

HALOALKANES & HALOARENES

1 MARK QUESTIONS(1-20)

1. What happens when tert-butyl alcohol is treated with Cu / at 573 K.?
2. Arrange the following halides in order of increasing S_N^2 reactivity :
 $\text{CH}_3 - \text{Cl}$, $\text{CH}_3 - \text{Br}$, $\text{CH}_3\text{CH}_2\text{Cl}$, $(\text{CH}_3)_2\text{CHCl}$
3. Alkyl halides, though polar, are immiscible with water. Why?
4. Grignard reagents should be prepared under anhydrous conditions. Why?
5. Which of the following two compounds would react faster by S_N^2 pathway: 1-bromobutane (OR) 2-bromobutane.
6. Allyl Chloride is more reactive than n-propyl Chloride towards nucleophilic substitution reactions. Explain.
7. Explain why is Chlorobenzene difficult to hydrolyse than ethyl chloride ?
8. $\text{R}-\text{Cl}$ is hydrolysed to $\text{R}-\text{OH}$ slowly but the reaction is rapid if a catalytic amount of KI is added to the reaction mixture. Why?
9. Why haloalkanes are more reactive than haloarenes.
10. Why do haloalkenes undergo nucleophilic substitution whereas haloarenes under go electrophilic substitution?
11. Aryl halides cannot be prepared by the action of sodium halide in the presence H_2SO_4 . Why?
12. Why is Sulphuric acid not used during the reaction of alcohols with KI ?
13. p- dichlorobenzene has highest m.p. than those of ortho and m-isomers.?
14. Although chlorine is an electron- withdrawing group, yet it is ortho and para directing in electrophilic aromatic substitution reactions. Why?
15. Explain why vinyl chloride is unreactive in nucleophilic substitution reaction?
16. Arrange the following compounds according to reactivity towards nucleophilic substitution reaction with reagents mentioned :-
 a. 4- nitro chloro benzene, 2,4 di nitro chloro benzene, 2,4,6, trinitrochlorobenzene with CH_3ONa
17. Arrange in order of boiling points.
 a. Bromobenzene, Bromoform, chloromethane, Dibromo-methane
 b. 1-chloropropane, Isopropyl chloride, 1-Chlorobutane.
18. Predict the reactivity in S_N1
 $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$, $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$
19. Why is vinyl chloride less reactive than ethyl chloride?
20. Chloroform is stored in dark coloured & sealed bottle. Why?

2 MARK QUESTIONS(21-30)

21. The treatment of alkyl chlorides with aqueous KOH lead to the formation of alcohols but in presence of alcoholic KOH alkenes are major products. Explain?
22. p-Dichlorobenzene has higher melting point and lower solubility than those of o- and m- isomers. Discuss.
23. Haloalkanes react with KCN to form alkyl cyanides as major product while AgCN form isocyanide as the chief product. Explain
24. Explain why is Chlorobenzene difficult to hydrolyse than ethyl chloride ?
25. Which compound will react faster in S_N^2 reaction with OH^- ?
 - a. CH_3Br and CH_3I (S_N^2)
 - b. $(CH_3)_3C-Cl$ or CH_3Cl (S_N^2)
26. Alcohols reacts with halogen acids to form haloalkenes but phenol does not form halobenzene. Explain
27. How the following conversions can be carried out?
 - a. Propene to propan-1-ol
 - b. 1-Bromopropane to 2-bromopropane
28. The treatment of alkyl chlorides with aq KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are the major products. Explain.
29. Tert-butyl chloride reacts with aq. NaOH by S_N^1 mechanism while n-butyl chloride reacts by S_N^2 mechanism. Why ?
30. Why alkyl halides are generally not prepared in laboratory by free radical halogenation of alkanes ?

