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Class 12

CHEMISTRY

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HaloAlkanes and HaloArenes

NCERT Solutions

Question 10.1.

Name the following halides according to IUPAC system and classify them as alkyl, allyl, and benzyl (primary, secondary, tertiary), and 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) $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$
- (viii) $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$
- (ix) $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$
- (x) $m\text{-ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_3$
- (xi) $o\text{-Br-C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

Answer:

(i) 2-chloro-3-methylbutane, (2° alkyl halide)

The Cl atom is attached with two alkyl groups therefore 2° alkyl halide.

(ii) 3-chloro-4-methylhexane (2° alkyl halide)

The Cl atom is attached with two alkyl groups therefore 2° alkyl halide.

(iii) 1-iodo-2,2-dimethylbutane (1° alkyl halide)

The atom I is attached with one alkyl group therefore 1° alkyl halide.

(iv) 1-bromo-3,3-dimethyl-1-phenylbutane (2° benzylic halide)

The atom Br is attached with two alkyl groups with the benzene group therefore 2° benzylic halide.

(v) 2-bromo-3-methylbutane (2° alkyl halide)

The atom Br is attached with two alkyl groups therefore 2° alkyl halide.

(vi) 1-bromo-2-ethyl-2-methylbutane (1° alkyl halide)

The atom Br is attached with one alkyl group therefore 1° alkyl halide.)

(viii) 3-chloro-3-methylpentane (3° alkyl halide)

The atom Cl is attached with three alkyl groups therefore 3° alkyl halide.

(viii) 3-chloro-5-methylhex-2-ene (vinylic halide)

The atom Cl is attached with the double bond i.e. at vinylic position therefore vinylic halide.)

(ix) 4-bromo-4-methylpent-2-ene (allylic halide)

The Br atom is attached with the carbon next to the double bond i.e. at allylic position therefore allylic halide.

(x) 1-chloro-4-(2-methylpropyl) benzene (aryl halide)

The Cl atom is attached with the benzene i.e. at aryl position therefore aryl halide.

(xi) 1-chloro-3-(2, 2-dimethylpropyl) benzene (1° benzylic halide)

The Cl is attached with one alkyl group at the benzene carbon therefore 1° benzylic halide.

(xii) 1-bromo-2-(1-methylpropyl) benzene (aryl halide)

The Br is attached with the benzene i.e. at aryl position therefore aryl halide.

Question 10.2.

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) $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Br}$

(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:

- (i) IUPAC name is :- 2-Bromo-3-chlorobutane
- (ii) IUPAC name is :- 1-Bromo-1-chloro-1,2,2-trifluoroethane
- (iii) IUPAC name is :- 1-bromo-4-chlorobut-2-yne
- (iv) IUPAC name is :- 2-(trichloromethyl)-1,1,1,2,3,3,3heptachloropropane
- (v) IUPAC name is :- 2-bromo-3,3-bis-(4-chlorophenyl)butane
- (vi) IUPAC name is :- 1-chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene

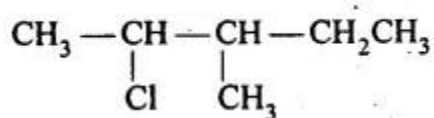
Question 10.3.

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:

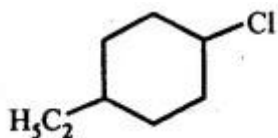
- (i) 2-Chloro-3-methylpentane



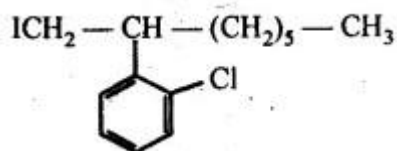
- (ii) p-Bromochlorobenzene



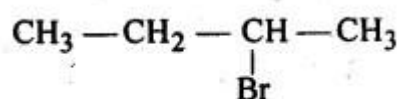
- (iii) 1-Chloro-4-ethylcyclohexane



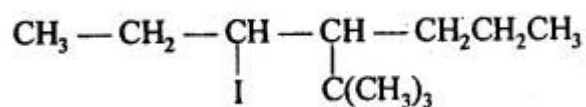
(iv) 2-(2-Chlorophenyl)-1-iodooctane



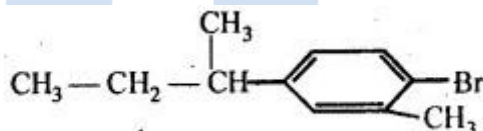
(v) Perfluorobenzene



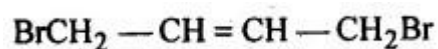
(vi) 4-tert-Butyl-3-iodoheptane



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



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



Question 10.4.

