Haloalkanes and Haloarenes

Chapter 10 Haloalkanes and Haloarenes Exercise Solutions

In text : Solutions of Questions on Page Number : **285**

Q1 :

Write structures of the following compounds:

(i) 2-Chloro-3-methylpentane

(ii) 1-Chloro-4-ethylcyclohexane

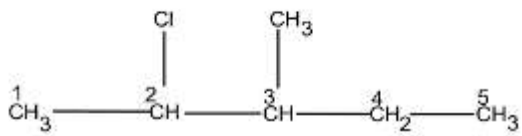
(iii) 4-tert. Butyl-3-iodoheptane

(iv) 1,4-Dibromobut-2-ene

(v) 1-Bromo-4-sec. butyl-2-methylbenzene

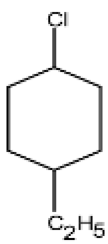
Answer :

(i)



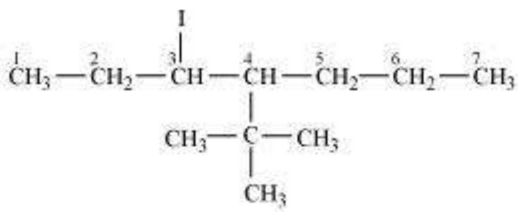
2-Chloro-3-methyl pentane

(ii)



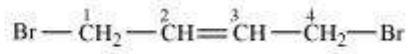
1-Chloro-4-ethylcyclohexane

(iii)



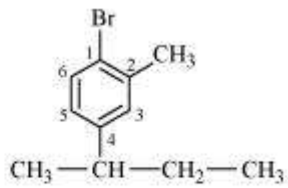
4- tert-Butyl-3-iodoheptane

(iv)



1, 4-Dibromobut-2-ene

(v)



1-Bromo-4-sec-butyl-2-methylbenzene

Q2 :

Why is sulphuric acid not used during the reaction of alcohols with KI?

Answer :

In the presence of sulphuric acid (H_2SO_4), KI produces HI

$$2KI + H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$

Since H_2SO_4 is an oxidizing agent, it oxidizes HI (produced in the reaction to I_{2}).

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$$

As a result, the reaction between alcohol and HI to produce alkyl iodide cannot occur. Therefore, sulphuric acid is not used during the reaction of alcohols with KI. Instead, a non-oxidizing acid such as H_3PO_4 is used.

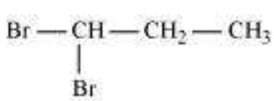
Q3 :

Write structures of different dihalogen derivatives of propane.

Answer :

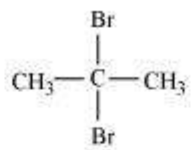
There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

(i)



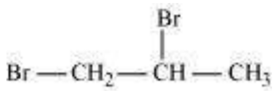
1, 1-Dibromopropane

(ii)



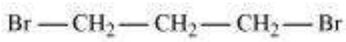
2, 2-Dibromopropane

(iii)



1, 2-Dibromopropane

(iv)



1, 3-Dibromopropane

Q4 :

Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

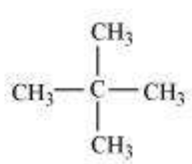
(i) A single monochloride.

(ii) Three isomeric monochlorides.

(iii) Four isomeric monochlorides.

Answer :

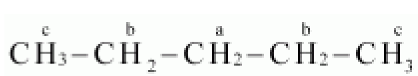
(i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula C_5H_{12}. This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.



Neopentane

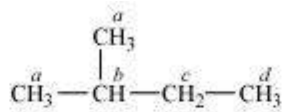
(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain three different types of H-atoms.

Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H atoms labelled as *a*, *b* and *c* in *n*-pentane.



n-Pentane

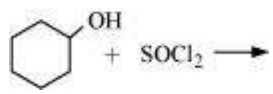
(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c,* and *d* in 2-methylbutane.



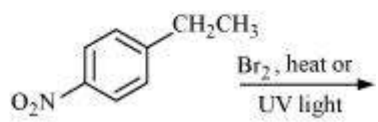
Q5 :

Draw the structures of major monohalo products in each of the following reactions:

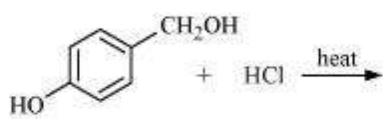
(i)



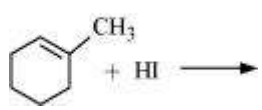
(ii)



(iii)



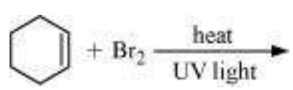
(iv)



(v)

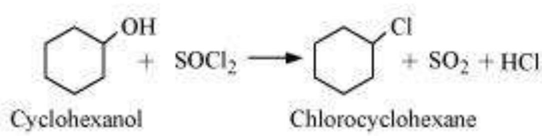
$CH_3CH_2Br + NaI \longrightarrow$

(vi)

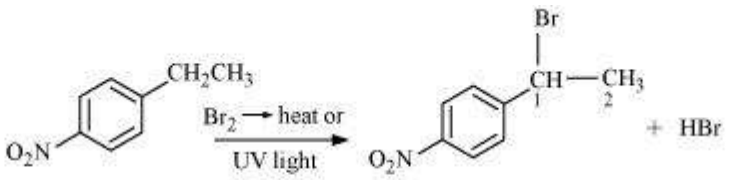


Answer :

(i)

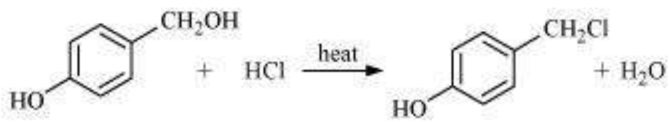


(ii)



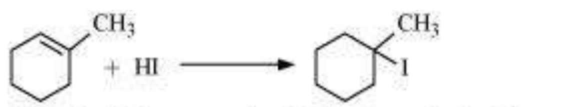
4 – Ethylnitrobenzene 4 – (1 – Bromoethyl) nitrobenzene

(iii)



4 – Hydroxymethylphenol 4 – Chloromethylphenol

(iv)

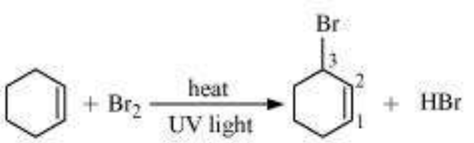


1 – Methylcyclohexene 1 – Iodo – 1 – methylcyclohexane

(v)

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + NaI \longrightarrow \underset{\text{Iodoethane}}{CH_3CH_2I} + NaBr$$

(vi)



Cyclohexene 3 – Bromocyclohexene

Q6 :

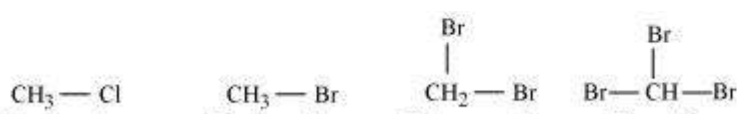
Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

Answer :

(i)



Chloromethane Bromomethane Dibromomethane Bromoform

For alkyl halides containing the same alkyl group, the boiling point increases with an increase in the atomic mass of the halogen atom.

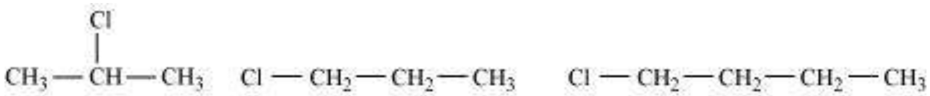
Since the atomic mass of Br is greater than that of Cl, the boiling point of bromomethane is higher than that of chloromethane.

Further, for alkyl halides containing the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of Dibromomethane is higher than that of chloromethane and bromomethane, but lower than that of bromoform.

Hence, the given set of compounds can be arranged in the order of their increasing boiling points as:

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

(ii)



Isopropyl chloride   1 – Chloropropane   1 – Chlorobutane

For alkyl halides containing the same halide, the boiling point increases with an increase in the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than that of isopropyl chloride and 1-chloropropane.

Further, the boiling point decreases with an increase in branching in the chain. Thus, the boiling point of isopropyl alcohol is lower than that of 1-chloropropane.

