
Chapter – 10 (Haloalkanes and Haloarenes)

Exercise Questions:

Question :1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl, vinyl, or aryl halides:

- I. $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_3$
- II. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)\text{Cl}$
- III. $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$
- IV. $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{Br})\text{C}_6\text{H}_5$
- V. $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{Br})\text{CH}_3$
- VI. $\text{CH}_3\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Br}$
- VII. $\text{CH}_3\text{C}(\text{Cl})(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3$
- VIII. $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$
- IX. $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$
- X. $\text{P-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$
- XI. $\text{M-ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_3$
- XII. $\text{O-Br-C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

Answer:

The IUPAC names of various compounds are given below in order:

- (1) 2-Chloro-3-methylbutane (secondary alkyl halide)
- (ii) 3-Chloro-4-methylhexane (secondary alkyl halide)
- (iii) 1-Iodo-2,2-dimethylbutane (primary alkyl halide)
- (iv) 1-Bromo-2,3-dimethyl-1-phenylbutane (secondary benzyl halide)
- (v) 2-Bromo-3-methylbutane (secondary alkyl halide)
- (vi) 1-Bromo-2-ethyl-2-methylbutane (primary alkyl halide)

- (vii) 3-Chloro-3-methylpentane (tertiary alkyl halide)
- (viii) 3-Chloro-5-methylhex-2-ene (vinyl halide)
- (ix) 4-Bromo-4-methylpent-2-ene (allyl halide)
- (x) 1-Chloro-4-(2-methylpropyl) benzene (aryl halide)
- (xi) 1-Chloromethyl-3-(2,2-dimethylpropyl) benzene (primary benzyl halide)
- (xii) 1-Bromo-2-(1-methylpropyl) benzene (aryl halide)

Question :2 Give the IUPAC names of the following compounds :

- I. $\text{CH}_3\text{CH}(\text{Cl})\text{CH}(\text{Br})\text{CH}_3$
- II. $\text{CHF}_2\text{CBrClF}$
- III. $\text{ClCH}_2\text{C}=\text{CCH}_2\text{Br}$
- IV. $(\text{CCl}_3)_3\text{CCl}$
- V. $\text{CH}_3\text{C}(\text{p-ClC}_6\text{H}_4)_2\text{CH}(\text{Br})\text{CH}_3$
- VI. $(\text{CH}_3)_3\text{CCH}=\text{ClC}_6\text{H}_4\text{-p}$

Answer:

The IUPAC names of various compounds are given below in order:

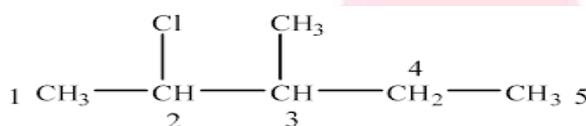
- (i) 2-Bromo-3-chlorobutane
- (ii) 1-Bromo-1-chloro-1,2,2-trifluoroethane
- (iii) 1-Bromo-4-chlorobut-2-yne
- (iv) 2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane
- (v) 2-Bromo-3,3-bis (4-chlororphenyl) butane
- (vi) 1-Chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene

Question :3 Write the structures of the following organic halogen compounds.

- I. **2-Chloro-3-methylpentane**

- II. P-Bromochlorobenzene
- III. 1-Chloro-4-ethylcyclohexane
- IV. 2-(2-Chlorophenyl) -1-iodooctane
- V. Perfluorobenzene
- VI. 4-tert-Butyl-3-iodoheptane
- VII. 1-Bromo-4-sec-butyl-2-methylbenzene
- VIII. 1,4-Dibromobut-2-ene

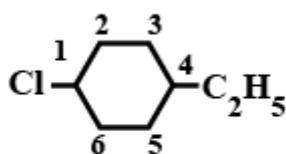
Answer:



i.) 2-chloro-3-methylpentane

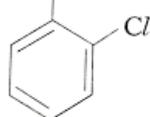
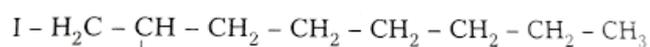


ii.)

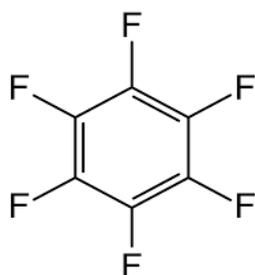


1-chloro-4-ethylcyclohexane

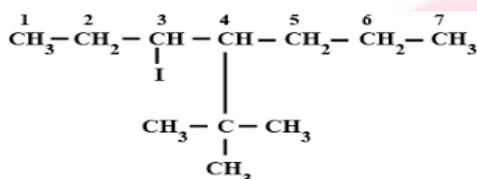
iii.)



iv.)

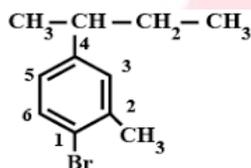


v.)



vi.)

4-tert-Butyl-3-iodoheptane



vii.)

1-Bromo - 4 sec - butyl - 2 - methyl benzene



viii.)

1,4-Dibromobut-2-ene

Question :4 Which one of the following has the highest dipole moment?

- I. CH_2Cl_2
- II. CHCl_3
- III. CCl_4

Answer:

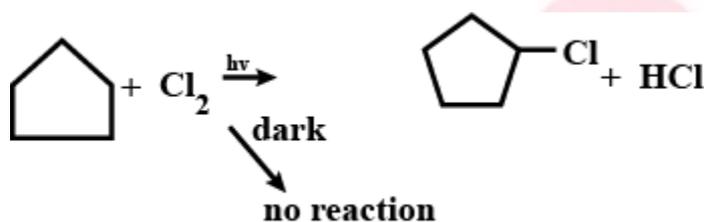
Dichloromethane has highest dipole moment among CH_2Cl_2 , CHCl_3 and CCl_4 . The decreasing order of dipole moments is $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$. These molecules have tetrahedral geometry due to sp^3 hybridization of carbon atom. In CCl_4 , the individual C-Cl bond dipoles cancel each other which results in zero dipole moment.

Hence, CCl_4 is non polar.