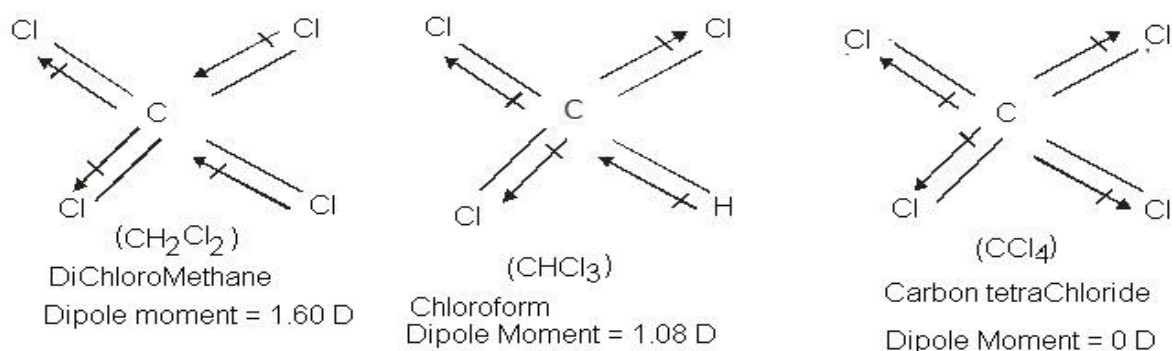
Which one of the following has the highest dipole moment?

(i) CH_2Cl_2

(ii) CHCl_3

(iii) CCl_4

Answer:



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.

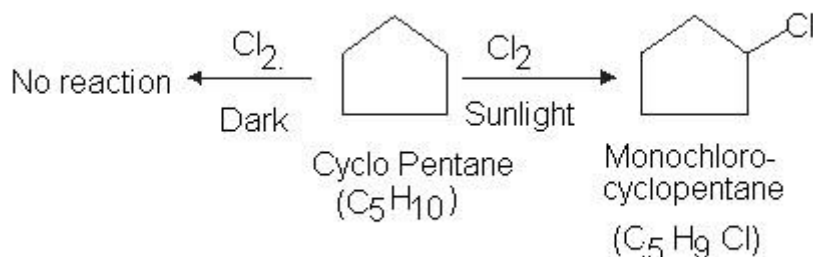
Hence, the given compounds can be arranged in the increasing order of their dipole moments as:



Question 10.5.

A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound $\text{C}_5\text{H}_9\text{Cl}$ in bright sunlight. Identify the hydrocarbon.

Answer:



A hydrocarbon with the molecular formula, C₅H₁₀ 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, C₅H₉Cl 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.

Question 10.6.

Write the isomers of the compound having formula C₄H₉Br.

Answer:

Double bond equivalent is used to find the level of unsaturation's present in an organic molecule.

$$\text{DBE} = \left(C + 1 - \left(\frac{H}{2} \right) + \left(\frac{X}{2} \right) - \left(\frac{N}{2} \right) \right)$$

Where C= number of carbon atoms present

H=number of hydrogen atoms present

N=number of nitrogen atoms present

X=number of halogen atoms present

Double bond equivalent (DBE) for C_4H_9Br

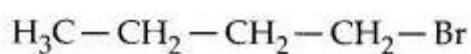
$$= (4 + 1 - \frac{9}{2}) + \frac{1}{2}$$

$$= 0$$

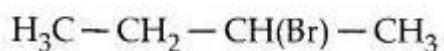
So none of the isomers has a ring or unsaturation, so the isomers are positions or chain isomers as shown below in the table:

The possible isomers of C_4H_9Br are following:-

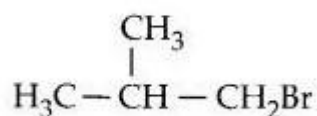
(i) 1-BromoButane



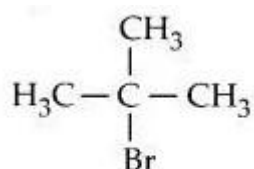
(ii) 2-BromoButane



(iii) 1-Bromo-2-methylpropane



(iv) 2-Bromo-2-methylpropane



Question 10.7.

Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol

(ii) 1-chlorobutane

(iii) but-1-ene.

