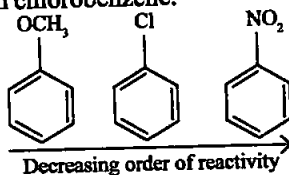
27. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile. Give reason.



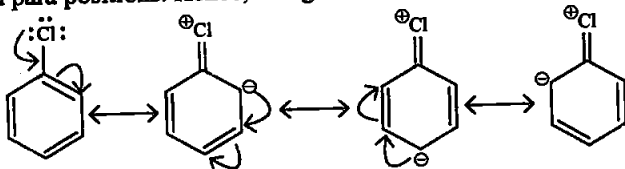
Ans. The methoxy group ( $-OCH_3$ ) is electron releasing group and increases electron density of benzene ring due to +R effect. Hence it makes anisole more reactive than benzene.



In case of Cl group it gives  $-I$  effect and +R effect. Its reactivity is less than methoxybenzene.  $-NO_2$  group gives  $-I$  effect and  $-R$  effect so it is less reactive than chlorobenzene.

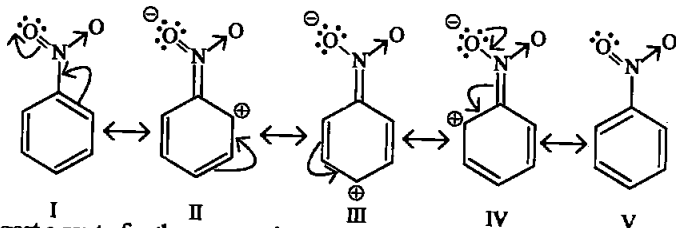


28. Despite their  $-I$  effect, halogens are *o*- and *p*-directing in haloarenes. Explain.  
Ans. Halogens present on benzene ring have  $-I$  and +R effect,  $-I$  effect deactivates the ring but +R effect increases the electron density on ortho and para positions. Hence, halogens are ortho and para directing.



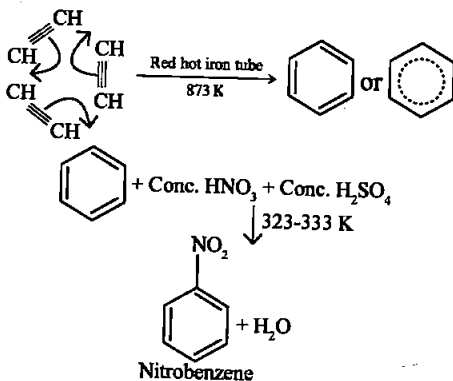
29. Why does presence of a nitro group make the benzene ring less reactive in comparison to the unsubstituted benzene ring. Explain.

Ans. Nitro group has  $-I$  and  $-R$  effect due to that benzene ring deactivates and electron density decreases on ortho and para positions as compared to meta positions.

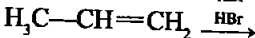
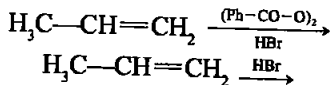


30. Suggest a route for the preparation of nitrobenzene starting from acetylene?

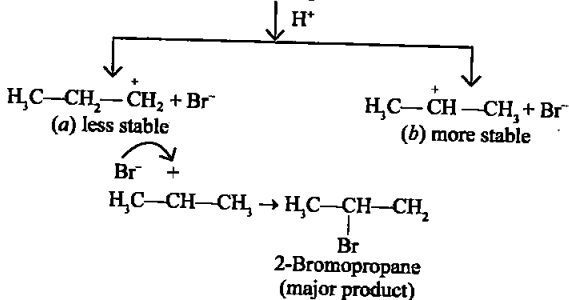
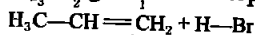
Ans. Ethyne when passed through red hot iron tube at 873 K undergoes cyclic polymerization to give benzene which upon subsequent nitration gives nitrobenzene.