3MARK QUESTIONS(31-40)

31. Haloalkanes undergo nucleophilic substitutions whereas Haloarenes undergo electrophilic substitutions.
32. Why alkyl halides are generally not prepared in laboratory by free radical halogenation of alkanes?
33. Why preparation of aryl iodide by electrophilic substitution requires presence of an oxidising agent? Why can aryl fluoride not be prepared by this method?
34. Why aryl halides are extremely less reactive towards nucleophilic substitution?
35. (i) Arrange in order of property indicated :
 $CH_3CH_2CH_2CH_2Br$, $(CH_3)_3Br$, $(CH_3)_3CHCH_2Br$
 (Increasing boiling point)
 (ii) CH_3F , CH_3I , CH_3Cl , CH_3Br (nucleophilic substitution)
36. Why does 2 bromopentane gives pent-2-ene as major product in elimination reaction ?
37. Complete the reaction :
 - (a) $CH_3OCH_3 + PCl_5 \longrightarrow$?
 - (b) $C_2H_5OCH_3 + HCl \longrightarrow$?
 - (c) $(C_2H_5)_2O + HCl \longrightarrow$?
38. Distinguish between the following pair of organic compounds
 i) CCl_4 and $CHCl_3$

ii) Chlorobenzene and Benzyl chloride

39. How are the following conversions carried out?

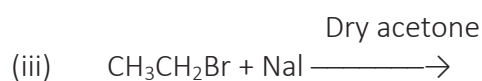
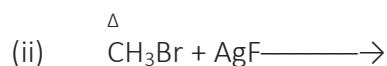
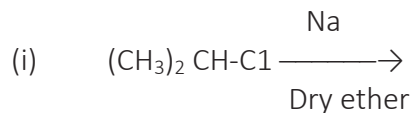
(i) Benzyl chloride \rightarrow Benzyl alcohol.

(ii) Ethyl magnesium chloride \rightarrow Propan-1-ol.

Cu / HCl

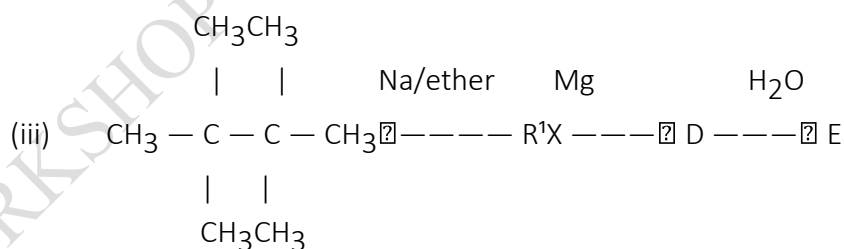
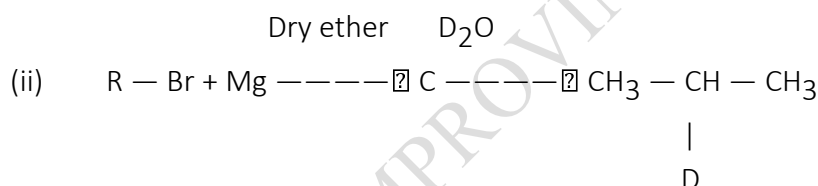
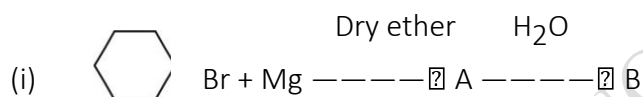
(iii) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow{\quad\quad\quad} \rightarrow$

40. Write the formula of main product formed in the following chemical reactions.

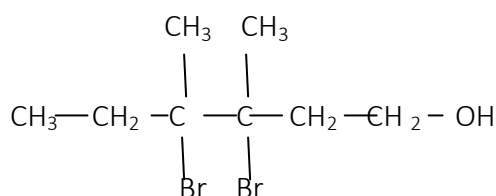


5 MARKS QUESTIONS(41-45)

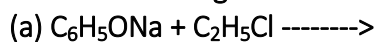
41. Identify A, B, C, D, E, R, R¹ in the following :



42.a) Give the IUPAC name of



b) Complete the following reactions:



(c) Preparation of haloalkane with Alkane and halogen using U.V light is least Preferred method. Explain?

43.a). p-dichlorobenzene has higher melting point and lower solubility than o- and m-isomer. Explain?

b) Which will have a higher boiling point?