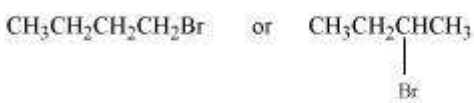
Hence, the given set of compounds can be arranged in the increasing order of their boiling points as:

Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

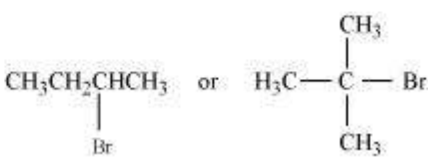
Q7 :

Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

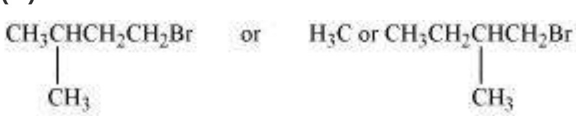
(i)



(ii)

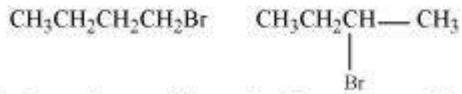


(iii)



Answer :

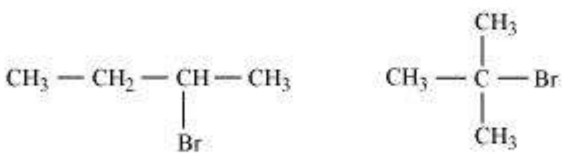
(i)



1 – Bromobutane (1°) 2 – Bromobutane (2°)

2-bromobutane is a 2° alkylhalide whereas 1-bromobutane is a 1° alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.

(ii)



2 – Bromobutane (2°) 2 – Bromo – 2 – methylpropane (3°)

2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3° alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.

(iii)

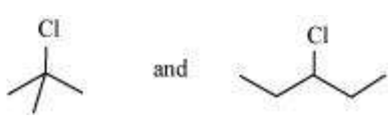
1 – Bromo – 3 – methylbutane (1°) 1 – Bromo – 2 – methylbutane (1°)

Both the alkyl halides are primary. However, the substituent $-CH_3$ is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by S_N2 mechanism.

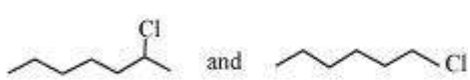
Q8 :

In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i)



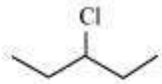
(ii)



Answer :

(i)

2 – Chloro – 2 – methylpropane (3°)
(I)



3 – chloropentane (2°)
(II)

S_N1 reaction proceeds via the formation of carbocation. The alkyl halide (I) is 3° while (II) is 2°. Therefore, (I) forms 3° carbocation while (II) forms 2° carbocation. Greater the stability of the carbocation, faster is the rate of S_N1 reaction. Since 3° carbocation is more stable than 2° carbocation. (I), i.e. 2-chloro-2-methylpropane, undergoes faster S_N1 reaction than (II) i.e., 3-chloropentane.

(ii)

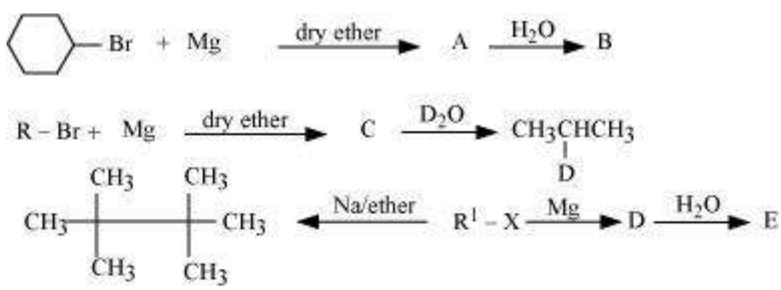
2 – chloroheptane (2°)
(I)

1 – chlorohexane (1°)
(II)

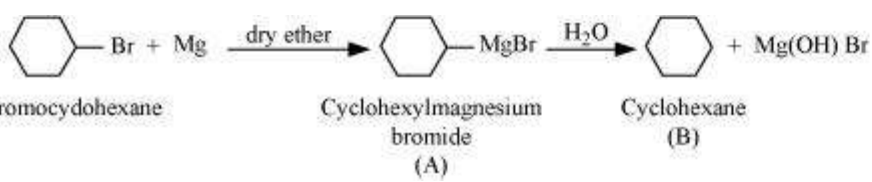
The alkyl halide (I) is 2° while (II) is 1°. 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2-chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

Q9 :

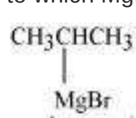
Identify A, B, C, D, E, R and R[1]in the following:



Answer :

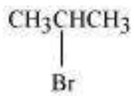


Since D of D_2O gets attached to the carbon atom to which MgBr is attached, C is

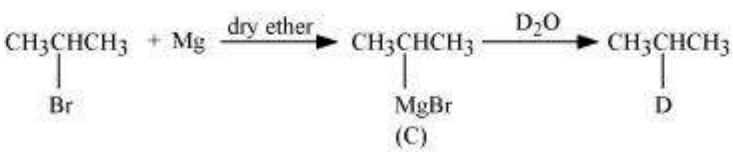


Isopropylmagnesium bromide

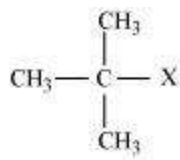
Therefore, the compound R - Br is



2 – Bromopropane

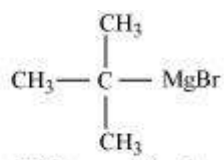


When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product. This is known as Wurtz reaction. Therefore, the halide, R^1-X, is



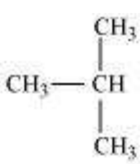
tert – Butylhalide

Therefore, compound D is

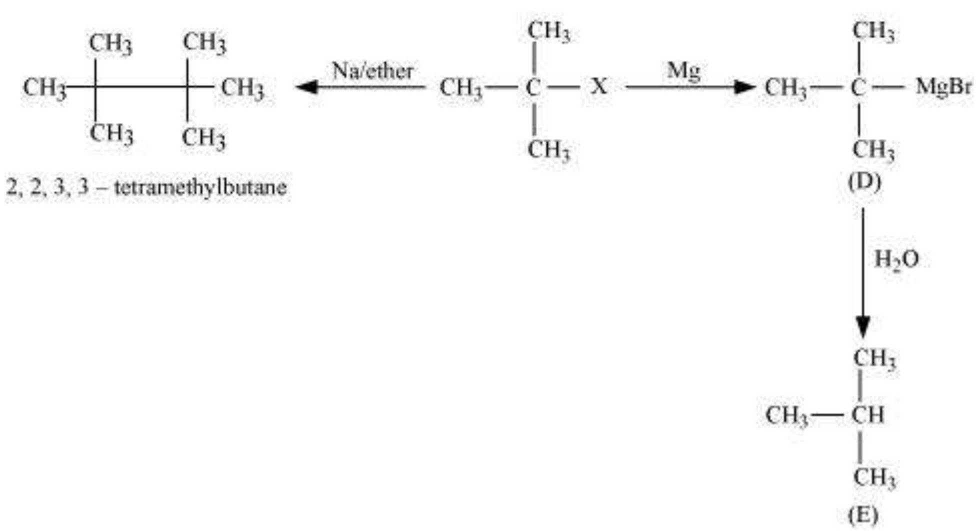


tert – Bulytmagnesiumbromide

And, compound E is



2 – Methylpropane



Exercise : Solutions of Questions on Page Number : **310**

Q1 :

Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

(i) $(CH_3)_2CHCH(Cl)CH_3$

(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(iii) $CH_3CH_2C(CH_3)_2CH_2I$

(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$

(v) $CH_3CH(CH_3)CH(Br)CH_3$

(vi) $CH_3C(C_2H_5)_2CH_2Br$

(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$

(viii) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$

(ix) $CH_3CH{=}CHC(Br)(CH_3)_2$

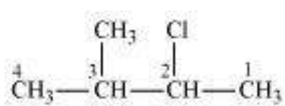
(x) *p*-$ClC_6H_4CH_2CH(CH_3)_2$

(xi) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$

(xii) *o*-Br-$C_6H_4CH(CH_3)CH_2CH_3$

Answer :

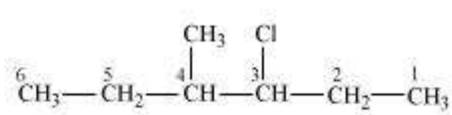
(i)



2-Chloro-3-methylbutane

(Secondary alkyl halide)

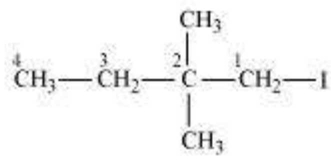
(ii)



3-Chloro-4-methyhexane

(Secondary alkyl halide)