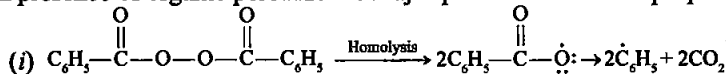
31. Predict the major product (s) of the following reactions and explain their formation.



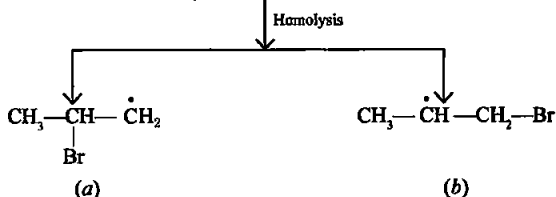
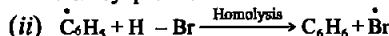
Ans. Addition of HBr to propene gives 2-Bromopropane.



In presence of organic peroxide the major product is 1-Bromopropane.

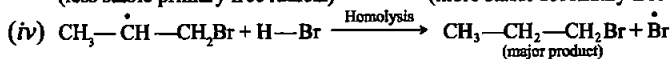


Benzoyl peroxide

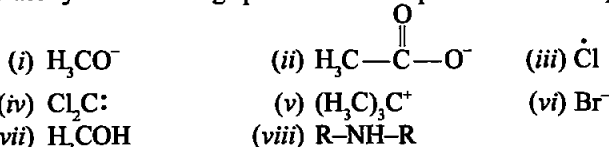


(less stable primary free radical)

(more stable secondary free radical)



32. Nucleophiles and electrophiles are reaction intermediates having electron rich and electron deficient centres respectively. Hence, they tend to attack electron deficient and electron rich centres respectively. Classify the following species as electrophiles and nucleophiles.



Ans. Electrophiles are electron seeking species or electron deficient species. These species may be neutral or positively charged.

(iii)  $\dot{\text{Cl}}$  (iv)  $\text{Cl}_2\text{C} \cdot$  (v)  $(\text{H}_3\text{C})_3\text{C}^+$  are electrophiles.

Nucleophiles are electron rich species and may be neutral or negatively charged.

(i)  $\text{H}_3\text{CO}^-$  (ii)  $\text{CH}_3\text{COO}^-$  (vi)  $\text{Br}^-$  (vii)  $\text{CH}_3\text{OH}$  (viii)  $\text{R}-\text{NH}-\text{R}$  are nucleophiles.

33. The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1 : 3.8 : 5. Calculate the percentages of all monochlorinated products obtained from 2-methylbutane.

Ans. In 2-methylbutane, there are 9 primary hydrogen, 2 secondary and 1 tertiary hydrogen atoms. The relative reactivity of 1°, 2° and 3° hydrogen atoms towards chlorination is 1: 3.8: 5.

Relative amount of product after chlorination = number of hydrogen atom X relative reactivity

Relative Amount	1°halide	2°halide	3° halide
	$9 \times 1 = 9$	$2 \times 3.8 = 7.6$	$1 \times 5 = 5$

Total amount of monochloro product =  $9 + 7.6 + 5 = 21.6$

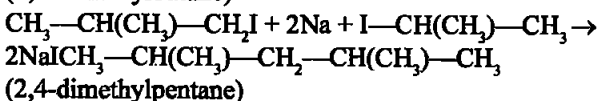
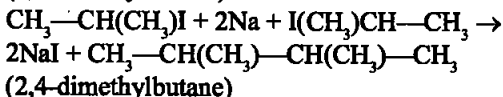
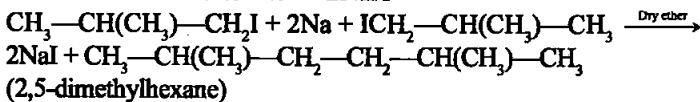
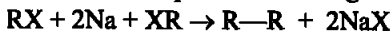
Percentage of 1° monochloro product =  $9 \times 100/21.6 = 41.7\%$

Percentage of 2° monochloro product =  $7.6 \times 100/21.6 = 35.2\%$

Percentage of 3° monochloro product =  $5 \times 100/21.6 = 23.1\%$

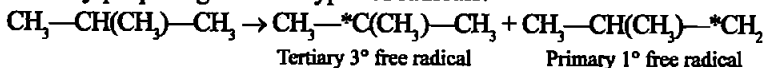
34. Write the structures and names of products obtained in the reactions of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane.