1 - Chloro ethane or - 2 methyl -2- chlorobutane

Give reasons?

c) Chloroform is not used as anesthetic nowadays. Why?

44.(a) p - nitro chlorobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structures as well.

(b) Allyl chloride is more reactive than n - propyl chloride towards nucleophilic substitution reaction. Explain why?

(c) Give IUPAC name of the following organic compound



45.a) Why do alcohols have higher boiling points than the halo alkanes of the same molecular mass?

b) Convert the following:

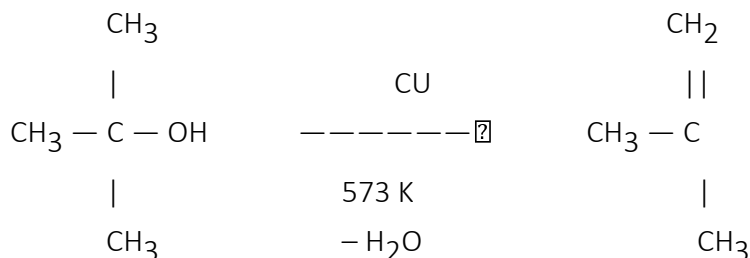
i) Benzene to aniline.

ii) Benzene to diphenyl

iii) Benzene to p-Chloro toluene.

ANSWERS1 MARK ANSWERS(1-20)

1. Dehydration reaction will take place. Isobutene will be formed.



2. $(\text{CH}_3)_2\text{CHCl} < \text{CH}_3\text{CH}_2\text{Cl} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br}$.

(Hint : As the size of the alkyl group increases SN^2 reactivity decreases.)

3. Alkyl halides cannot form H-bonds with water molecules and hence are insoluble in water.

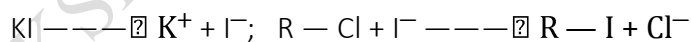
4. Because Grignard reagents have a very strong affinity for H^+ ions. In presence of water, they abstract H^+ ions from water and form alkanes. To prevent this, they should be prepared under anhydrous conditions.

5. The reactivity in SN^2 reaction depends upon the extent of steric hindrance. i-bromobutane is a 1° alkyl halide and 2-bromobutane is a 2° alkyl halide. Since there will be some steric hindrance in 2° alkyl halide than in 1° alkyl halide, therefore 1° -bromobutane will react faster than 2-bromobutane in SN^2 reaction.

6. Allyl Chloride readily undergoes ionization to produce resonance stabilized allyl carbocation. Since carbocations are reactive species they readily combine with OH^- ions to form allyl alcohol.

7. The lone pair of electrons of Chlorine in Chlorobenzene participates into resonance with the benzene ring. As a result $\text{C} - \text{Cl}$ bond acquires a partial double bond character. Therefore, this $\text{C} - \text{Cl}$ bond is stronger than $\text{C} - \text{Cl}$ bond in ethyl chloride which is a pure single bond. As such the Chlorobenzene is difficult to hydrolyse than ethyl chloride.

8. Iodide ion is a powerful nucleophile and hence reacts rapidly with RCl to form RI .



9. In haloarenes, there is double bond character b/w carbon and halogen due to resonance effect which makes them less reactive.

10. Due to more electro negative nature of halide atom in haloalkanes carbon atom becomes slightly positive and is easily attacked by nucleophilic reagents.

While in haloarenes due to resonance, carbon atom becomes slightly negative and attacked by electrophilic reagents.