Question :5 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

Answer:

The molecular formula of hydrocarbon is C_5H_{10} . It satisfies the general formula C_nH_{2n} . It suggests that the hydrocarbon is either alkene or cycloalkane. It does not react with chlorine in dark. Hence, it cannot be alkene. Hence, it is cycloalkane. It gives a single monochloro compound C_5H_9Cl in bright sunlight. Hence, the hydrocarbon is cyclopentane.

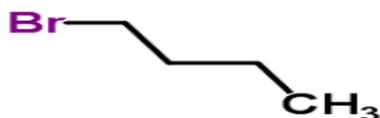


Question :6 Write the isomers of the compound having formula C_4H_9Br .

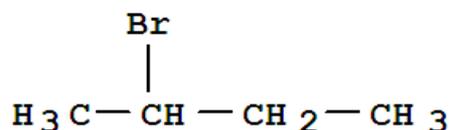
Answer:

There are four isomers of the compound having formula C_4H_9Br .

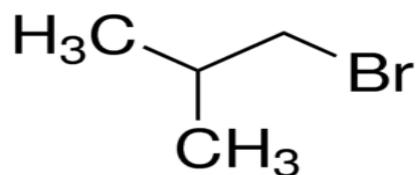
i.) 1 – Bromobutane



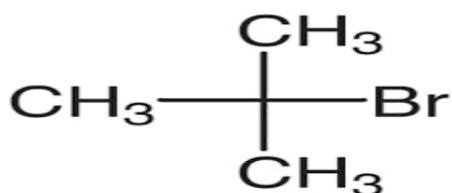
ii.) 2 – Bromobutane



iii.) 1 – Bromo – 2 – methylpropane



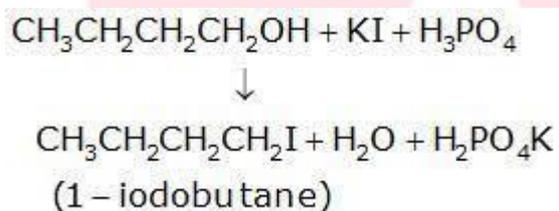
iv.) 2 - Bromo - 2 - methylpropane



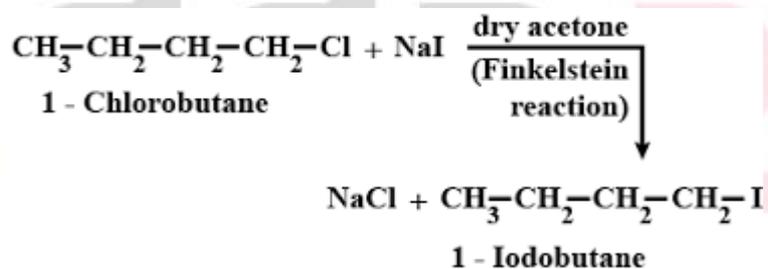
Question :7 Write the equations for the preparation of 1-iodobutane from

- I. 1-butanol
- II. 1-chlorobutane
- III. But-1-ene.

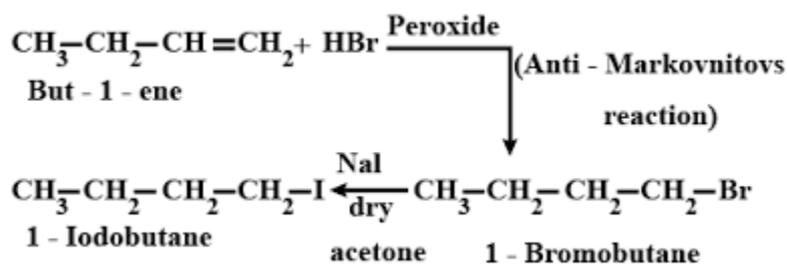
Answer:



i.)



ii.)



iii.)

Question :8 What are ambident nucleophiles? Explain with an example.

Answer:

The nucleophiles that can attack through two different sites are known as ambident nucleophiles. For example, cyanide ion is an ambident nucleophile. It can attack through either C atom or N atom to form alkyl cyanide or alkyl isocyanide.

Question :9 Which compound in each of the following pairs will react faster in SN2 reaction with -OH?

- I. **CH₃Br or CH₃I**
- II. **(CH₃)₃CCl or CH₃Cl**

Answer:

- i.) In S_N2 mechanism, the order in which the halides react to some alkyl group is constant. This is because the halide ion becomes a better leaving group when the size of the ion increases.
R-F << R-Cl << R-Br << R-I
Hence, the reactivity of CH₃I is faster as compared to CH₃Br in S_N2 reaction with OH⁻.
- ii.) In SN2 mechanism, the nucleophile attacks at the atom bearing the leaving group. The attack of nucleophile in (CH₃)₃CCl at the carbon atom is hindered as the carbon atoms contain bulky group.
However, CH₃Cl does not consist of bulky substituents on the carbon atom bearing the leaving group.
Hence, the reactivity of CH₃Cl is faster as compared to (CH₃)₃CCl in SN2 reaction with OH⁻.

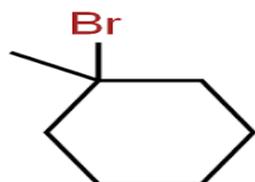
Question :10 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

- I. **1-Bromo-1-methylcyclohexane**
- II. **2-Chloro-2-methylbutane**

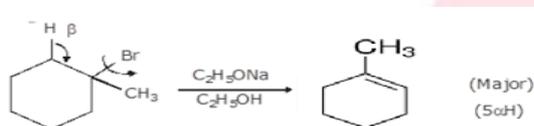
III. 2,2,3-Trimethyl-3-bromopentane

Answer:

- i.) 1-bromo-1-methylcyclohexane.

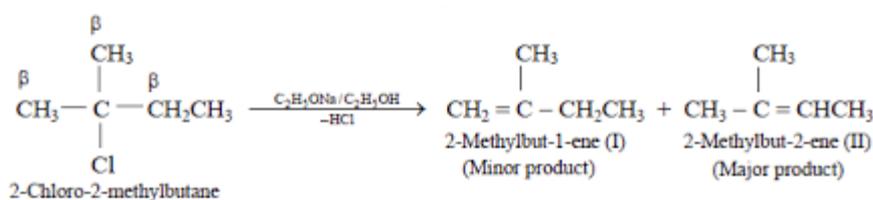


In given compound, all beta-hydrogen atoms are equivalent. Thus, dehydrohalogenation of this compound gives only one alkene.