Ans. Products obtained are based on Wurtz reaction. *n*-alkyl halide on treatment with Na metal in presence of ether gives alkane having double carbon atoms.



35. Write hydrocarbon radicals that can be formed as intermediates during monochlorination of 2-methylpropane? Which of them is more stable? Give reasons.

Ans. 2-methylpropane gives two types of radicals:



Tertiary 3° free radical is more stable because it has 9  $\alpha$  Hydrogen and due to hyperconjugation structures it is stabilized.

Primary 1° free radical is less stable because of only 1  $\alpha$  hydrogen and one hyperconjugative structure.

36. An alkane  $\text{C}_8\text{H}_{18}$  is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.

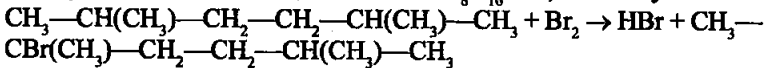
Ans.  $2\text{C}_4\text{H}_9\text{X} + 2\text{Na} \rightarrow \text{C}_8\text{H}_{16} + 2\text{NaI}$

$\text{C}_8\text{H}_{16} + \text{Br}_2 \rightarrow$  Single isomer of tertiary bromide.

$\text{C}_4\text{H}_9\text{X}$  can be *n*-Butyl halide =  $\text{CH}_3-(\text{CH}_2)_2-\text{CH}_2\text{X}$  (It is primary halide)

And  $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2\text{X}$

$2\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2\text{X} + 2\text{Na} \rightarrow 2\text{NaX} + \text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_3$ . This compound gives only one isomer of tertiary bromide. Therefore, the name of  $\text{C}_8\text{H}_{16}$  is 2,5-dimethylhexane.



2-Bromo 2,5-dimethylhexane.

37. The ring systems having following characteristics are aromatic.

(i) Planar ring containing conjugated  $\pi$  bonds.

- (ii) Complete delocalisation of the  $\pi$ -electrons in ring system i.e. each atom in the ring has unhybridised p-orbital, and  
 (iii) Presence of  $(4n + 2)$   $\pi$ -electrons in the ring where  $n$  is an integer ( $n = 0, 1, 2, \dots$ ) [Huckel rule].

Using this information classify the following compounds as aromatic/nonaromatic.



(A)



(B)



(C)



(D)



(E)










(F)

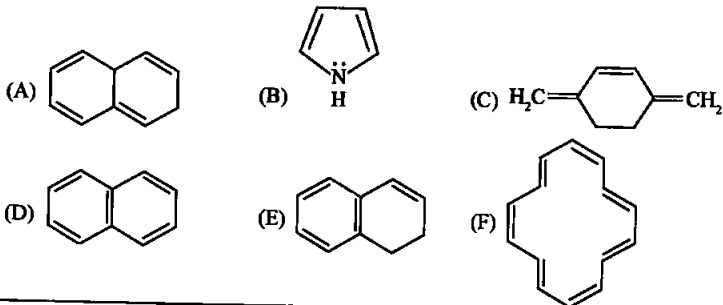


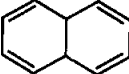
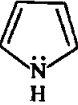

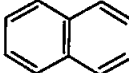
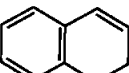
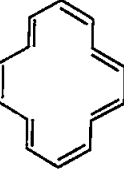
(G)

Ans.