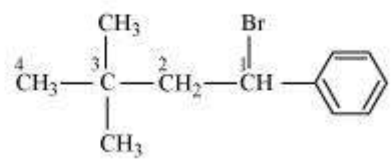
(iii)



1-Iodo-2, 2 -dimethylbutane

(Primary alkyl halide)

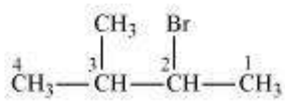
(iv)



1-Bromo-3, 3-dimethyl-1-phenylbutane

(Secondary benzyl halide)

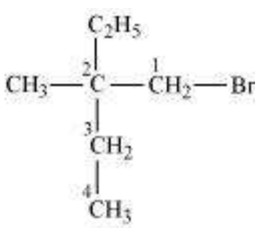
(v)



2-Bromo-3-methylbutane

(Secondary alkyl halide)

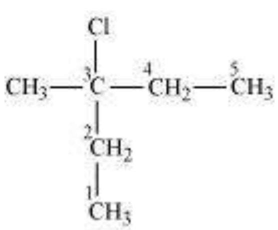
(vi)



1-Bromo-2-ethyl-2-methylbutane

(Primary alkyl halide)

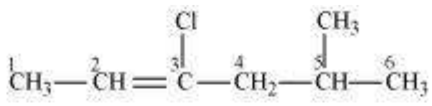
(vii)



3-Chloro-3-methylpentane

(Tertiary alkyl halide)

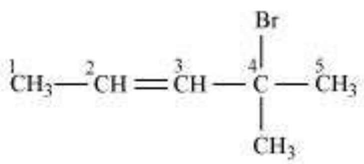
(viii)



3-Chloro-5-methylhex-2-ene

(Vinyl halide)

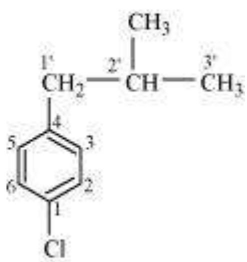
(ix)



4-Bromo-4-methylpent-2-ene

(Allyl halide)

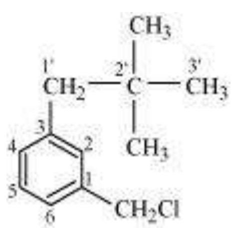
(x)



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)

Q2 :

Give the IUPAC names of the following compounds:

(i) $CH_3CH(Cl)CH(Br)CH_3$

(ii) $CHF_2CBrClF$

(iii) $ClCH_2C$Ã¢â€°Â¡CCH_2Br

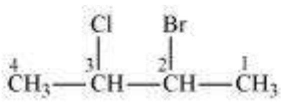
(iv) $(CCl_3)_3CCl$

(v) $CH_3C($*p*$-ClC_6H_4)_2CH(Br)CH_3$

(vi) $(CH_3)_3CCH=CClC_6H_4I$-*p*

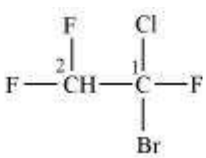
Answer :

(i)



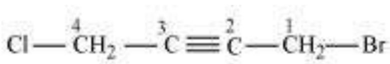
2-Bromo-3-chlorobutane

(ii)



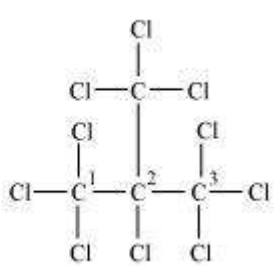
1-Bromo-1-chloro-1, 2, 2-trifluoroethane

(iii)



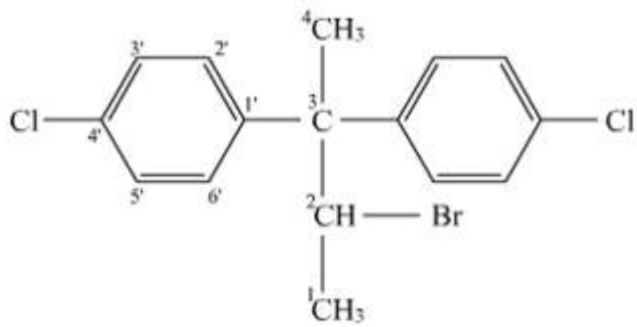
1-Bromo-4-chlorobut-2-yne

(iv)



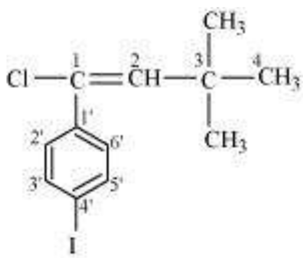
2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

(v)



2-Bromo-3, 3-bis(4-chlorophenyl) butane

(vi)



1-chloro-1-(4-iodophenyl)-3, 3-dimethylbut-1-ene

Q3 :

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

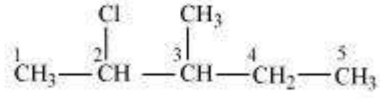
(vi) 4-tert-Butyl-3-iodoheptane

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene

(viii) 1,4-Dibromobut-2-ene

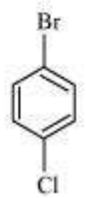
Answer :

(i)



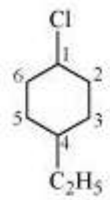
2-Chloro-3-methylpentane

(ii)



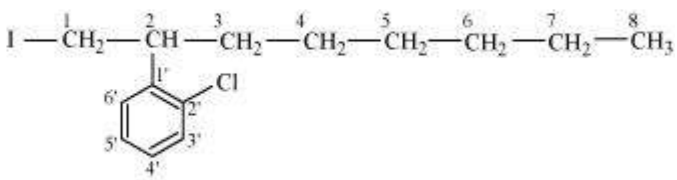
p-Bromochlorobenzene

(iii)



1-Chloro-4-ethylcyclohexane

(iv)

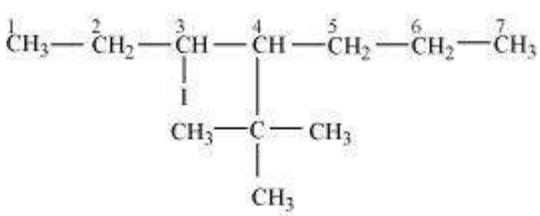


2-(2-Chlorophenyl)-1-iodooctane

(v)

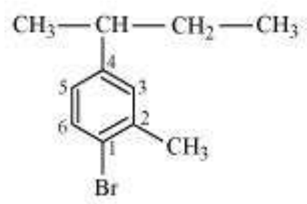
Perfluorobenzene

(vi)



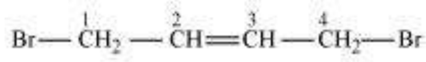
4-Tert-Butyl-3-iodoheptane

(vii)



1-Bromo-4-sec-butyl-2-methylbenzene

(viii)



1,4-Dibromobut-2-ene

Q4 :

Which one of the following has the highest dipole moment?

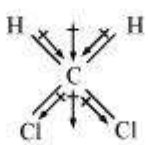
(i) CH_2Cl_2

(ii) $CHCl_3$

(iii) CCl_4

Answer :

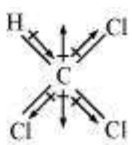
(i)



Dichlormethane (CH_2Cl_2)

ÃŽÂ¼ = 1.60D

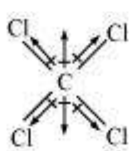
(ii)



Chloroform ($CHCl_3$)

ÃŽÂ¼ = 1.08D

(iii)



Carbon tetrachloride (CCl_4)

ÃŽÂ¼ = 0D

CCl_4 is a symmetrical molecule. Therefore, the dipole moments of all four C-Cl bonds cancel each other. Hence, its resultant dipole moment is zero.

As shown in the above figure, in $CHCl_3$, the resultant of dipole moments of two C-Cl bonds is opposed by the resultant of dipole moments of one C-H bond and one C-Cl bond. Since the resultant of one C-H bond and one C-Cl bond dipole moments is smaller than two C-Cl bonds, the opposition is to a small extent. As a result, $CHCl_3$ has a small dipole moment of 1.08 D.

On the other hand, in case of CH_2Cl_2, the resultant of the dipole moments of two C-Cl bonds is strengthened by the resultant of the dipole moments of two C-H bonds. As a result, CH_2Cl_2 has a higher dipole moment of 1.60 D than $CHCl_3$i.e., CH_2Cl_2 has the highest dipole moment.