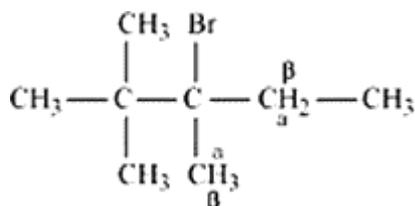
- ii.)

Saytzeff's rule implies that in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced. Therefore, alkene (I) i.e., 2-methylbut-2-ene is the major product in this reaction.

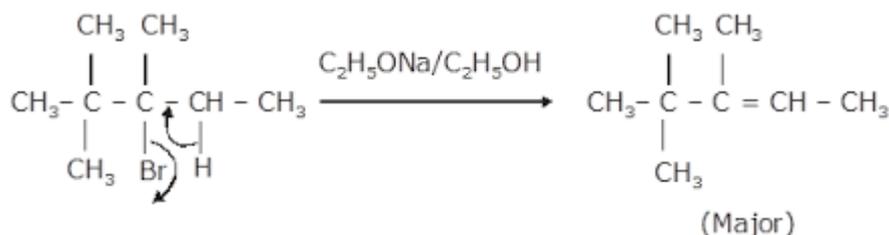


- (iii)

2,2,3-Trimethyl-3-bromopentane



In the given compound, there are two different sets of equivalent β -hydrogen atoms labelled as a and b. Thus, dehydrohalogenation of the compound yields two alkenes.

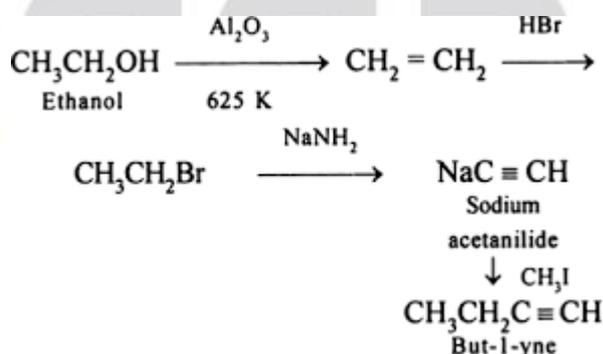


According to Saytzeff's rule, in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to the doubly bonded carbon atom is preferably formed. Hence, alkene (I) i.e., 3,4,4-trimethylpent-2-ene is the major product in this reaction.

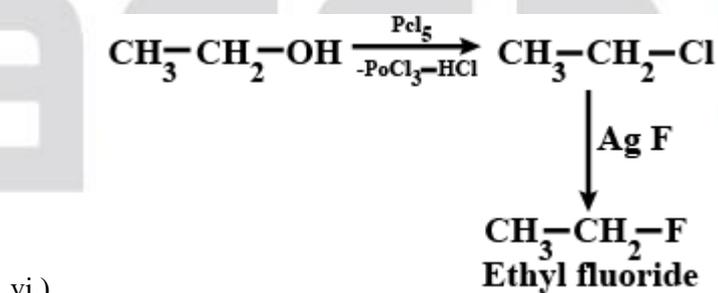
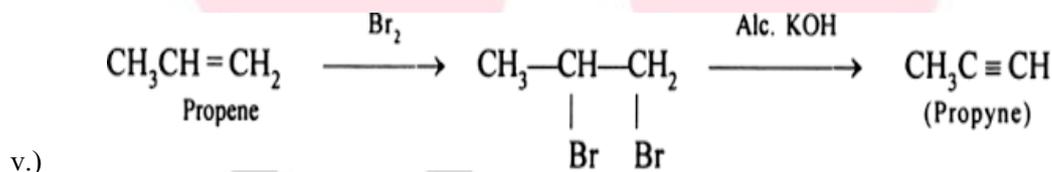
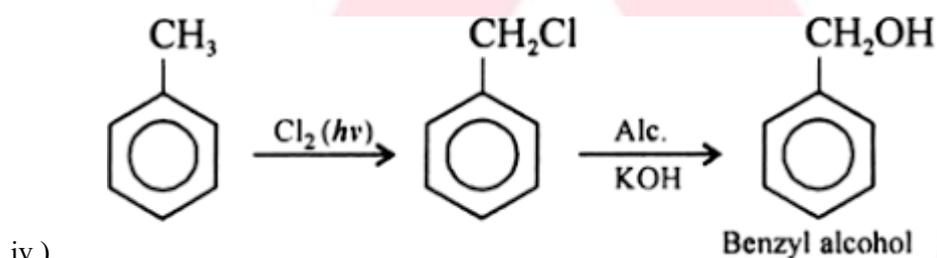
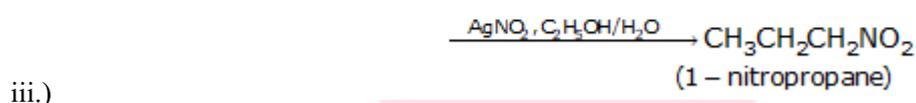
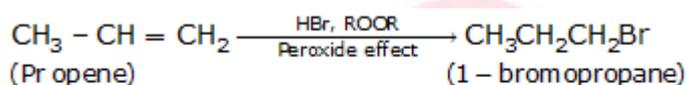
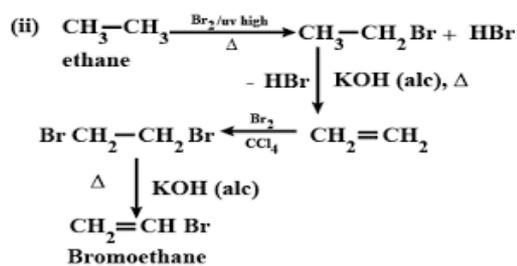
Question :11 How will you bring about the following conversions?

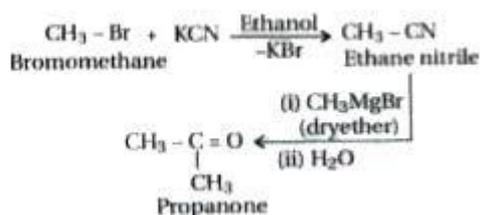
- I. Ethanol to but-1-yne
- II. Ethane to bromoethene
- III. Propene to 1-nitropropane
- IV. Toluene to benzyl alcohol
- V. Propene to propyne
- VI. Ethanol to Ethyl fluoride
- VII. Bromomethane to propanone
- VIII. But-1-ene to but-2-ene
- IX. 1-Chlorobutane to n-octane
- X. Benzene to violently.