 (A)	The ring is planar, has complete delocalisation of $\pi$ electrons, presence of $6\pi$ -electrons is there. It is aromatic.
 (B)	The ring is non-planar, has incomplete delocalisation of $\pi$ -electrons, presence of $6\pi$ -electrons is there. It is non-aromatic.
 (C)	The ring is planar, has complete delocalisation of $\pi$ -electrons, $6\pi$ -electrons are present. It is aromatic.
 (D)	The ring is planar, has incomplete delocalisation of $\pi$ -electrons, has $4\pi$ electrons. It is non-aromatic.
 (E)	The ring is planar, has complete delocalisation of $\pi$ -electrons, Huckel rule obeyed. It is aromatic.
 (F)	The ring is planar, has complete delocalisation of $\pi$ -electrons, Huckel rule obeyed. It is aromatic.
 (G)	The ring is planar, has incomplete delocalisation of $\pi$ -electrons, has $8\pi$ -electrons. It is non-aromatic.

38. Which of the following compounds are aromatic according to Huckel's rule?

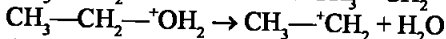
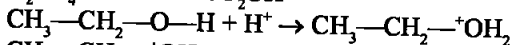
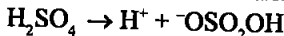


(A) 	The compound has $8\pi$ electrons. It is non aromatic.
(B) 	This compound has delocalised $6\pi$ electrons, follows Huckel rule. It is aromatic.
(C) 	In this compound $6\pi$ electrons are not present in the ring hence nonaromatic.
(D) 	It is aromatic obeying Huckel's rule. It has $10$ delocalised $\pi$ -electrons.
(E) 	It has $8\pi$ -electrons, out of which $6\pi$ -electrons are delocalised. Follows Huckel rule. It is aromatic.
(F) 	In this compound $14\pi$ electrons are in conjugation and in the planar ring. It is also aromatic. It follows Huckel's rule.

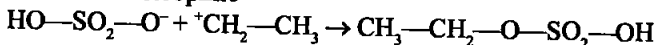
39. Suggest a route to prepare ethyl hydrogensulphate ( $\text{CH}_3\text{—CH}_2\text{—OSO}_2\text{—OH}$ ) starting from ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ).

Ans. Preparation of ethyl hydrogensulphate [ $\text{CH}_3\text{CH}_2\text{—OSO}_2\text{—OH}$ ] starting from ethanol.

**Step-1:** Protonation of alcohol and formation of carbocation



**Step-2:** Attack of nucleophile



#### IV. MATCHING TYPE

40. Match the reagent from Column I which on reaction with  $\text{CH}_3\text{—CH=CH}_2$  gives some product given in Column II as per the codes given below:

Column I	Column II
(i) $\text{O}_3/\text{Zn} + \text{H}_2\text{O}$	(a) Acetic acid and $\text{CO}_2$
(ii) $\text{KMnO}_4/\text{H}^+$	(b) Propan-1-ol
(iii) $\text{KMnO}_4/\text{OH}^-$	(c) Propan-2-ol
(iv) $\text{H}_2\text{O}/\text{H}^+$	(d) Acetaldehyde and formaldehyde
(v) $\text{B}_2\text{H}_6/\text{NaOH}$ and $\text{H}_2\text{O}_2$	(e) Propane-1, 2-diol

Ans. (i) → (d); (ii) → (a); (iii) → (e); (iv) → (c); (v) → (b)