Hence, the given compounds can be arranged in the increasing order of their dipole moments as:

$CCl_4 < CHCl_3 < CH_2Cl_2$

Q5 :

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 :

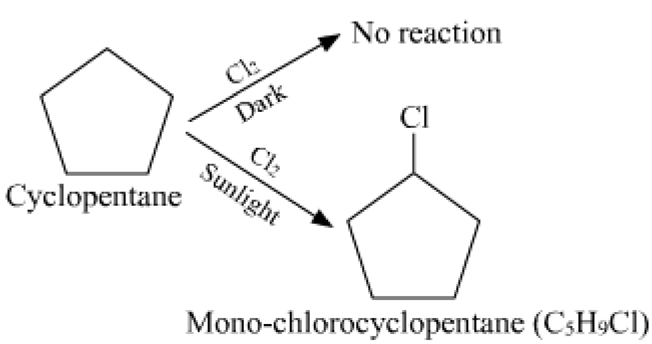
A hydrocarbon with the molecular formula, C_5H_{10} belongs to the group with a general molecular formula C_nH_{2n}. Therefore, it may either be an alkene or a cycloalkane.

Since hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane.

Further, the hydrocarbon gives a single monochloro compound, C_5H_9Cl by reacting with chlorine in bright sunlight. Since a single monochloro compound is formed, the hydrocarbon must contain H-atoms that are all equivalent. Also, as all H-atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.

Cyclopentane (C_5H_{10})

The reactions involved in the question are:



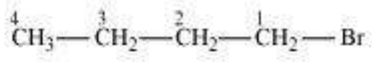
Q6 :

Write the isomers of the compound having formula C_4H_9Br.

Answer :

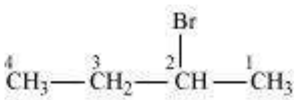
There are four isomers of the compound having the formula C_4H_9Br. These isomers are given below.

(a)



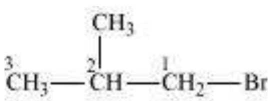
1-Bromobutane

(b)



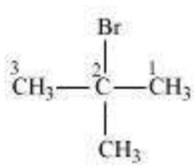
2-Bromobutane

(c)



1-Bromo-2-methylpropane

(d)



2-Bromo-2-methylpropane

Q7 :

Write the equations for the preparation of 1-iodobutane from

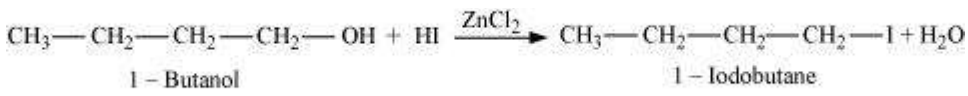
(i) 1-butanol

(ii) 1-chlorobutane

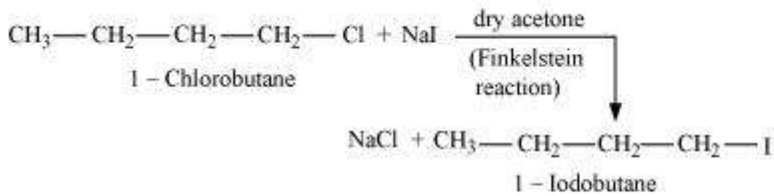
(iii) but-1-ene.

Answer :

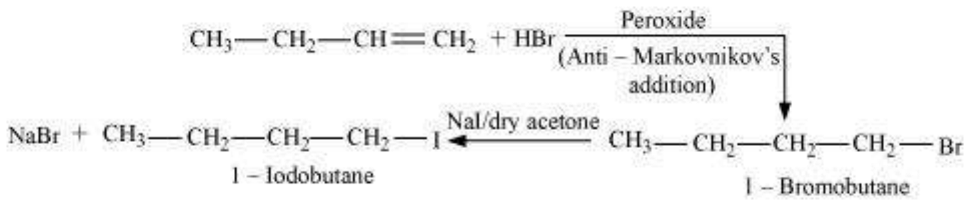
(i)



(ii)



(iii)



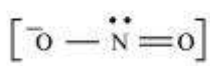
Q8 :

What are ambident nucleophiles? Explain with an example.

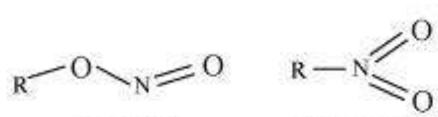
Answer :

Ambident nucleophiles are nucleophiles having two nucleophilic sites. Thus, ambident nucleophiles have two sites through which they can attack.

For example, nitrite ion is an ambident nucleophile.



Nitrite ion can attack through oxygen resulting in the formation of alkyl nitrites. Also, it can attack through nitrogen resulting in the formation of nitroalkanes.



Alkylnitrite Nitroalkane

Q9 :

Which compound in each of the following pairs will react faster in S_N2 reaction with OH^-?

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

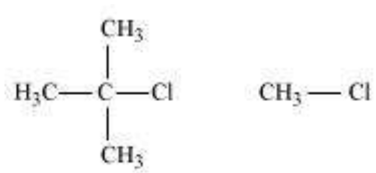
Answer :

(i) In the S_N2 mechanism, the reactivity of halides for the same alkyl group increases in the order. This happens because as the size increases, the halide ion becomes a better leaving group.

R-F << R-Cl < R-Br < R-I

Therefore, CH_3I will react faster than CH_3Br in S_N2 reactions with OH^-.

(ii)



The S_N2 mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in case of $(CH_3)_3CCl$, the attack of the nucleophile at the carbon atom is hindered because of the presence of bulky substituents on that carbon atom bearing the leaving group. On the other hand, there are no bulky substituents on the carbon atom bearing the leaving group in CH_3Cl. Hence, CH_3Cl reacts faster than $(CH_3)_3CCl$ in S_N2 reaction with OH^-.

Q10 :

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)

In the given compound, there are two types of ÃŽÂ²-hydrogen atoms are present. Thus, dehydrohalogenation of this compound gives two alkenes.

”‹

(ii)

In the given compound, there are two different sets of equivalent ÃŽÂ²-hydrogen atoms labelled as *a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.

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 ÃŽÂ²-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.

Q11 :

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 biphenyl.

Answer :

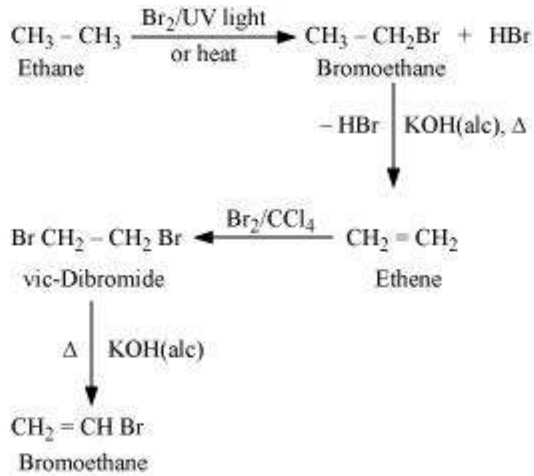
(i)

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{SOCl_2\text{, Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2 + HCl$$

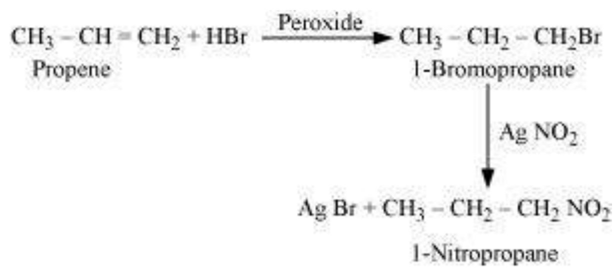
$$\underset{\text{Ethyne}}{HC \equiv CH} + NaNH_2 \xrightarrow{\text{Liq. }NH_3} \underset{\text{Sodium acetylide}}{HC \equiv \overset{-}{C}\overset{+}{N}a}$$

$$\underset{\text{Chloroethane}}{CH_3CH_2-Cl} + HC \equiv \overset{-}{C}\overset{+}{N}a \longrightarrow \underset{\text{But}-1-\text{yne}}{CH_3CH_2C \equiv CH} + NaCl$$

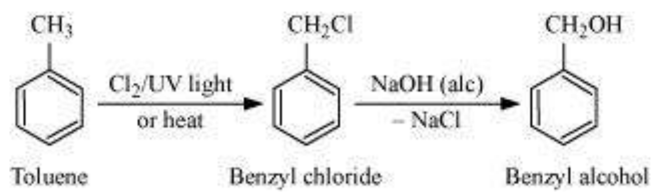
(ii)