11. Due to resonance the carbon- oxygen bond in phenols has partial double bond and it is stronger than carbon oxygen single bond.
12. It is because HI formed will get oxidized to I₂ by concentrated Sulphuric acid which is an oxidizing agent.
13. p- dichlorobenzene is symmetrical, fits into crystal lattice more readily and has higher melting point.
14. Ans. Chlorobenzene is resonance hybrid, there is -ve charge at O and para positions, electrophillic substitution reaction will take place at O and para position due to +R effect. +R effect is dominating over - I effect. .
15. Vinyl chloride is unreactive in nucleophilic substitution reaction because of double bond character between C=Cl bond which is difficult to break.
16. 2,4,6, trinitrochlorobenzene > 2,4 dinitrochlorobenzene > 4- nitrochlorobenzene
17. Ans. (a) chloromethane < Bromobenzene < Dibromo-methane < , Bromoform
(b) , Isopropyl chloride < 1-chloropropane < 1-Chlorobutane
 $3^\circ > 2^\circ > 1^\circ$ (SN¹)
18. $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br} > \text{C}_6\text{H}_5(\text{C}_6\text{H}_5)\text{Br} > \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br} > \text{C}_6\text{H}_5\text{CH}_2\text{Br}$
 $(3^\circ) \quad (2^\circ) \quad (2^\circ) \quad (1^\circ)$
19. Due to the sp² hybridization and resonance in vinyl chloride.
20. Because it undergoes oxidation and converting to poisonous gas phosgene.

2 mark questions(21-30)

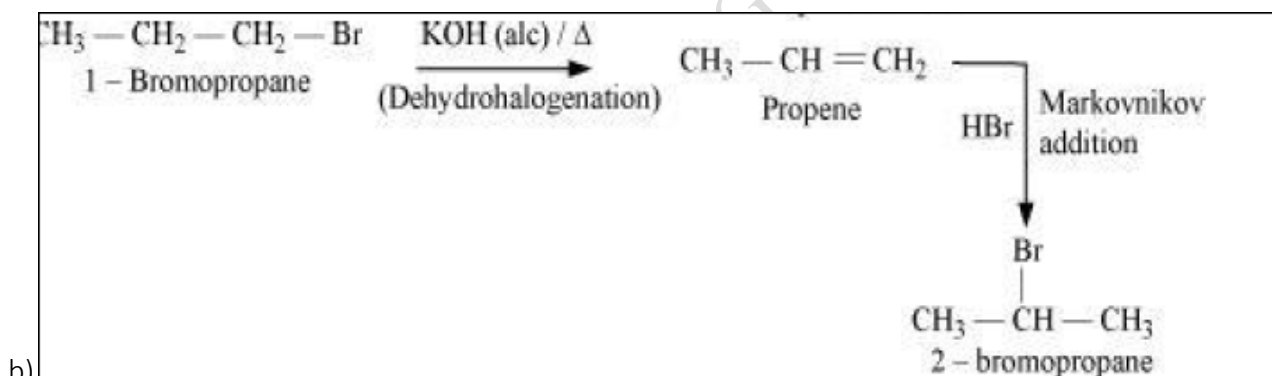
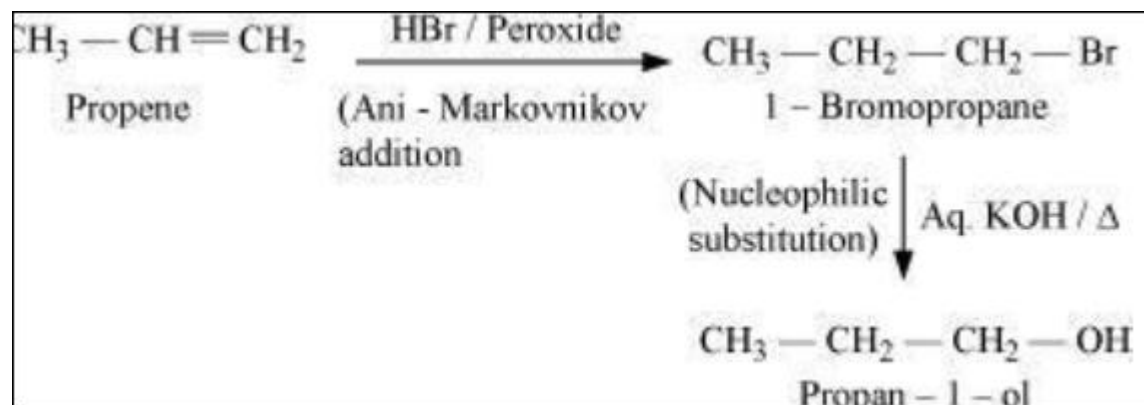
21. In aqueous KOH, OH⁻ is nucleophile which replaces another nucleophile.
 $\text{R-X} + \text{KOH} \rightarrow \text{R-OH} + \text{KX}$
 Where as in alcoholic KOH
 $\text{C}_2\text{H}_5\text{OH} + \text{KOH} \rightarrow \text{C}_2\text{H}_5\text{O}^- + \text{K}^+$
 $\text{CH}_3\text{CH}_2\text{-Cl} + \text{alcoholic KOH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{C}_2\text{H}_5\text{OH}$
 $(\text{C}_2\text{H}_5\text{O}^-)$
22. The p-isomer being more symmetrical fits closely in the crystal lattice and thus has stronger intermolecular forces of attraction than those of o- and m- isomers. Since during melting or dissolution, the crystal lattice breaks, therefore a larger amount of energy is needed to melt or dissolve the p- isomer than the corresponding o- and meta isomers.
23. KCN is an ionic compound and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through Carbon atom and not through nitrogen atom since C — C bond is more stable than C — N bond. However AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.
24. The lone pair of electrons of Chlorine in Chlorobenzene participates into resonance with the benzene ring. As a result C — Cl bond acquires a partial double bond character. Therefore, this C — Cl bond is