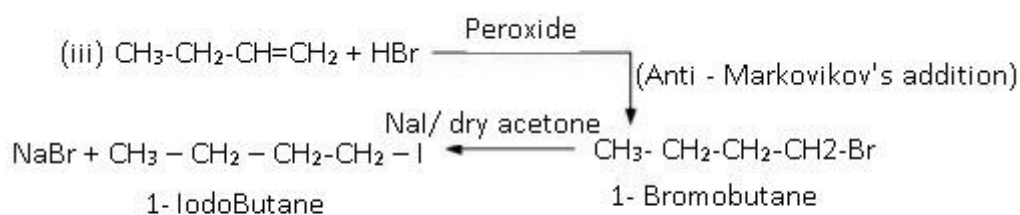
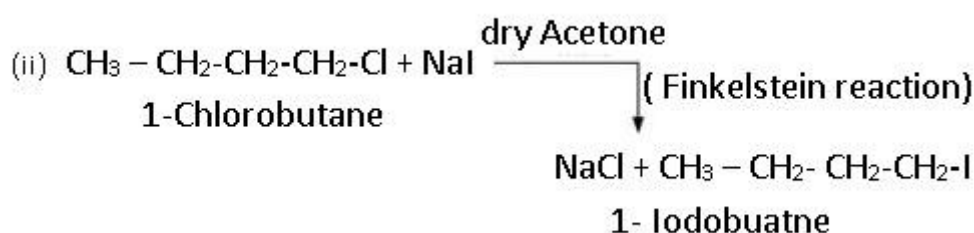
Answer:

1-butanol is treated with KI in the presence of H_3PO_4 where the OH is being replaced by the iodine and gives H_2O and KH_2PO_4 as the by-product with 1iodobutane as the final product.



1- Butanol

1-IodoButane

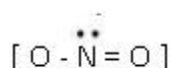


Question 10.8.

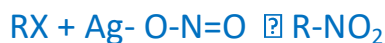
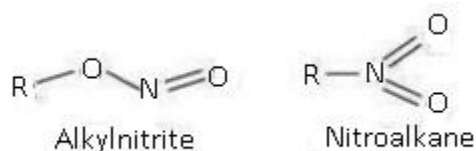
What are ambident nucleophiles? Explain with an example.

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.



Nitroalkane



Alkyl nitrite

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.

Question 10.9.

Which compound in each of the following pairs will react faster in $\text{S}_{\text{N}}2$ reaction with $-\text{OH}^-$?

(i) CH_3Br or CH_3I

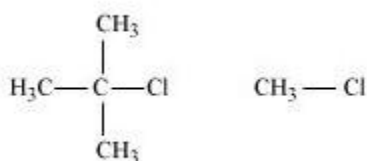
(ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl .

Answer:

(i) In the $\text{S}_{\text{N}}2$ 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.



Therefore, CH_3I will react faster than CH_3Br in $\text{S}_{\text{N}}2$ reactions with OH^- .



(ii) The $\text{S}_{\text{N}}2$ mechanism involves the attack of the nucleophile at the atom

bearing the leaving group. But, in case of $(\text{CH}_3)_3\text{CCl}$, 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 $(\text{CH}_3)_3\text{CCl}$ in $\text{S}_{\text{N}}2$ reaction with OH^- .

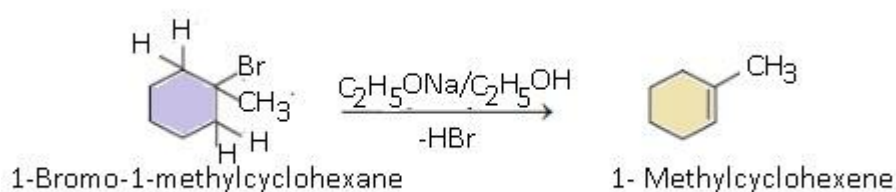
Question 10.10.

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

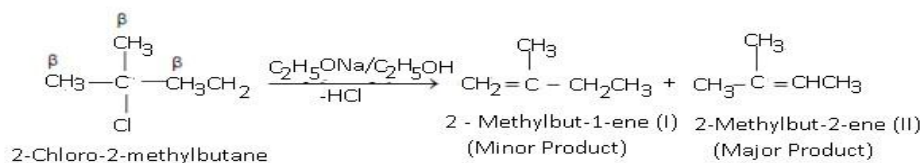
- (i) 1-Bromo-1-methylcyclohexane
- (ii) 2-Chloro-2-methylbutane
- (iii) 2,2,3-Trimethyl-3-bromopentane

Answer:

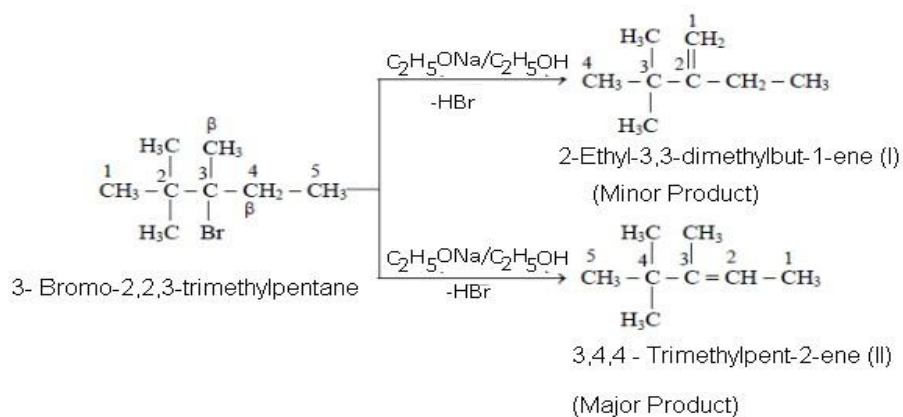
(i) In 1-Bromo-1-methylcyclohexane, the β -hydrogen atoms on either side of the Br atoms are equivalent, therefore, only one type of product i.e., 1-methylcyclohexene is formed.



(ii) 2-Chloro-2-methylbutane has two different sets of equivalent β hydrogen atoms and hence, in principle can give two alkenes (I and II). But according to Saytzeff's rule, more highly substituted alkene (II), being more stable, is the major product.



(iii) 3-Bromo-2, 2, 3-trimethylpentane has two different sets of β -hydrogen atoms and hence, in principle, can give two alkenes (I and II). But according to Saytzeff's rule, more highly substituted alkene (II), being more stable, is the major product.



Question 10.11.

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

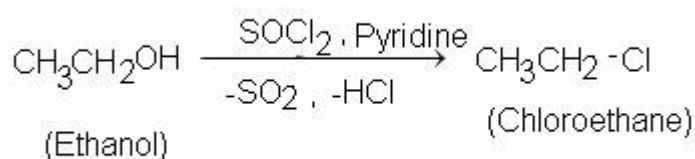
(ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.

Answer:

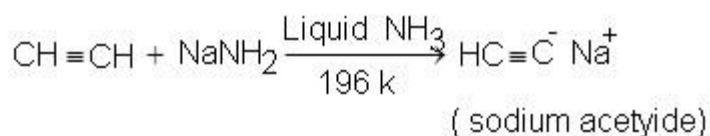
(i) Ethanol to but-1-yne

Since the conversion of ethanol to but-1-yne involves the addition the two extra carbons that is why the conversion is carried out in 3 steps

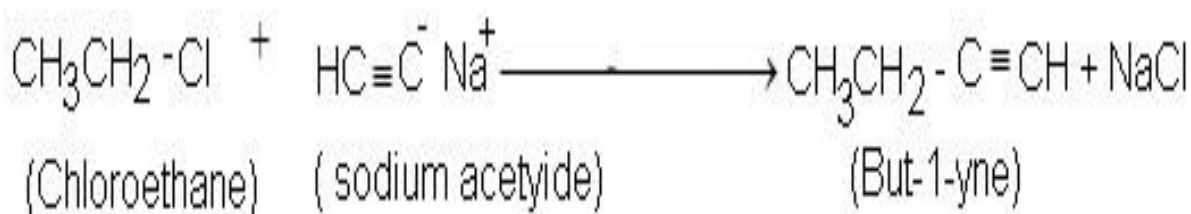
1. In the first step ethanol is treated with thionyl chloride (SOCl₂) in the presence of pyridine to give chloroethane.



2. In the second step the acetylene is treated with sodamide (NaNH₂) in the presence of liquid ammonia to give sodium acetylide.

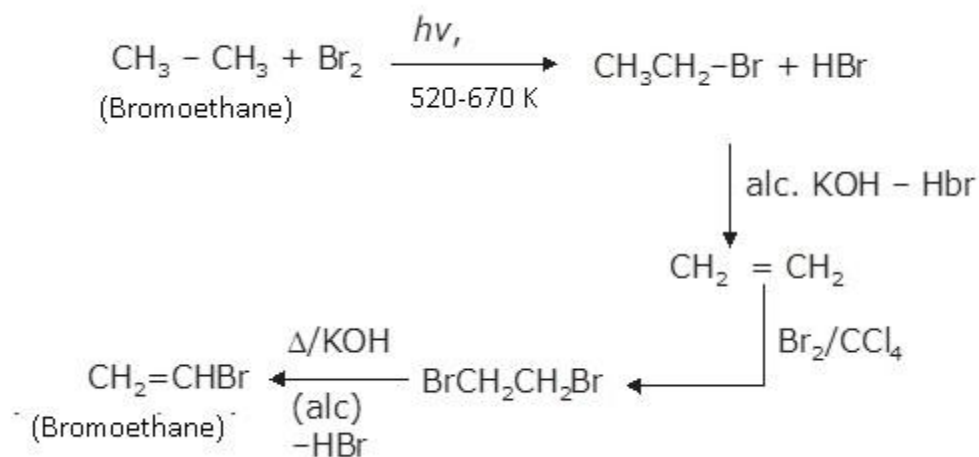


3. The last step involves the reaction between chloroethane and sodium acetylide to give the final product as the But-1-yne and NaCl as the by-product.