Answer:

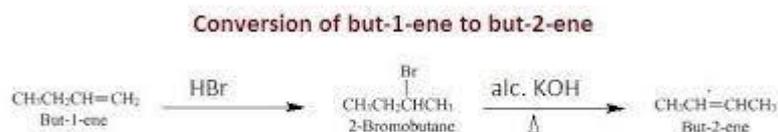


i.)

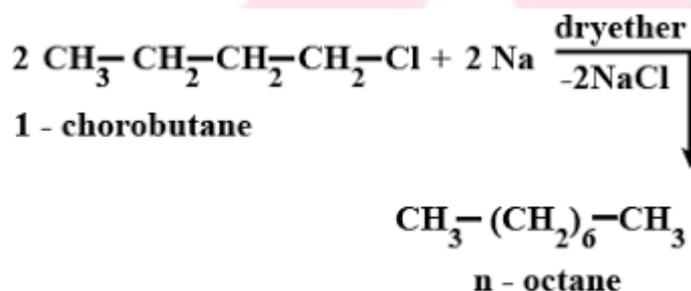




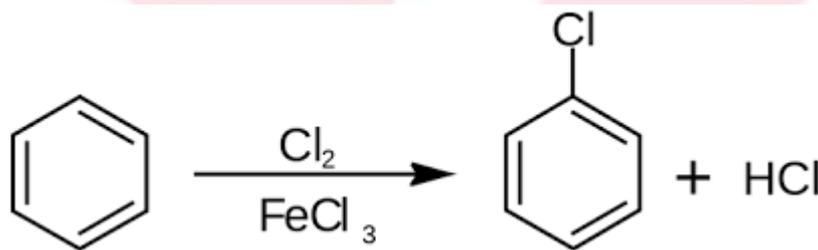
vii.)



viii.)



ix.)



x.)

Question :12 Explain why

- I. The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
- II. Alkyl halides ,though polar, are immiscible with water?
- III. Grignard reagents should be prepared under anhydrous conditions?

Answer:

 i.)In chlorobenzene, the Cl-atom is linked to a sp² hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to a sp³ hybridized carbon atom. Now, sp² hybridized carbon has more s-character

than sp^3 hybridized carbon atom. Therefore, the former is more electronegative than the latter. Therefore, the density of electrons of C - Cl bond near the Cl-atom is less in chlorobenzene than in cyclohexyl chloride.

Moreover, the - R effect of the benzene ring of chlorobenzene decreases the electron density of the C - Cl bond near the Cl-atom. As a result, the polarity of the C - Cl bond in chlorobenzene decreases. Hence, the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(ii) To be miscible with water, the solute-water force of attraction must be stronger than the solute-solute and water-water forces of attraction. Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the alkyl halide-alkyl halide and water-water forces of attraction. Hence, alkyl halides (though polar) are immiscible with water.

(iii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes. Therefore, Grignard reagents should be prepared under anhydrous conditions.

Question :13 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform .

Answer:

Uses of Freon - 12

Freon-12 (dichlorodifluoromethane, CF_2Cl_2) is commonly known as CFC. It is used as a refrigerant in refrigerators and air conditioners. It is also used in aerosol spray propellants such as body sprays, hair sprays, etc. However, it damages the ozone layer. Hence, its manufacture was banned in the United States and many other countries in 1994.

Uses of DDT

DDT (p, p-dichlorodiphenyltrichloroethane) is one of the best known insecticides. It is very effective against mosquitoes and lice. But due its harmful effects, it was banned in the United States in 1973.

Uses of carbon tetrachloride (CCl_4)

(i) It is used for manufacturing refrigerants and propellants for aerosol cans.

(ii) It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

(iii) It is used as a solvent in the manufacture of pharmaceutical products.

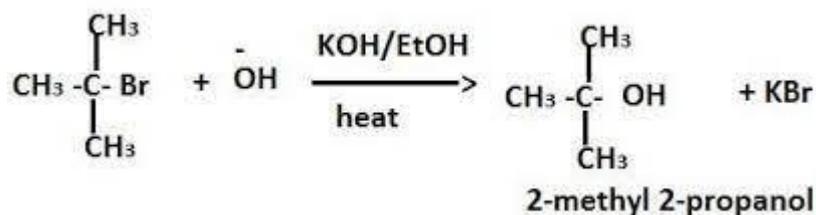
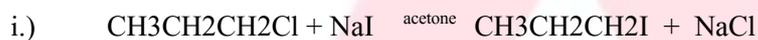
Uses of iodoform (CHI_3)

Iodoform was used earlier as an antiseptic, but now it has been replaced by other formulations-containing iodine-due to its objectionable smell. The antiseptic property of iodoform is only due to the liberation of free iodine when it comes in contact with the skin.

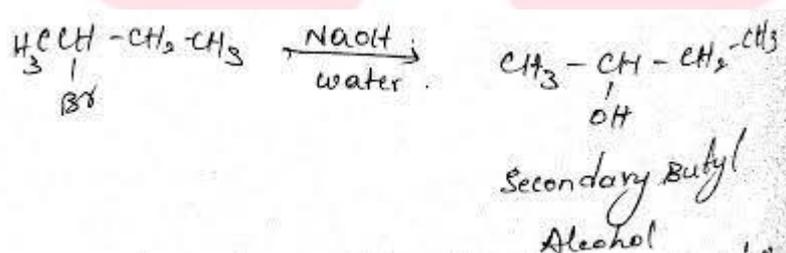
Question :14 Write the structure of the major organic product in each of the following reactions :

- I. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaI} \xrightarrow[\text{heat}]{\text{acetone}}$
- II. $(\text{CH}_3)_3\text{CBr} + \text{KOH} \xrightarrow[\text{heat}]{\text{ethanol}}$
- III. $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3 + \text{NaOH} \xrightarrow{\text{water}}$
- IV. $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \xrightarrow{\text{aq. ethanol}}$
- V. $\text{C}_6\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{Cl} \rightarrow$
- VI. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \rightarrow$
- VII. $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{peroxide}}$
- VIII. $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{HBr} \rightarrow$