stronger than C — Cl bond in ethyl chloride which is a pure single bond. As such the Chlorobenzene is difficult to hydrolyse than ethyl chloride.

25.a) CH_3I will react faster than CH_3Br b) CH_3Cl will react faster than CH_3F

26. The C-O bond in phenol acquires partial double bond character due to resonance and hence is not cleaved by X^- ions to form halobenzenes. But in alcohols a pure C — O bond is maintained and can be cleaved by X^- ions.

27.a)



b)

28. In aq. solution, KOH is almost completely ionised to give OH^- ions which being a strong nucleophile brings about a substitution reaction to form alcohols. Further in aq. solution, OH^- ions are highly solvated (hydrated).

This solution reduces the basic character of OH^- ions which fail to abstract a hydrogen from the β -carbon of the alkyl halide to form an alkene.

However an alcoholic solution of KOH contains alkoxide (RO^-) ions which being a much stronger base than OH^- ions preferentially abstracts a hydrogen from the β -carbon of the alkyl halide to form alkene.

29. Tert-butyl chloride reacts via SN^1 mechanism because the heterolytic cleavage of $\text{C} - \text{Cl}$ bond in tert-butyl chloride gives 3 carbocation which is highly stable and favourable for SN^1 mechanism. Moreover, tert-butyl chloride (3°) being a bulky molecule has steric hindrance which will not allow SN^2 mechanism to take place. Hence only SN^1 mechanism can occur in tert-butyl chloride. However n-butyl chloride (1°) reacts via SN^2 because 'C' of $\text{C} - \text{Cl}$ bond is less crowded and favourable for nucleophile to attack from back side results in the formation of transition state. It has less steric hindrance which is a favourable factor for SN^2 mechanism.

30. It is because :

- (i) It gives a mixture of isomeric monohalogenated products whose boiling points are so close that they cannot be separated easily.
- (ii) Polyhalogenation may also take place, thereby making the mixture more complex and hence difficult to separate.

3 MARK QUESTIONS(31-40)

31. Haloalkanes are more polar than haloarenes.

☐ C-atom carrying the halogen in haloalkanes is more e^- deficient than that in haloarenes.

☐ Haloalkanes undergo nucleophilic substitution readily

In haloarenes, the lone pair of electrons present on the halogen atom goes into resonance with the aryl ring. The aryl ring being rich in electron density, undergoes electrophilic substitutions.

32. It is because :

- (i) It gives a mixture of isomeric monohalogenated products whose boiling points are so close that they cannot be separated easily.
- (ii) Polyhalogenation may also take place, thereby making the mixture more complex and hence difficult to separate.

33. Reactions with I_2 are reversible in nature and require presence of oxidising agent (HNO_3 , etc.) to oxidise HI formed during iodination and promote forward reaction.

Fluoro compounds cannot be prepared due to high reactivity of fluorine.