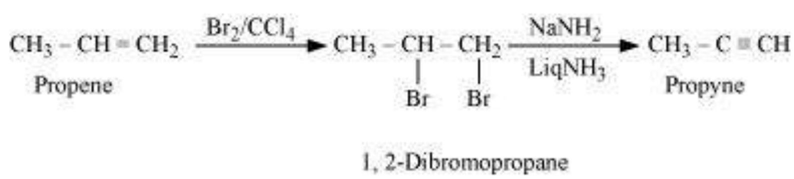
(iii)



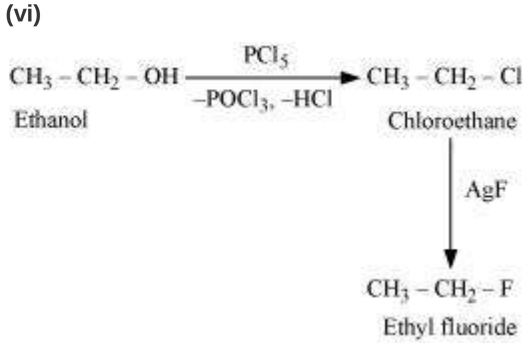
(iv)



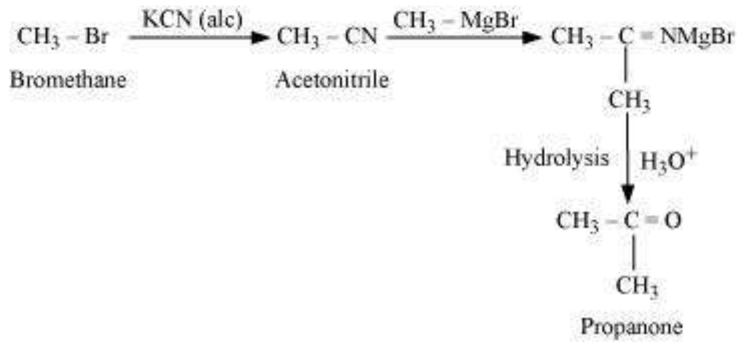
(v)



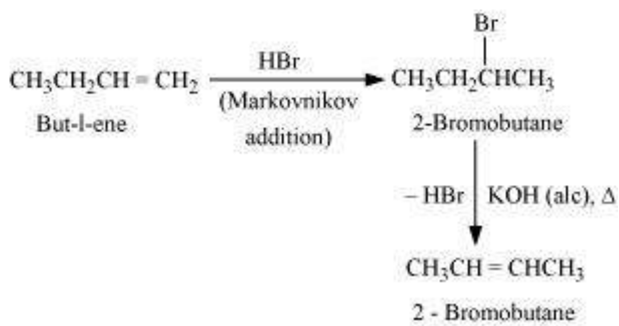
(vi)



(vii)



(viii)

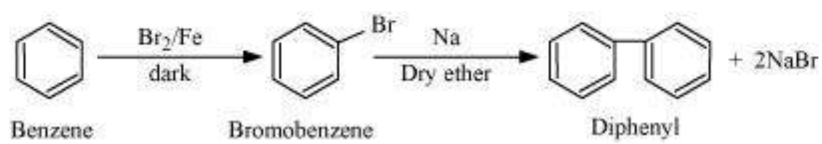


(ix)

$$2CH_3CH_2CH_2CH_2-Cl+2Na \xrightarrow[-2NaCl]{\text{dry ether}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

1 – Chlordrutane n – Octane

(x)



Q12 :

Explain why

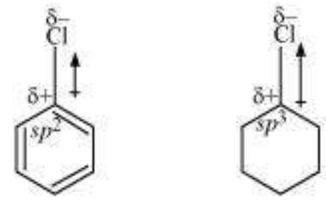
(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

Answer :

(i)



Chlorobenzene Cyclohexyl chloride

In chlorobenzene, the Cl-atom is linked to a sp^2 hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to asp^3 hybridized carbon atom. Now, sp^2 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 cydohexyl 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.

$$\underset{\text{Grigrard reagent}}{\overset{\delta-}{R}\overset{\delta+}{Mg}\overset{\delta-}{X}} + H_2O \longrightarrow \underset{\text{Alkane}}{R-H} + Mg(OH)X$$

Therefore, Grignard reagents should be prepared under anhydrous conditions.

Q13 :

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 carbontetrachloride (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.

(iv) Until the mid 1960's, carbon tetrachloride was widely used as a cleaning fluid, a degreasing agent in industries, a spot reamer in homes, and a fire extinguisher.

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.

Q14 :

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

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$

(ii) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}$

(iv) $CH_3CH_2Br + KCN \xrightarrow{\text{aq.ethanol}}$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(vii) $CH_3CH_2CH=CH_2 + HBr \xrightarrow{\text{Peroxide}}$

(viii) $CH_3CH=C(CH_3)_2 + HBr \longrightarrow$

Answer :

(i)

$$\underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + NaI \xrightarrow[\text{heat}]{\text{acetone}} \underset{\text{1-Iodopropane}}{CH_3CH_2CH_2I} + NaCl$$

$$\begin{pmatrix}\text{Finkelstein} \\ \text{reaction}\end{pmatrix}$$

(ii)

$$\underset{\text{2-Bromo-2-methylpropane}}{(CH_3)_3CBr} + KOH \xrightarrow[\text{heat}]{\text{ethanol}} \begin{array}{c} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \end{array} + KBr + H_2O$$

(Dehydrohalogenation)

2-Methylpropene

(iii)

$$\underset{\text{2-Bromobutane}}{CH_3CH(Br)CH_2CH_3} + NaOH \xrightarrow{\text{water}} \underset{\text{Butan-2-ol}}{CH_3CH(OH)CH_2CH_3} + NaBr$$

(iv) $$\underset{\text{Bromobutane}}{CH_3CH_2Br} + KCN \xrightarrow[\text{(Nucleophilic substitution)}]{\text{aq. ethanol}} \underset{\text{Cyanoethane}}{CH_3CH_2CN} + KBr$$

(v) $$\underset{\text{Sodium phenoxide}}{C_6H_5ONa} + \underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow[\text{(Williamson synthesis)}]{} \underset{\text{Phenetole}}{C_6H_5-O-C_2H_5} + NaCl$$

(vi) $$\underset{1-\text{Propanol}}{CH_3CH_2CH_2OH} + SOCl_2 \longrightarrow \underset{1-\text{Chloropropane}}{CH_3CH_2CH_2Cl} + SO_2 + HCl$$

(vii) $$\underset{\text{But}-1-\text{ene}}{CH_3CH_2CH=CH_2} + HBr \xrightarrow[\text{(Anti-Markovnikov's addition)}]{\text{Peroxide}} \underset{1-\text{Bromobutane}}{CH_3CH_2CH_2CH_2-Br}$$

(viii)

Q15 :

Write the mechanism of the following reaction:

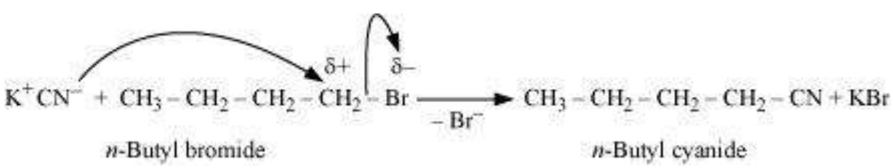
$$nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$$

Answer :

The given reaction is:

$$nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$$

The given reaction is an S_N2 reaction. In this reaction, CN^- acts as the nucleophile and attacks the carbon atom to which Br is attached. CN^- ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



Q16 :

Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

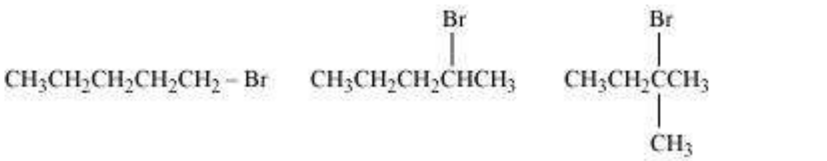
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(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 :

(i)



1-Bromopentane (1°) 2-Bromopentane (2°) 2-Bromo-2-methylbutane (3°)

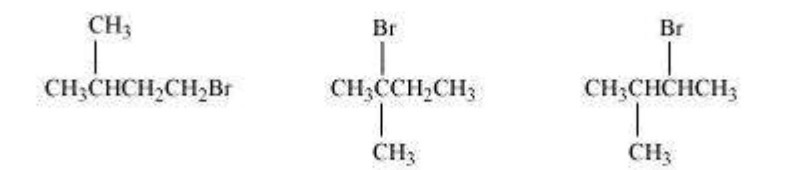
An S_N2 reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards S_N2 displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases in the following order.