**Explanation:**

Column I	Column II
(i) $\text{O}_3/\text{Zn} + \text{H}_2\text{O}$	On ozonolysis alkene gives two carbonyl compounds. $\text{CH}_3\text{—CH=CH}_2 + \text{O}_3 \rightarrow \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_3\text{—CH} \quad \text{CH}_2 \\   \quad   \\ \text{O} \quad \text{O} \\ \text{Propene ozonide} \end{array}$ $\downarrow \text{Zn} + \text{H}_2\text{O}$ $\text{CH}_3\text{CHO} + \text{HCHO}$ Ethanal      Methanal
(ii) $\text{KMnO}_4/\text{H}^+$	On reacting with $\text{KMnO}_4$ in acidic medium, propene gives $\text{CH}_3\text{COOH}$ and $\text{CO}_2$ . $\text{CH}_3\text{—CH=CH}_2 + \text{KMnO}_4/\text{H}^+ \rightarrow \text{CH}_3\text{COOH} + \text{CO}_2$
(iii) $\text{KMnO}_4/\text{OH}^-$	Propene decolourized the colour of alkaline $\text{KMnO}_4$ . $\text{CH}_3\text{—CH=CH}_2 + \text{H}_2\text{O} + \text{O} \xrightarrow[273\text{ K}]{\text{dil. KMnO}_4}$ $\text{CH}_3\text{CH(OH)CH}_2\text{OH}$ Propane-1, 2-diol
(iv) $\text{H}_2\text{O}/\text{H}^+$	Addition of $\text{H}_2\text{O}$ to propene gives propanol-2. $\text{CH}_3\text{—CH=CH}_2 + \text{H}^+/\text{OH}^- \rightarrow \text{CH}_3\text{—CH(OH)—CH}_3$
(v) $\text{B}_2\text{H}_6/\text{NaOH}$ and $\text{H}_2\text{O}_2$	Propanol-1 is formed. $\text{CH}_3\text{—CH=CH}_2 + (\text{H—BH}_2)_2 \rightarrow \begin{array}{c} \text{CH}_3\text{—CH—CH}_2 \\   \quad   \\ \text{H} \quad \text{BH}_2 \\ \downarrow \\ \text{CH}_3\text{—CH=CH}_2 \end{array}$ $(\text{CH}_3\text{—CH}_2\text{—CH}_2)_3\text{B} \xleftarrow{\text{CH}_3\text{—CH=CH}_2} (\text{CH}_3\text{—CH}_2\text{—CH}_2)_2\text{BH}$ $\text{H}_2\text{O} \downarrow 3\text{H}_2\text{O}_2, \text{OH}^-$ $3\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH} + \text{B(OH)}_3$ Propan-1-ol



41. Match the hydrocarbons in Column I with the boiling points given in Column II.

Column I	Column II
(i) <i>n</i> -Pentane	(a) 282.5 K
(ii) <i>iso</i> -Pentane	(b) 309 K
(iii) <i>neo</i> -Pentane	(c) 301 K

Ans. (i) → (b); (ii) → (c); (iii) → (a)

**Explanation:**

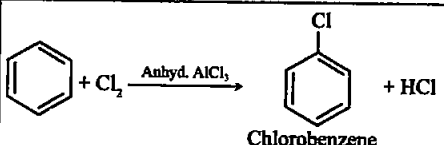
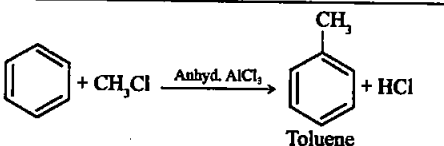
Column I	Column II
(i) <i>n</i> -Pentane	In <i>n</i> -pentane there is no branching and surface area. Hence, more Vander Waal's forces. Therefore boiling point is high.
(ii) <i>iso</i> -Pentane	Molar mass is same but one branch is there which reduces its surface area. Hence, the boiling point is less.
(iii) <i>neo</i> -Pentane	In this compound two side chains are there having the same molar mass. Therefore its boiling point is lowest amongst all three compounds.