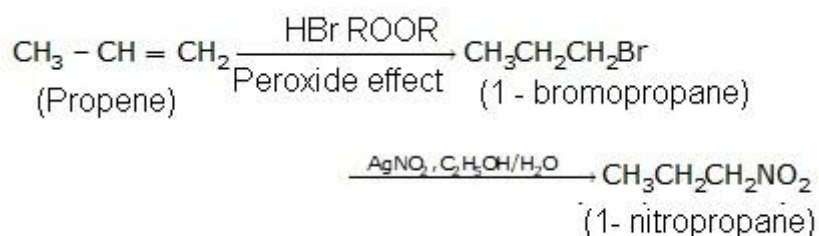


(ii) Ethane to bromoethene

The Bromination of ethane (Br_2 in the presence of light at 520-670K) gives bromoethane which on further treatment with alcoholic KOH results in the alkene called ethane which again on Bromination with Br_2/CCl_4 gives Dibromide(vicinal bromide) called 1,2-dibromoethane which on treatment with alcoholic KOH gives bromoethene as the final product.

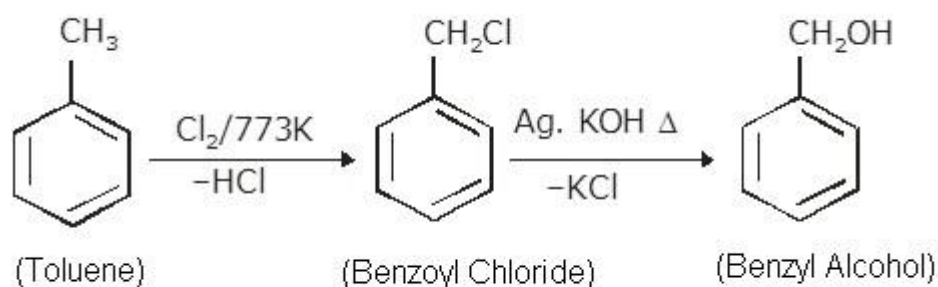


(iii) Propene on treatment with HBr in the presence of peroxide (antiMarkownikoff's rule which states the negative part i.e. Br- goes to the carbon which has more number of hydrogens and positive part i.e. H^+ goes to the carbon which has lesser number of hydrogens) gives 1-bromopropane which on treatment with silver nitrite in the presence of alcohol or water gives 1-nitropropane as the final product.

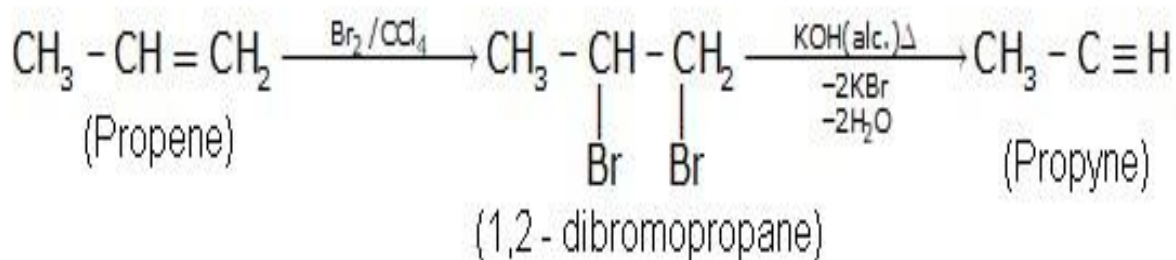


(iv) Chlorination of toluene (Cl_2 at 773K) gives benzyl chloride with the removal of HCl. Benzyl Chloride on further treatment with dilute KOH in the presence of heat gives benzyl alcohol as the final