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

Hence, the increasing order of reactivity towards S_N^2 displacement is:

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

(ii)



1-Bromo-3-methylbutane (1°) 2-Bromo-2-methylbutane (3°) 2-Bromo-3-methylbutane (2°)

Since steric hindrance in alkyl halides increases in the order of 1° < 2° < 3°, the increasing order of reactivity towards S_N2 displacement is

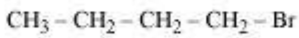
3° < 2° < 1°.

Hence, the given set of compounds can be arranged in the increasing order of their reactivity towards S_N^2 displacement as:

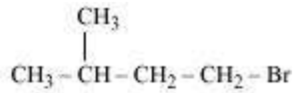
2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane

[2-Bromo-3-methylbutane is incorrectly given in NCERT]

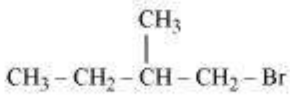
(iii)



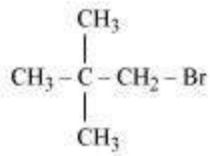
1-Bromobutane



1-Bromo-3-methylbutane



1-Bromo-2-methylbutane



1-Bromo-2, 2-dimethylpropane

The steric hindrance to the nucleophile in the S_N2 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 S_N2 displacement is:

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

Q17 :

Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

Answer :

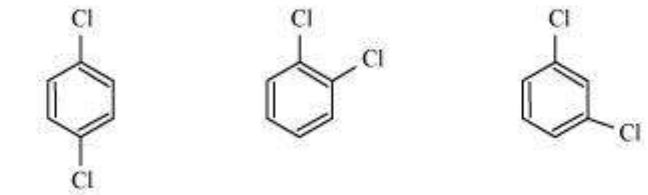
Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. Now, forms 1°-carbocation, while forms 2°-carbocation, which is more stable than 1°-carbocation. Hence, is hydrolyzed more easily than by aqueous KOH.

Q18 :

***p*-Dichlorobenzene has higher m.p. and lower solubility than those of *o*- and**

***m*-isomers. Discuss.**

Answer :



p-Dichlorobenzene *o*-Dichlorobenzene *m*-Dichlorobenzene

p-Dichlorobenzene is more symmetrical than *o*-and *m*-isomers. For this reason, it fits more closely than *o*-and *m*-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of *p*-dichlorobenzene. As a result, *p*-dichlorobenzene has a higher melting point and lower solubility than *o*-and *m*-isomers.

Q19 :

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

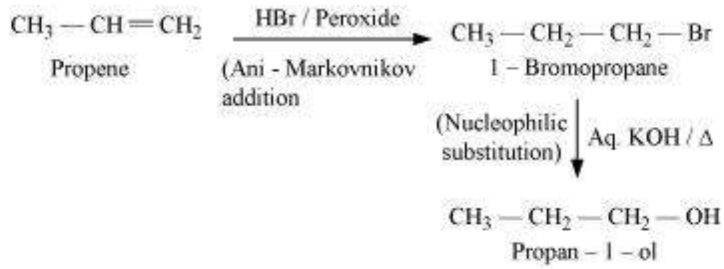
(xviii) Benzene to diphenyl

(xix) *tert*-Butyl bromide to isobutyl bromide

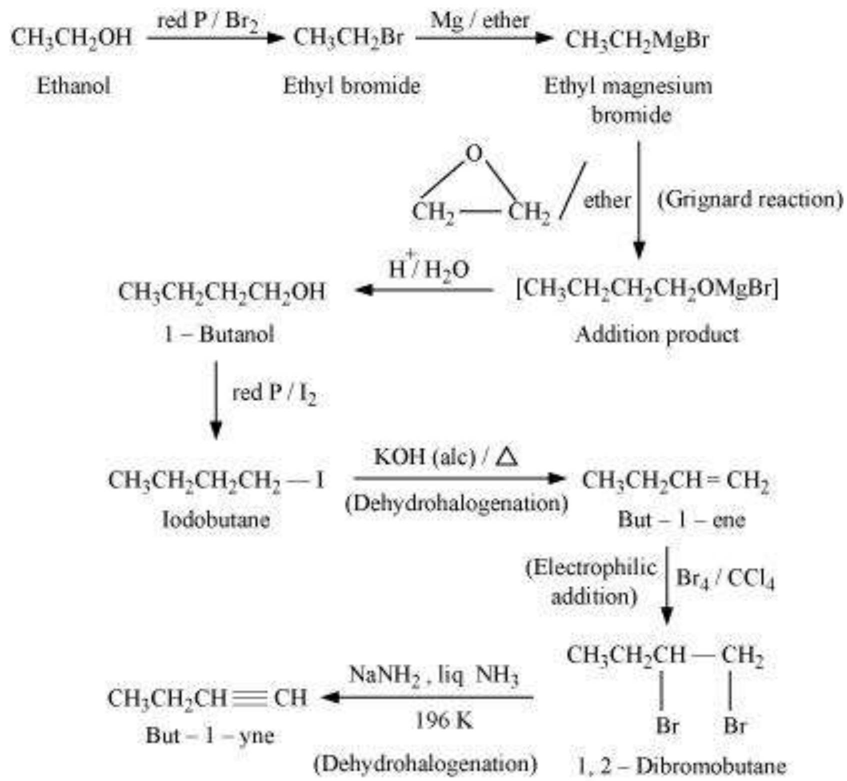
(xx) Aniline to phenylisocyanide

Answer :

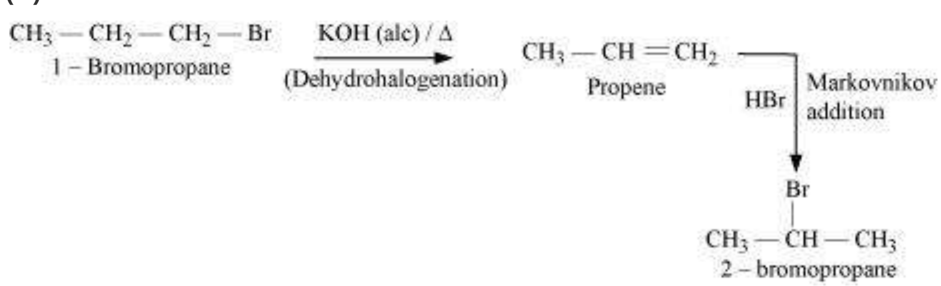
(i)


CH3 — CH = CH2
Propene
HBr / Peroxide
(Ani - Markovnikov
addition
CH3 — CH2 — CH2 — Br
1 – Bromopropane
(Nucleophilic
substitution)
Aq. KOH / Δ
CH3 — CH2 — CH2 — OH
Propan – 1 – ol

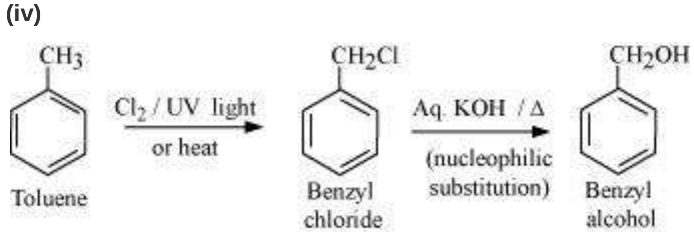
(ii)


CH3CH2OH
Ethanol
red P / Br2
CH3CH2Br
Ethyl bromide
Mg / ether
CH3CH2MgBr
Ethyl magnesium
bromide
O
CH2 — CH2
ether
(Grignard reaction)
H+ / H2O
CH3CH2CH2CH2OH
1 – Butanol
[CH3CH2CH2CH2OMgBr]
Addition product
red P / I2
CH3CH2CH2CH2 — I
Iodobutane
KOH (alc) / Δ
(Dehydrohalogenation)
CH3CH2CH = CH2
But – 1 – ene
(Electrophilic
addition)
Br4 / CCl4
CH3CH2CH — CH2
Br Br
1, 2 – Dibromobutane
NaNH2 , liq. NH3
196 K
(Dehydrohalogenation)
CH3CH2CH ≡ CH
But – 1 – yne