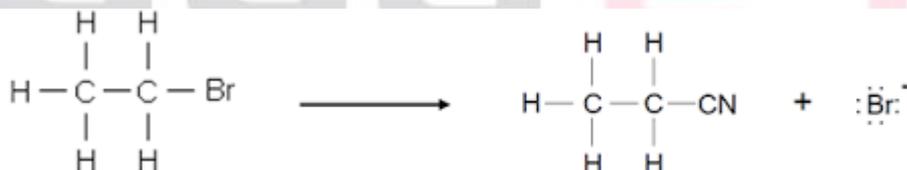
Answer:



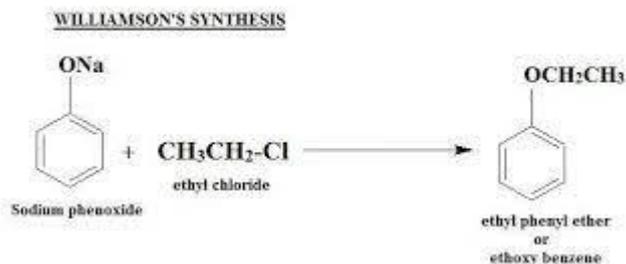
ii.)



iii.)



iv.)



v.)



Question :15 Write the mechanism of the following reaction :



Answer:

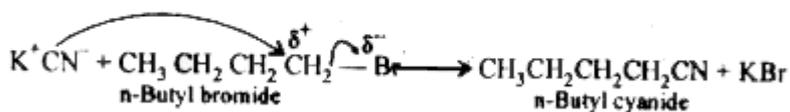
The given reaction is :



It is a nucleophilic substitution reaction in which stronger nucleophile CN^- is replacing weaker nucleophile Br^- .

It will follow $\text{S}_\text{N}2$ mechanism.

$$\text{Rate} = k [\text{C}_3\text{H}_7\text{CH}_2\text{Br}] [\text{CN}^-]$$



Question :16 Arrange the compounds of each set in order of reactivity towards $\text{S}_\text{N}2$ displacement :

I. 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

II. 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

III. 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

Answer:

An SN₂ reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards SN₂ displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases in the following order.

1-Bromopentane < 2-bromopentane < 2-Bromo-2-methylbutane

Hence, the increasing order of reactivity towards SN₂ displacement is:

2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

(ii) Since steric hindrance in alkyl halides increases in the order of $1^\circ < 2^\circ < 3^\circ$, the increasing order of reactivity towards SN₂ displacement is $3^\circ < 2^\circ < 1^\circ$.

Hence, the given set of compounds can be arranged in the increasing order of their reactivity towards SN₂ displacement as:

2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane

(iii) The steric hindrance to the nucleophile in the SN₂ mechanism increases with a decrease in the distance of the substituents from the atom containing the leaving group. Further, the steric hindrance increases with an increase in the number of substituents. Therefore, the increasing order of steric hindrances in the given compounds is as below:

1-Bromobutane < 1-Bromo-3-methylbutane < 1-Bromo-2-methylbutane < 1-Bromo-2, 2-dimethylpropane

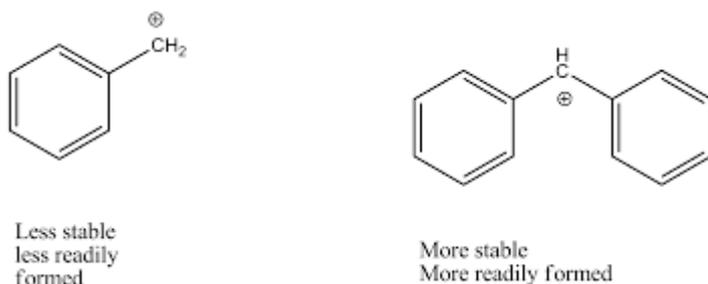
Hence, the increasing order of reactivity of the given compounds towards SN₂ displacement is:

1-Bromo-2, 2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3-methylbutane < 1-Bromobutane

Question :17 Out of C₆H₅CH₂Cl and C₆H₅CHClC₆H₅, which is more easily hydrolysed by aqueous KOH.

Answer:

$C_6H_5CHClC_6H_5$ is more easily hydrolysed by aqueous KOH. It involves formation of a secondary carbocation which is stabilized by resonance with two phenyl groups. On the other hand, during hydrolysis of $C_6H_5CH_2Cl$, a primary carbocation is formed which is stabilized by resonance with only one phenyl group and is less stable and less readily formed.



Question :18 p-Dichlorobenzene has higher m.p. and solubility than those of o-and m- isomers. Discuss.

Answer:

In the case of dichlorobenzenes, the para isomer is more symmetrical than ortho and meta isomers. Hence, in the crystal lattice, para isomer fits more closely than ortho and meta isomers.

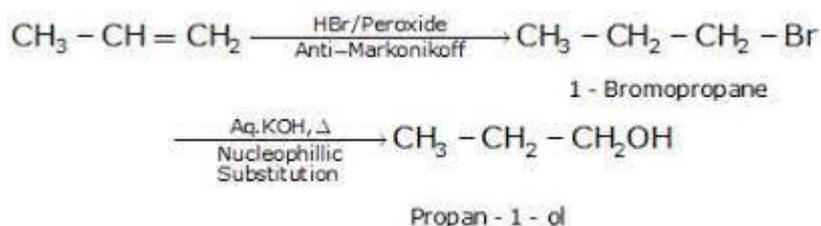
Due to this, more energy is required to break the crystal lattice of the para isomer. Hence, p-Dichlorobenzene has a higher melting point than those of o- and m-isomers.

Question :19 How the following conversions can be carried out?