34.(i) Resonance effect :

Due to resonance $\text{C} - \text{Cl}$ bond acquires partial double bond character.

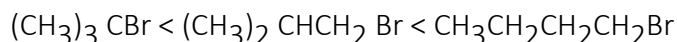
- (ii) Difference in hybridisation of Carbon in $\text{C} - \text{X}$ bond :
in haloarene C-atom attached to halogen is sp^2 hybrid while sp^3 in haloalkane.

C — X bond length in sp^2 hybrid is shorter and hence stronger and difficult to break.

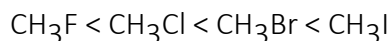
(iii) Instability of phenyl cation

(iv) Possible repulsion of nucleophile to approach e^- rich arenes.

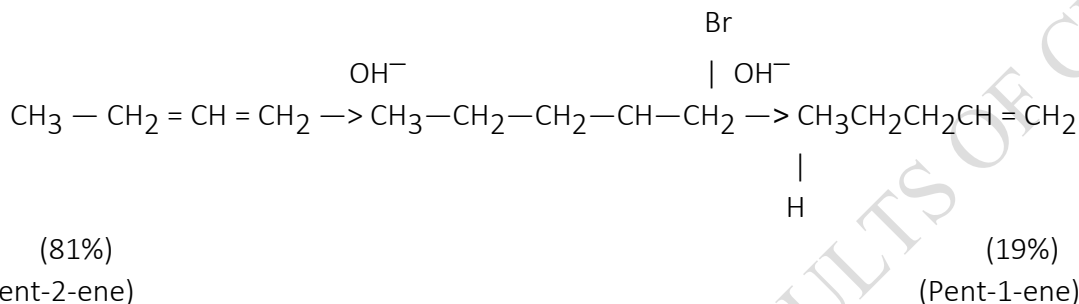
35.(i) B. P. decreases with increase in branching due to decrease in Van der Waals forces of attraction.



(ii) Reactivity increases as C — X bond dissociation energy decreases.



36.



This is because of Saytzeff's rule — In dehydrohalogen reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.

37. (a) $2 CH_3Cl$

(b) $CH_3Cl + C_2H_5OH$

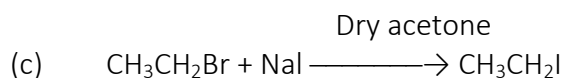
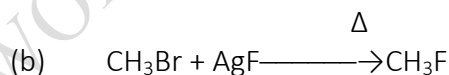
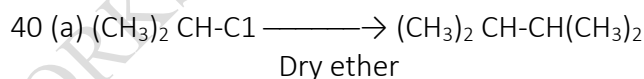
(c) $C_2H_5Cl + C_2H_5OH$

38. i) Carblamine reaction : chloroform gives offensive smell due to formation isocyanide but CCl_4 don't.

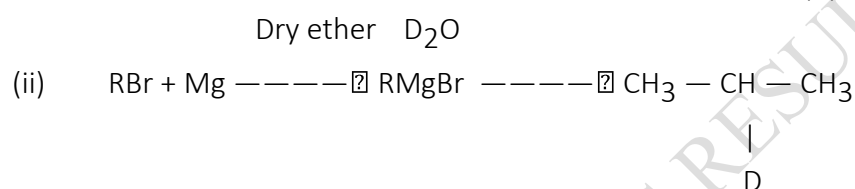
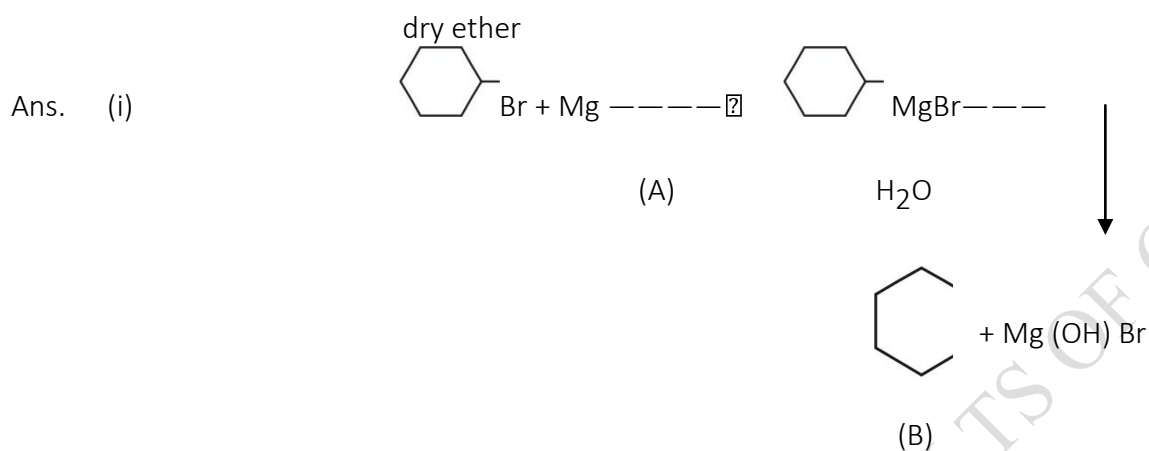
ii) Diazotisation test will be given by benzyl chloride.