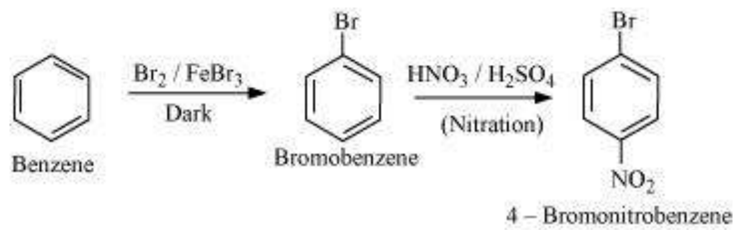
(iii)


CH3 — CH2 — CH2 — Br
1 – Bromopropane
KOH (alc) / Δ
(Dehydrohalogenation)
CH3 — CH = CH2
Propene
HBr
Markovnikov
addition
Br
CH3 — CH — CH3
2 – bromopropane

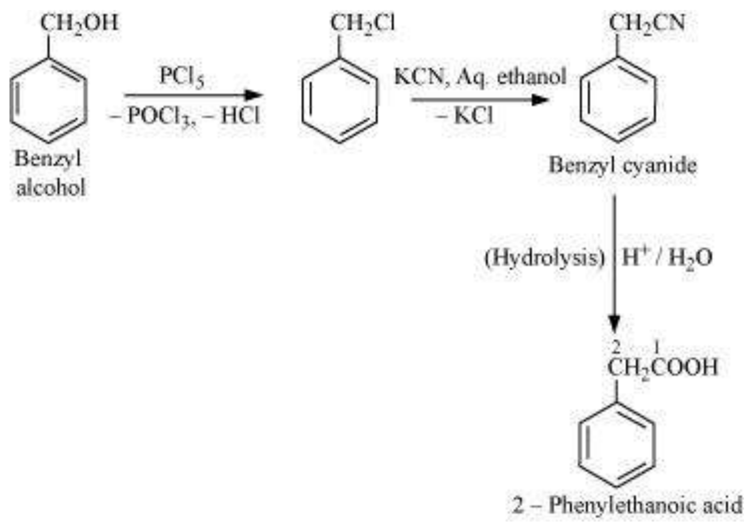
(iv)


CH3
Toluene
Cl2 / UV light
or heat
CH2Cl
Benzyl
chloride
Aq. KOH / Δ
(nucleophilic
substitution)
CH2OH
Benzyl
alcohol

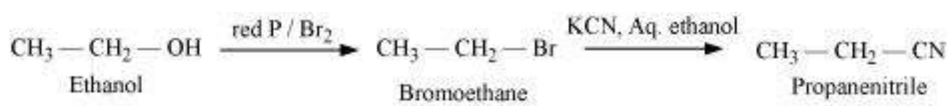
(v)



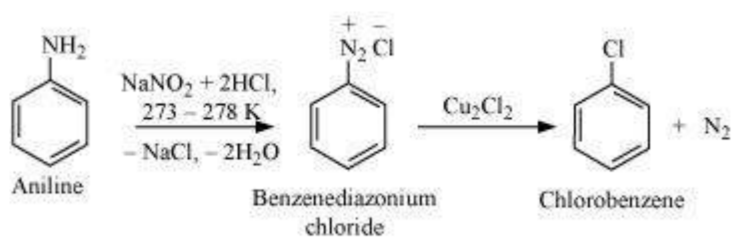
(vi)



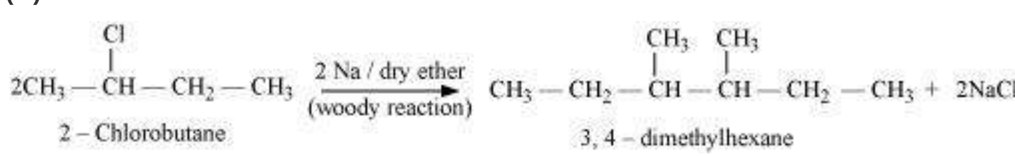
(vii)



(viii)

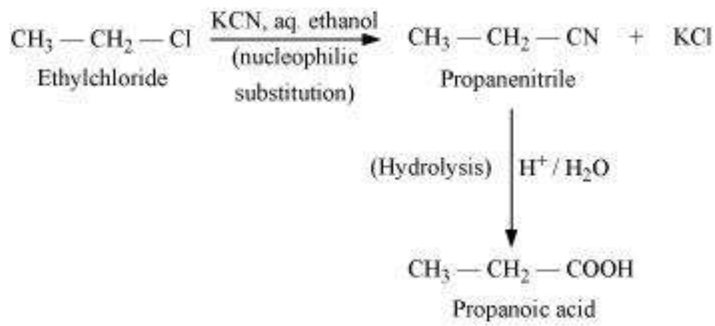


(ix)

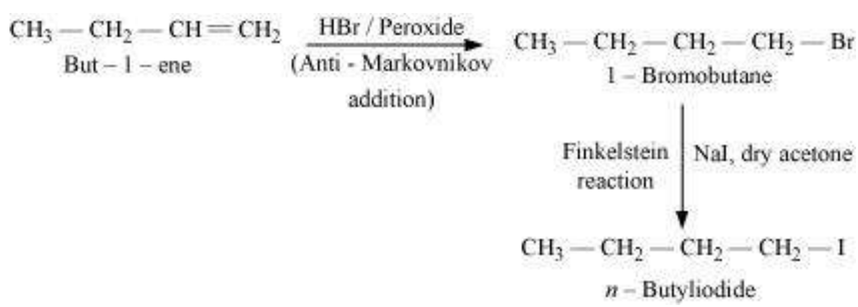


(x)

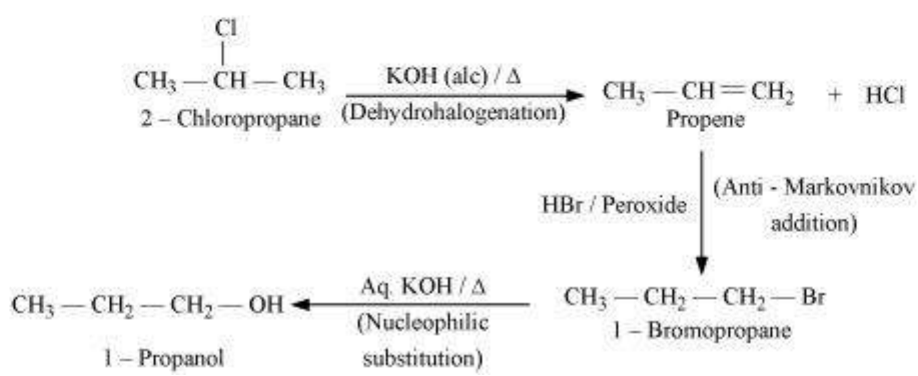
(xi)



(xii)



(xiii)



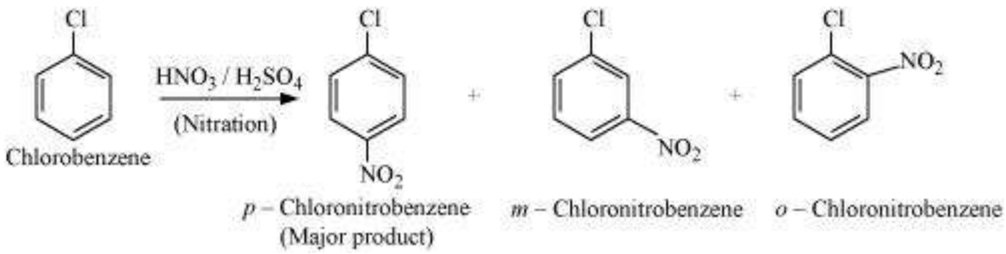
(xiv)

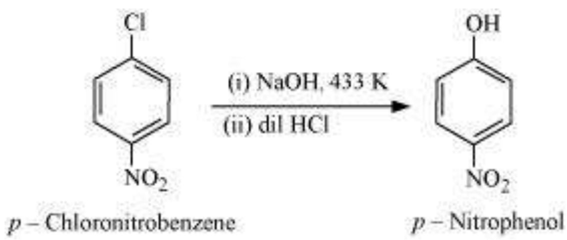
$$\underset{\text{Isopropyl alcohol}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_3} \xrightarrow[\text{(Oxidation)}]{CrO_3} \underset{\text{Propanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$

$$\downarrow \text{NaOI (Iodoform reaction)}$$

$$CH_3-\overset{O}{\overset{\|}{C}}-ONa + \underset{\text{Iodoform}}{CHI_3}$$

(xv)





(xvi)

$$\underset{\text{2 – Bromopropane}}{CH_3-\overset{Br}{\overset{|}{C}H}-CH_3} \xrightarrow[\text{Dehydrohalogenation}]{\text{KOH (alc) / }\Delta} \underset{\text{Propene}}{CH_3-CH=CH_2} + HBr$$