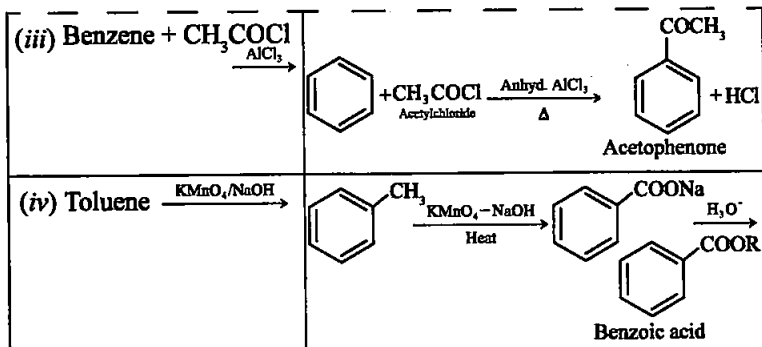
42. Match the following reactants in Column I with the corresponding reaction products in Column II.

Column I	Column II
(i) Benzene + Cl <sub>2</sub> $\xrightarrow{\text{AlCl}_3}$	(a) Benzoic acid
(ii) Benzene + CH <sub>3</sub> Cl $\xrightarrow{\text{AlCl}_3}$	(b) Methyl phenyl ketone
(iii) Benzene + CH <sub>3</sub> COCl $\xrightarrow{\text{AlCl}_3}$	(c) Toluene
(iv) Toluene $\xrightarrow{\text{KMnO}_4/\text{NaOH}}$	(d) Chlorobenzene
	(e) Benzene hexachloride

Ans. (i) → (d); (ii) → (c); (iii) → (b); (iv) → (a)

**Explanation:**

Column I	Column II
(i) Benzene + Cl <sub>2</sub> $\xrightarrow{\text{AlCl}_3}$	 <p style="text-align: center;">Chlorobenzene</p>
(ii) Benzene + CH <sub>3</sub> Cl $\xrightarrow{\text{AlCl}_3}$	 <p style="text-align: center;">Toluene</p>

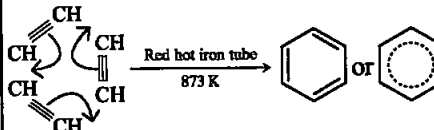


43. Match the reactions given in Column I with the reaction types in Column II.

Column I	Column II
(i) $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{OH}$	(a) Hydrogenation
(ii) $\text{CH}_2=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{Pd}} \text{CH}_3-\text{CH}_3$	(b) Halogenation
(iii) $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 \rightarrow \text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl}$	(c) Polymerisation
(iv) $3 \text{CH}\equiv\text{CH} \xrightarrow[\text{Heat}]{\text{Cu tube}} \text{C}_6\text{H}_6$	(d) Hydration
	(e) Condensation

Ans. (i) → (d); (ii) → (a); (iii) → (b); (iv) → (c)

Explanation:

Column I	Column II
(i) $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{OH}$	Hydration means addition of water molecule. $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3-\text{CH}_2\text{OH}$
(ii) $\text{CH}_2=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{Pd}} \text{CH}_3-\text{CH}_3$	Hydrogenation is addition of $\text{H}_2$ in presence of catalyst. $\text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3-\text{CH}_3$
(iii) $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 \rightarrow \text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl}$	Halogenation means addition of halogens. $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 \rightarrow \text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl}$
(iv) $3 \text{CH}\equiv\text{CH} \xrightarrow[\text{Heat}]{\text{Cu tube}} \text{C}_6\text{H}_6$	Polymerization means more number of smaller molecules combine and give one bigger molecule. 

## V. ASSERTION AND REASON TYPE

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

44. Assertion (A) : The compound cyclooctatetraene has the following structural formula:



It is cyclic and has conjugated  $8\pi$ -electron system but it is not an aromatic compound.

- Reason (R) :  $(4n + 2)\pi$  electrons rule does not hold good and ring is not planar.

- (i) Both A and R are correct and R is the correct explanation of A.  
 (ii) Both A and R are correct but R is not the correct explanation of A.  
 (iii) Both A and R are not correct.  
 (iv) A is not correct but R is correct.