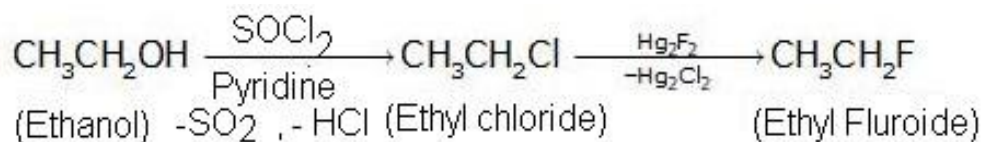
product.(dilute KOH removes Cl from the benzyl chloride and replaces it by OH)



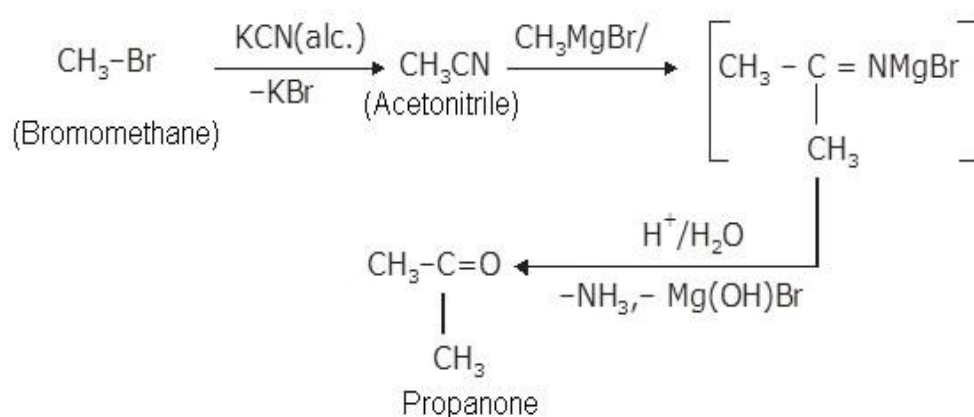
(v) Propene is treated with Br_2/CCl_4 i.e. bromination of alkene takes place to give dibromides, in this case 1,2-dibromopropane which on further treatment with alcoholic KOH gives propyne.(two times removal of KBr)



(vi) Ethanol in treatment with thionyl chloride (SOCl_2) in the presence of pyridine gives ethyl chloride with the evolution of SO_2 gas. The ethyl chloride on treatment with mercury fluoride gives ethyl fluoride (the Cl of ethyl chloride is being replaced by F from Hg_2F_2).



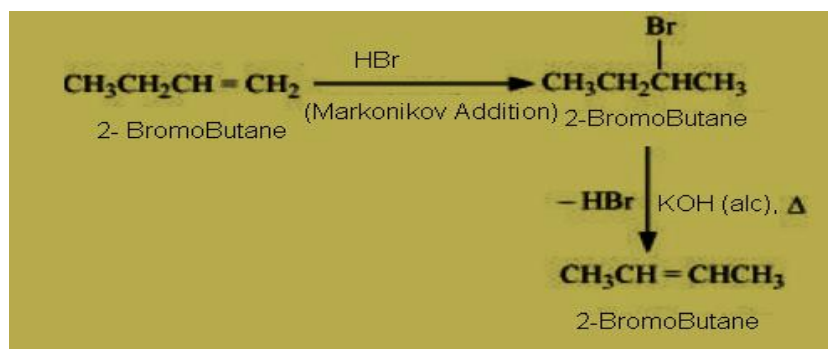
(vii) Bromoethane on treatment with alcoholic KCN forms Acetonitrile with the removal of KBr. CN is added in the case where there is a need to increase the number of carbons. Further the acetonitrile is treated with CH_3MgBr (Grignard reagent) in the presence of ether, the intermediate so formed is hydrolysed, and the product formation takes place i.e. Propanone and NH_3 is obtained as the by-product.



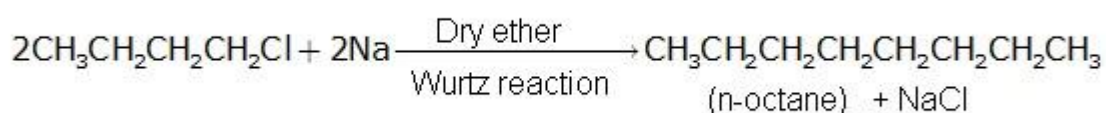
This reaction happens according to Markownikoff's rule

Now reacting this with alcoholic KOH gives alkenes



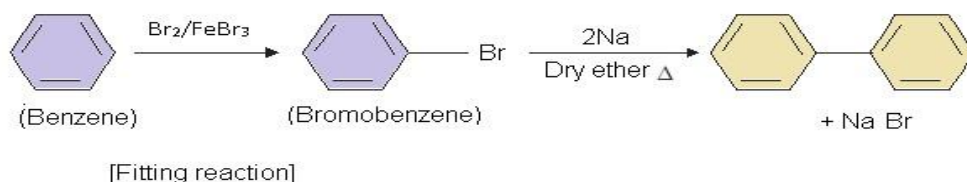


(ix) The conversion of 1-chlorobutane to n-octane in the presence of Na metal and dry ether is called Wurtz reaction. Two equivalent chlorobutane reacts to give n-octane as a final product and NaCl as the by-product.