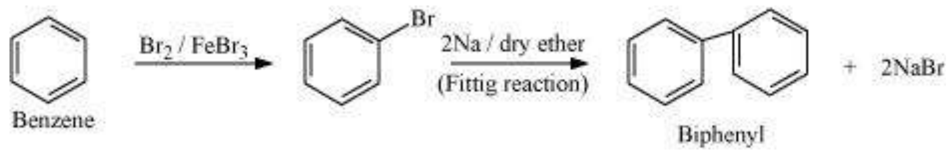
$$\downarrow \text{HBr / Peroxide (Anti–Markovnikov addition)}$$

$$\underset{\text{1 – Bromopropane}}{CH_3-CH_2-CH_2-Br}$$

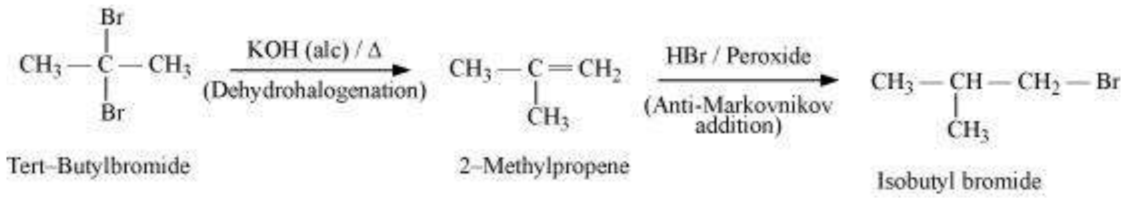
(xvii)

$$\underset{\text{Chloroethane}}{CH_3-CH_2-Cl} \xrightarrow[\text{(Wurtz reaction)}]{\text{2 Na / dry ether}} \underset{\text{Butane}}{CH_3-CH_2-CH_2-CH_3} + 2NaCl$$

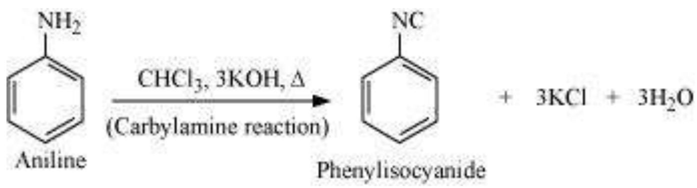
(xviii)



(xix)



(xx)



Q20 :

The treatment of alkyl chlorides with aqueous KOH leads to the formation of

alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Answer :

In an aqueous solution, KOH almost completely ionizes to give OH^- ions. OH^- ion is a strong nucleophile, which leads the alkyl chloride to undergo a substitution reaction to form alcohol.

$$\underset{\text{Alkyl chloride}}{R-Cl} + KOH_{(aq)} \longrightarrow \underset{\text{Alcohol}}{R-OH} + KCl$$

On the other hand, an alcoholic solution of KOH contains alkoxide (RO^-) ion, which is a strong base. Thus, it can abstract a hydrogen from the ÃŽÂ²-carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.

$$\underset{\text{Alkyl chloride}}{R-\underset{\beta}{C}H_2-\underset{\alpha}{C}H_2-Cl} + KOH(alc) \longrightarrow \underset{\text{Alkene}}{R-CH=CH_2} + KCl + H_2O$$

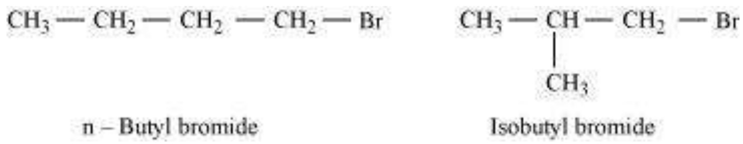
OH^- ion is a much weaker base than RO^- ion. Also, OH^- ion is highly solvated in an aqueous solution and as a result, the basic character of OH^- ion decreases. Therefore, it cannot abstract a hydrogen from the ÃŽÂ²-carbon.

Q21 :

Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b).Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18}which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

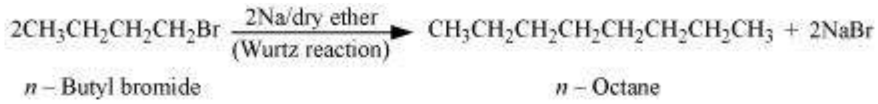
Answer :

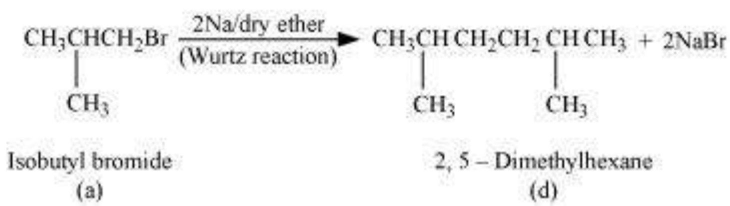
There are two primary alkyl halides having the formula, C_4H_9Br. They are *n* - bulyl bromide and isobutyl bromide.



Therefore, compound (a) is either *n*-butyl bromide or isobutyl bromide.

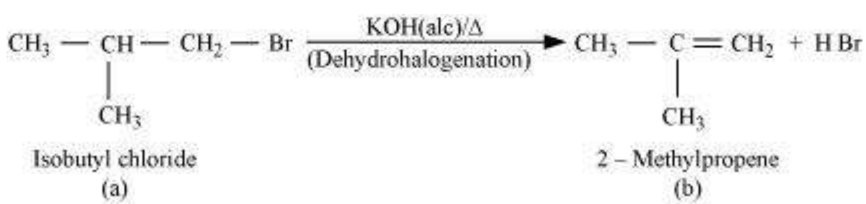
Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, $C_8H_{18,}$ which is different from the compound formed when *n*-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.



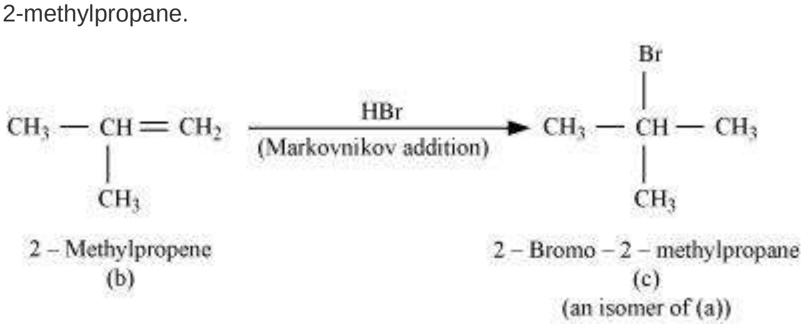


Thus, compound (d) is 2, 5-dimethylhexane.

It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2-methylpropene.



Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2-bromo-2-methylpropane.



Q22 :

What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

(ii) bromobenzene is treated with Mg 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,

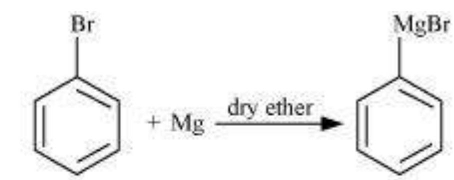
(vi) methyl chloride is treated with KCN.

Answer :

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

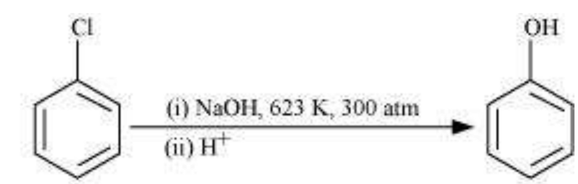
$$\underset{n-\text{Butyl chloride}}{CH_3-CH_2-CH_2-CH_2-Cl} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}/\Delta} \underset{\text{But-l-ene}}{CH_3-CH_2-CH=CH_2} + KCl + H_2O$$

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



Bromobenzene Phenylmagensium bromide

(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.



Chlorobenzene Phenol

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

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} \xrightarrow[\text{(Hydrolysis)}]{KOH_{(aq)}} \underset{\text{Ethanol}}{CH_3-CH_2-OH} + KCl$$

(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.

$$\underset{\text{Methyl bromide}}{2\,CH_3-Br} + 2\,Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

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

$$\underset{\text{Methyl chloride}}{CH_3-Cl} + KCN \xrightarrow[\text{Nucleophilic substitution}]{} \underset{\text{Methyl cyanide}}{CH_3-CN} + KCl$$