Ans. (i)

**Explanation:** Both A and R are correct, and R is correct explanation of A. Aromaticity is shown by compounds possessing following characteristics:

- Planarity
- Complete delocalization of the  $\pi$  electrons in the ring.
- Presence of  $(4n + 2)\pi$  electrons in the ring where  $n$  is an integer ( $4 = 0, 1, 2, \dots$ ). This is often referred to as **Hückel Rule**.

45. Assertion (A) : Toluene on Friedal Crafts methylation gives *o*- and *p*-xylene.

Reason (R) :  $\text{CH}_3$ -group bonded to benzene ring increases electron density at *o*- and *p*-position.

- (i) Both A and R are correct and R is the correct explanation of A.  
 (ii) Both A and R are correct but R is not the correct explanation of A.  
 (iii) Both A and R are not correct.  
 (iv) A is not correct but R is correct.

Ans. (i)

**Explanation:** Toluene has  $-\text{CH}_3$  group attached to benzene ring.  $\text{CH}_3$  group activates benzene ring due to hyperconjugation effect, and increases electron density on ortho and para positions for the attack of electrophiles.

46. Assertion (A) : Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

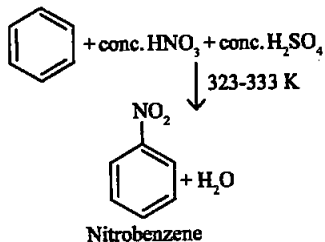
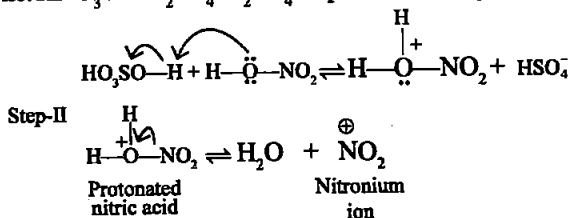
Reason (R) : The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile,  $\text{NO}_2^+$ .

- (i) Both A and R are correct and R is the correct explanation of A.  
 (ii) Both A and R are correct but R is not the correct explanation of A.

- (iii) Both A and R are not correct.  
 (iv) A is not correct but R is correct.

Ans. (i)

**Explanation:** In nitration, benzene is treated with nitrating mixture, i.e. conc.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .  $\text{H}_2\text{SO}_4$  helps in furnishing  $\text{NO}_2^+$  (Electrophile).



47. Assertion (A) : Among isomeric pentanes, 2, 2-dimethylpentane has highest boiling point.

Reason (R) : Branching does not affect the boiling point.

- (i) Both A and R are correct and R is the correct explanation of A.  
 (ii) Both A and R are correct but R is not the correct explanation of A.  
 (iii) Both A and R are not correct.  
 (iv) A is not correct but R is correct.

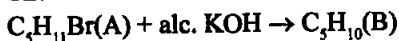
Ans. (iii)

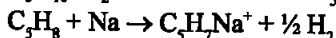
**Explanation:** Among isomeric pentanes 2, 2-dimethylpentane has lowest boiling point and on branching boiling point decreases.

## VI. LONG ANSWER TYPE

48. An alkyl halide  $\text{C}_5\text{H}_{11}\text{Br}$ (A) reacts with ethanolic KOH to give an alkene 'B', which reacts with  $\text{Br}_2$  to give a compound 'C', which on dehydrobromination gives an alkyne 'D'. On treatment with sodium metal in liquid ammonia one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight chain alkane. Identify A, B, C and D. Give the reactions involved.

Ans. The reactions involved in identification of A, B, C and D are as follows:





Hydrogenation of alkyne (D) gives straight chain alkane hence all the compounds A, B, C and D must be straight chain compounds. Alkyne gives sodium alkenyde which proves D is terminal alkyne.

49. 896 mL vapour of a hydrocarbon 'A' having carbon 87.80% and hydrogen 12.19% weighs 3.28g at STP. Hydrogenation of 'A' gives 2-methylpentane. Also 'A' on hydration in the presence of  $H_2SO_4$  and  $HgSO_4$  gives a ketone 'B' having molecular formula  $C_6H_{12}O$ . The ketone 'B' gives a positive iodoform test. Find the structure of 'A' and give the reactions involved.