(xx) The conversion of benzene to biphenyl using Na and dry ether is called FITTIG reaction.

Firstly, the benzene is treated with $\text{Br}_2/\text{FeBr}_3$ results in the formation of bromobenzene. It is an electrophilic substitution. Further the bromobenzene is treated with Na metal in presence of dry ether to form biphenyl as the final product and NaBr as the by-product. If instead of Na metal, bromobenzene is treated with Cu metal then the reaction is called Ullmann's reaction. The final product obtained in this reaction will also be biphenyl.



Question 10.12.

Explain why

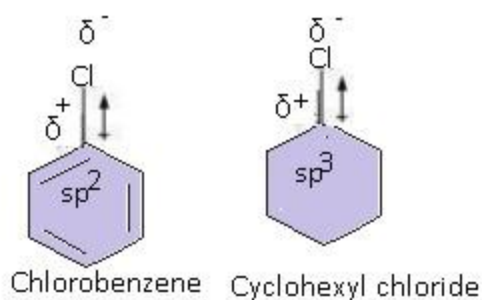
- (i) The dipole moment of chlorobenzene is lower than that of cyclohexylchloride?
- (ii) Alkyl halides, though polar, are immiscible with water?
- (iii) Grignard reagents should be prepared under anhydrous conditions?

Answer:

(i) In chlorobenzene, the Cl-atom is linked to a sp^2 hybridized carbon atom. In cyclohexylchloride, the Cl-atom is linked to a sp^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 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 10.13.

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.

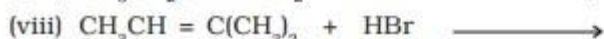
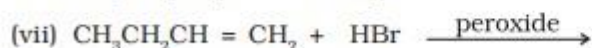
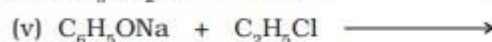
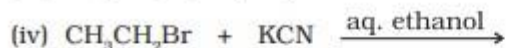
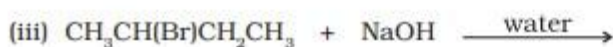
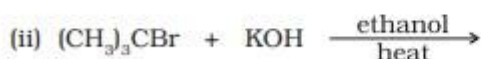
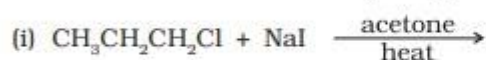
(iv) Until the mid-1960's, carbon tetrachloride was widely used as a cleaning fluid, a degreasing agent in industries, a spot remover in homes, and a fire extinguisher.

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.

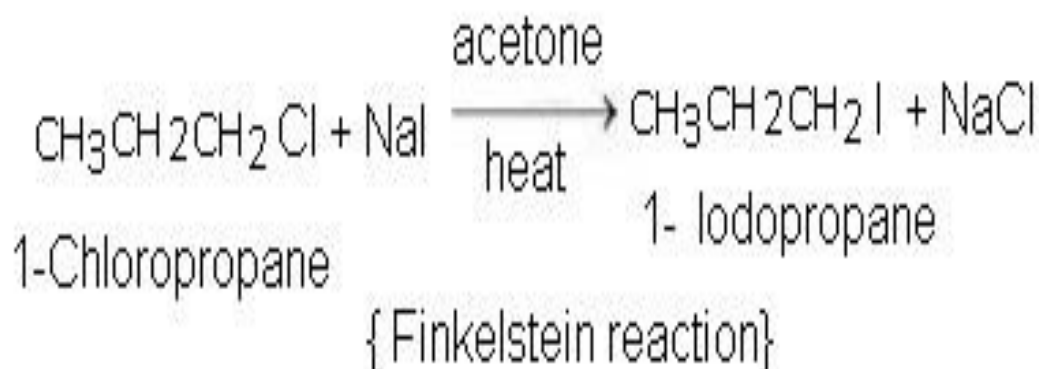
Question 10.14.