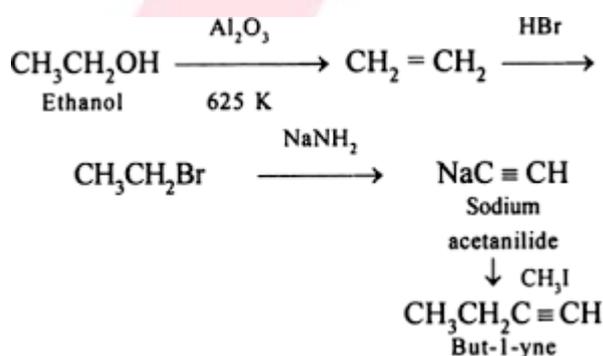
- I. Propene to propan-1-ol
- II. Ethanol to but-1-yne
- III. 1-Bromopropane to 2-bromopropane
- IV. Toluene to benzyl alcohol
- V. Benzene to 4-bromonitrobenzene
- VI. Benzyl alcohol to 2-phenylethanoic acid
- VII. Ethanol to propanenitrile
- VIII. Aniline to chlorobenzene
- IX. 2-Chlorobutane to 3,4-dimethylhexane
- X. 2-Methyl-1-propene to 2-chloro-2-methylpropane
- XI. Ethyl chloride to propanoic acid
- XII. But-1-ene to n-butyliodide

- XIII. 2-Chloropropane to 1-propanol**
XIV. Isopropyl alcohol to iodoform
XV. Chlorobenzene to p-nitrophenol
XVI. 2-Bromopropane to 1-bromopropane
XVII. Chloroethane to butane
XVIII. Benzene to diphenyl
XIX. Tert-Butyl bromide to isobutyl bromide
XX. Aniline to phenylisocyanide

Answer:



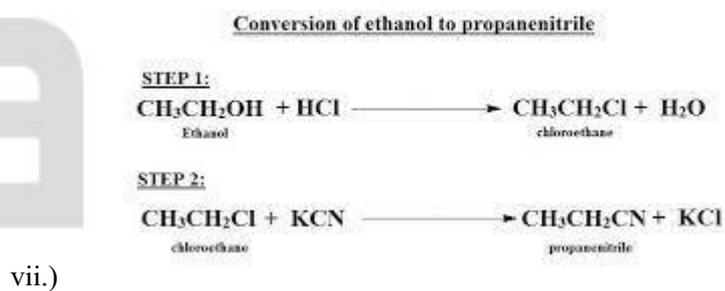
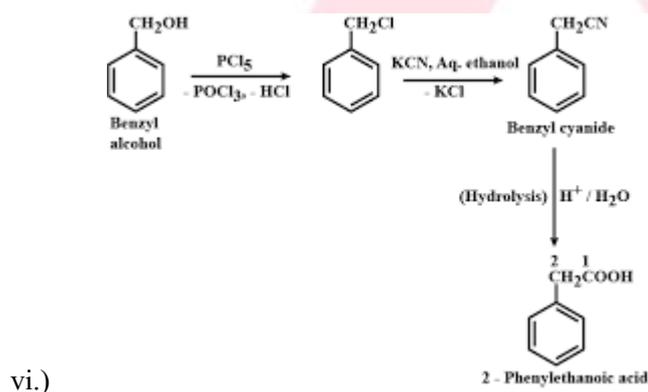
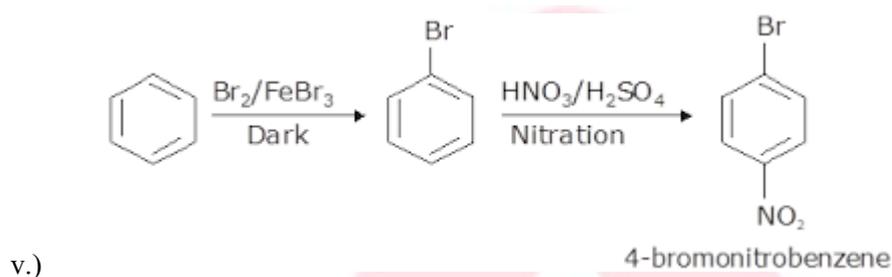
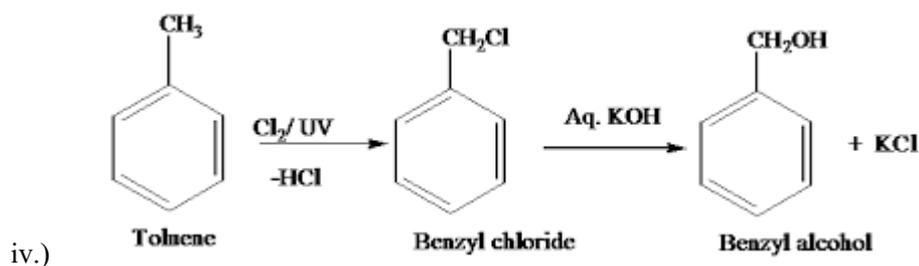
i.)