39.i) Hydrolysis with water.

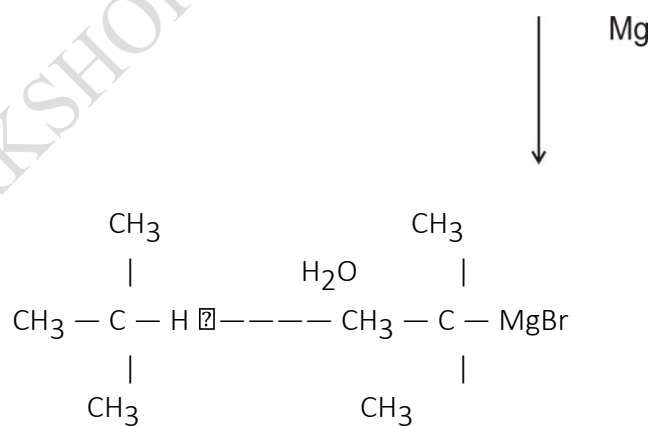
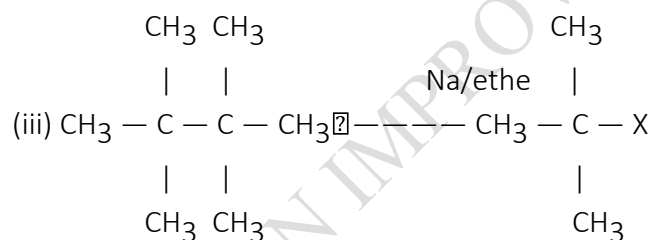
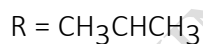
ii) Nucleophilic addition with HCHO followed by hydrolysis.



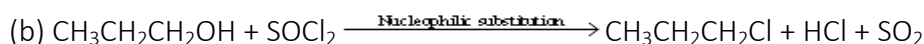
5 MARK ANSWERS(41-45)



Here



42. a) 3,4-dibromo-3,4-dimethylhexan-1-ol.



c) Due to formation of mixed halides primary, secondary tertiary.

43.a) The p-isomer being more symmetrical fits directly in the crystal lattice and thus has stronger inter molecular forces of attraction than o- and m- isomers. During melting or dissolution, the crystal lattice breaks. Therefore, a large amount of energy is needed to melt or dissolve the p-isomer than the resultant o- and m- isomers.

b) 1-chloro pentane

Surface area and hence Van der Waal's forces of attraction decreases on branching.

c) Due to the formation of poisonous gas during oxidation.

44(a) In this reaction a carbanion intermediate is formed. This is stabilized by Resonance in p-nitrochloro benzene Resonance Structure

(b) In allyl chloride, the carbocation formed is stabilised due to resonance while the carbocation formed from n - propyl chloride i.e. is less stable, so allyl chloride is more reactive towards nucleophilic substitution reaction.

(c) Chlorophenylmethane

45 a) Alcohols are capable of forming intermolecular H-bonds .