Ans. To calculate molar mass of hydrocarbon A it is given that 896 ml of hydrocarbon 'A'  $C_xH_y$  weighs 3.28 g at STP.

$$22400 \text{ ml of } C_xH_y \text{ has mass} = 3.28 \times 22400 \text{ ml} / 896 \text{ ml} = 831 \text{ g/mol.}$$

Hence, the molar mass of A = 831 g/mol.

Element	Percentage	Atomic mass	Relative ratio	Relative no. of atoms	Simplest ratio
C	87.8%	12	7.31	1	3
H	12.19%	1	12.19	1.66	4.98=5

Thus, empirical formula =  $C_3H_5$

Empirical formula weight =  $3 \times 12 + 5 = 41$ .

Molecular formula = (Empirical formula) $_n$

$$n = \text{Mol. Mass} / \text{empirical mass} = 831 / 41 = 2.02.$$

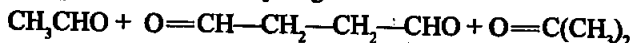
Molecular formula =  $[C_3H_5]_2 = C_6H_{10}$

To determine the structure of (A) and (B):

$C_6H_{10}$  on hydrogenation with 2 moles of  $H_2$  gives  $C_6H_{12}$  and structure is 2-methylpentane. (A) on hydration in presence of dil.  $H_2SO_4$  and  $HgSO_4$  gives  $C_6H_{12}O$  which gives Iodoform test positive. Hence, structure of A =  $(CH_3)_2CH-CH-C\equiv CH$  (4-methyl pent-1-yne) and (B) is 4-methyl pentanone-2.

50. An unsaturated hydrocarbon 'A' adds two molecules of  $H_2$  and on reductive ozonolysis gives butane-1,4-dial, ethanal and propanone. Give the structure of 'A', write its IUPAC name and explain the reactions involved.

Ans. Compound A on ozonolysis gives

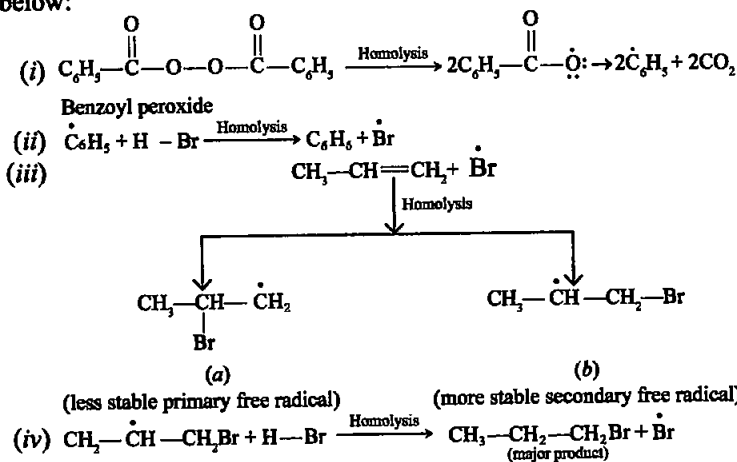


The structure of A is  $CH_3-CH=CH-CH_2-CH_2-CH=C(CH_3)_2$

IUPAC name: 2-methyl octa 2,6 diene.

51. In the presence of peroxide addition of HBr to propene takes place according to anti Markovnikov's rule but peroxide effect is not seen in the case of HCl and HI. Explain.

Ans. Peroxide effect proceeds via free radical chain mechanism as given below:



Peroxide effect is observed only in the case of HBr and not seen in case of HI and HCl. This is due to the fact that the H—Cl bond is stronger than B—Br bond. Also, bond energy of H—Cl bond is higher than H—Br. H—Cl bond is not cleaved by the free radical whereas the H—I bond is weaker and iodine free radicals combine to form iodine molecules.