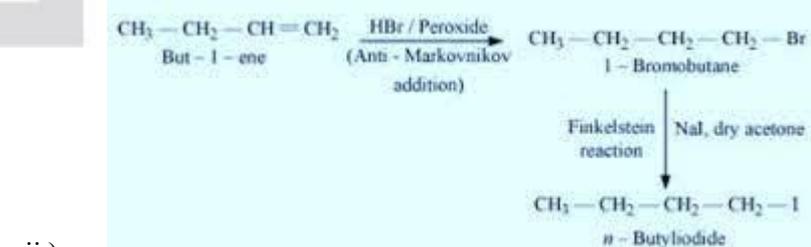
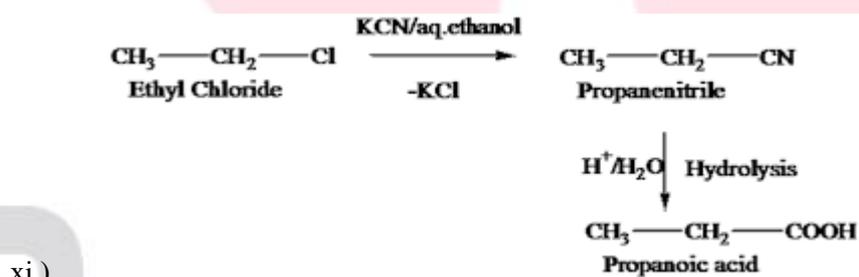
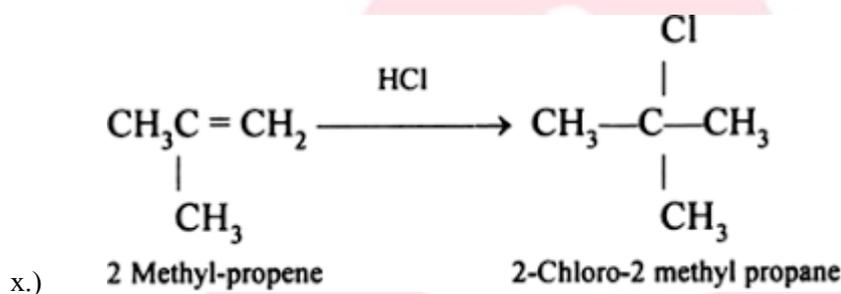
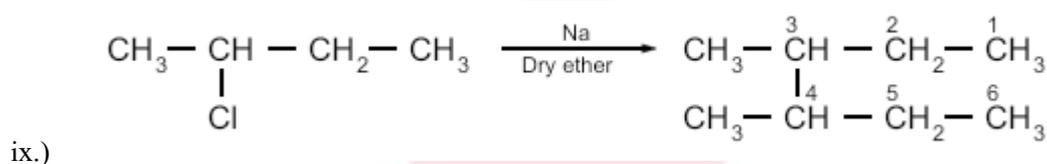
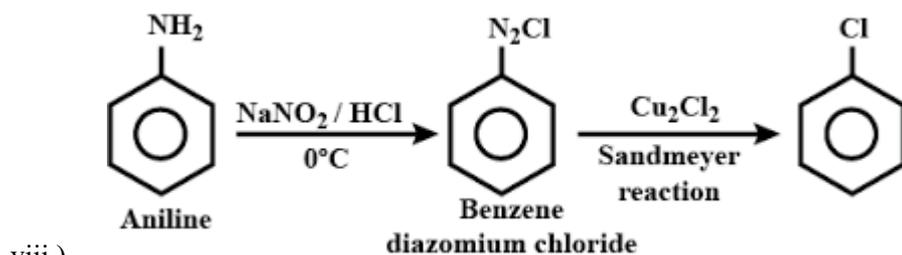


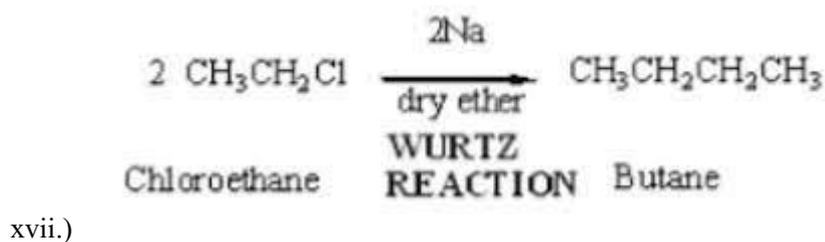
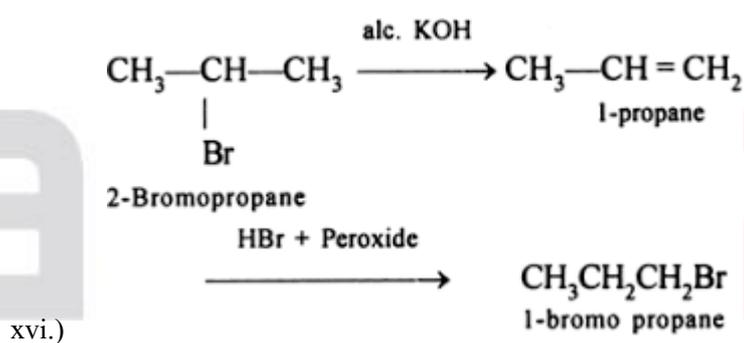
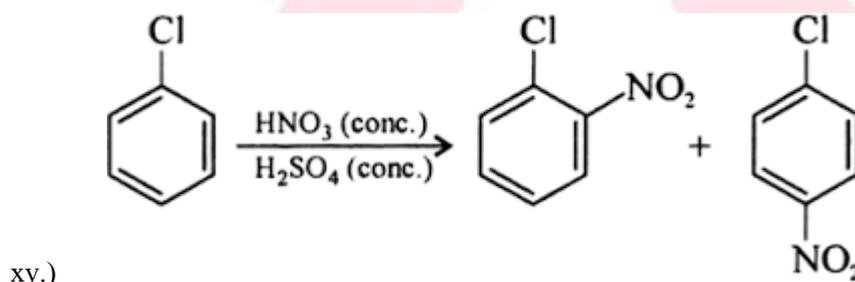
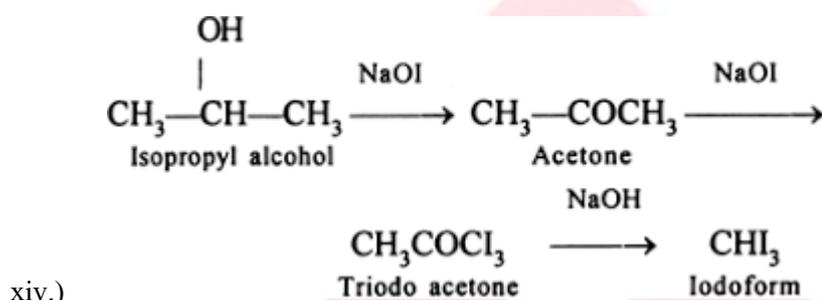
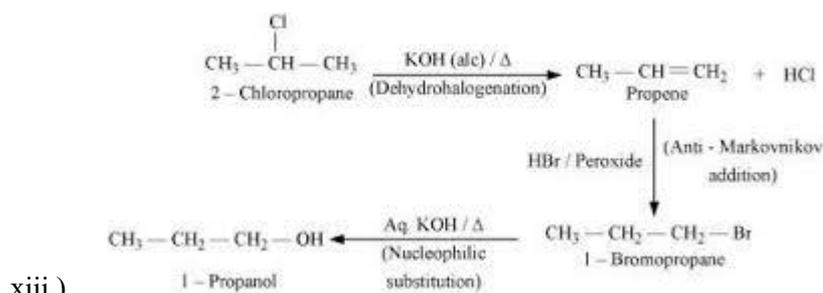
ii.)



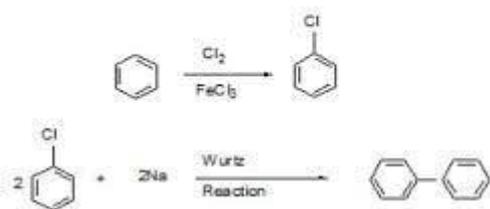
iii.)



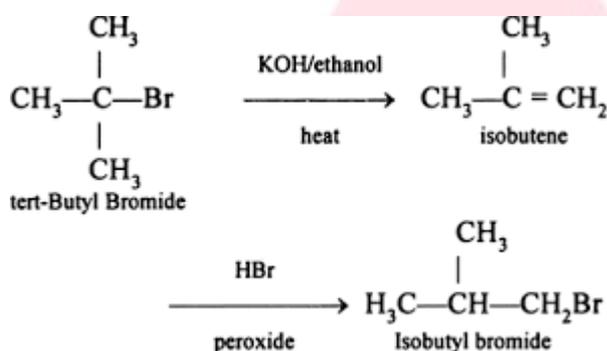




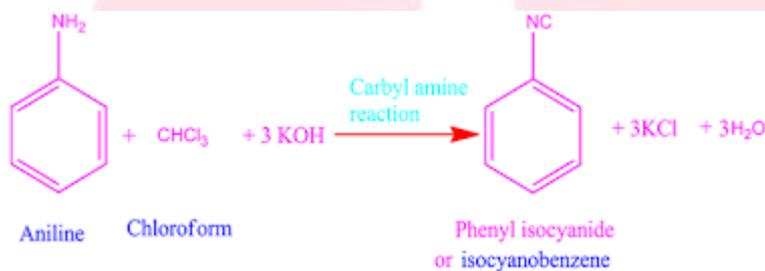
It can be prepared from benzene in a following way:



xviii.)



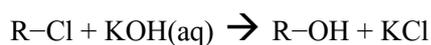
xix.)



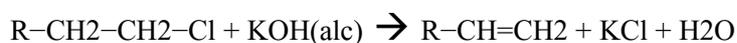
xx.)

Question :20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkenes are major products. Explain.

Answer:



The ionization of aqueous KOH produces hydroxide ions which are strong nucleophiles. Hence, alkyl chlorides undergo substitution to form alcohol.



Alcoholic KOH solution gives alkoxide ion which is a strong base. It abstracts β hydrogen atom of alkyl chloride. A molecule of HCl is eliminated and an alkene is formed.

The basicity of hydroxide ion is much lower than the basicity of alkoxide ion as hydroxide ion is significantly hydrated in aqueous solution.

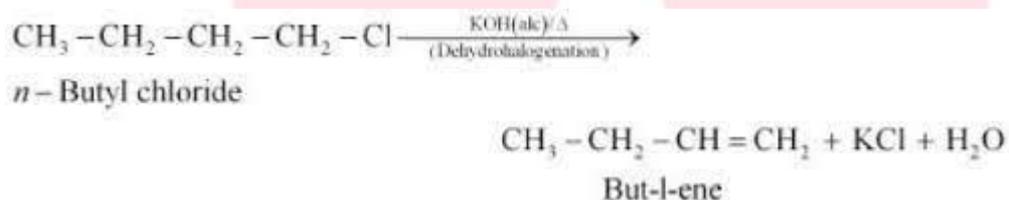
Hence, hydroxide ion cannot abstract β hydrogen atom of alkyl chloride.

Question :21 What happens when

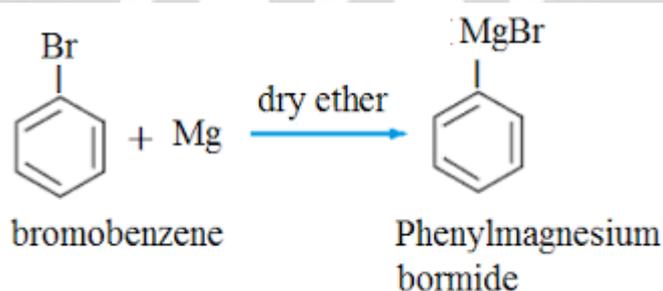
- I. N-butyl chloride is treated with alcoholic KOH.**
- II. Bromobenzene is treated with Me in the presence of dry ether**
- III. Chlorobenzene is subjected to hydrolysis.**
- IV. Ethyl chloride is treated with aqueous KOH**
- V. Methyl bromide is treated with sodium in the presence of dry ether**
- VI. Methyl chloride is treated with KCN?**

Answer:

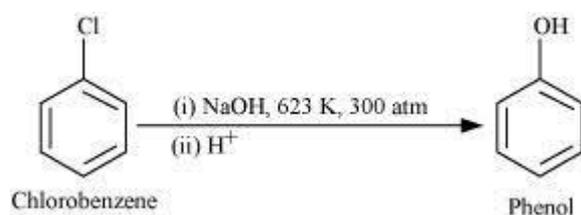
(i) When n - butyl chloride is treated with alcoholic KOH, the formation of but - 1 - ene takes place. This reaction is a dehydrohalogenation reaction.



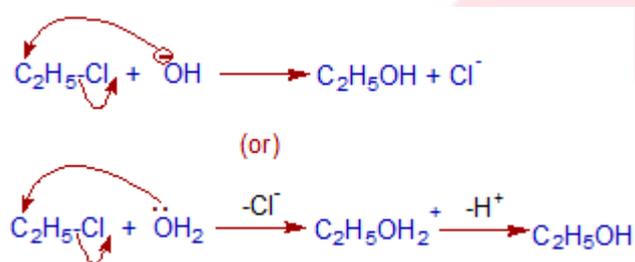
(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.



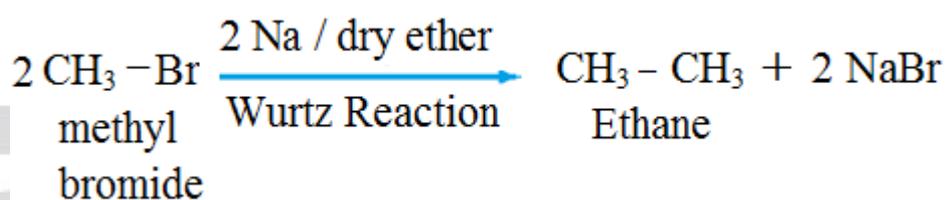
(iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.



(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.



(v) When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction.



(vi) When methyl chloride is treated with KCN, it undergoes a substitution reaction to give methyl cyanide.