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



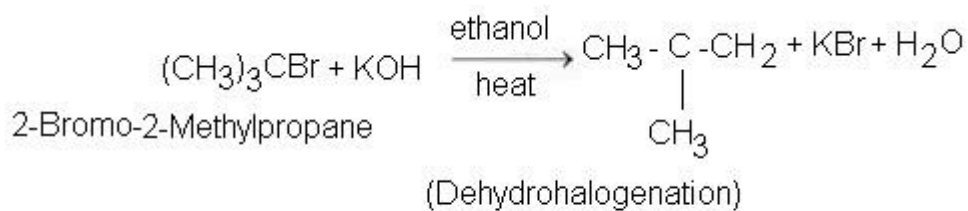
Answer:

(i)



(ii)

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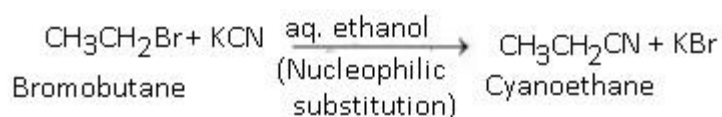
(iii)



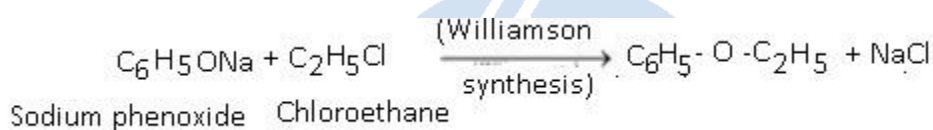
2-Bromobutane

Butan-2-ol

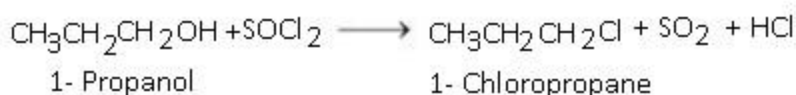
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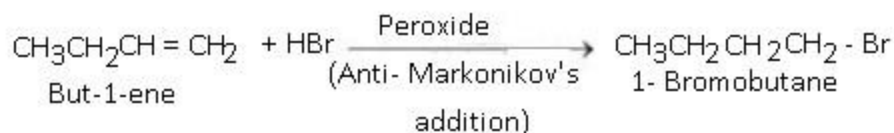
(v)



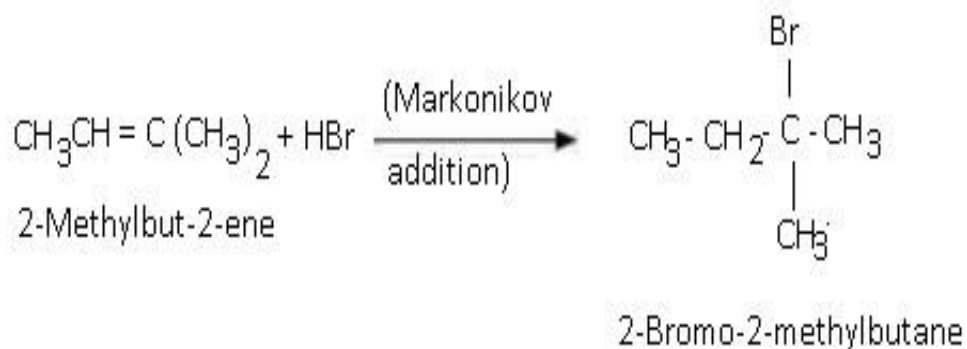
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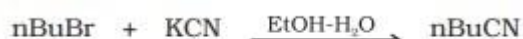
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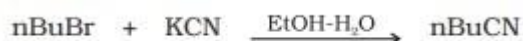
(viii)


Question 10.15.

Write the mechanism of the following reaction:-


Answer:

The given reaction is a nucleophilic reaction:

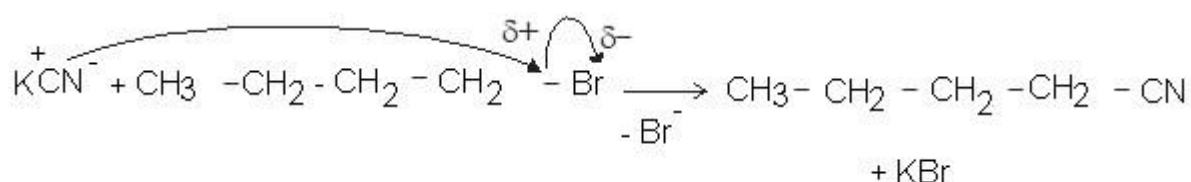


The given reaction is an S_N2 reaction. In this reaction, CN acts as the stronger nucleophile and attacks the carbon atom to which Br is attached in nBuBr.

And, CN⁻ ion is an ambident nucleophile and can attack through both C and N.

In this case, it attacks through the C-atom.

The mechanism is shown below:



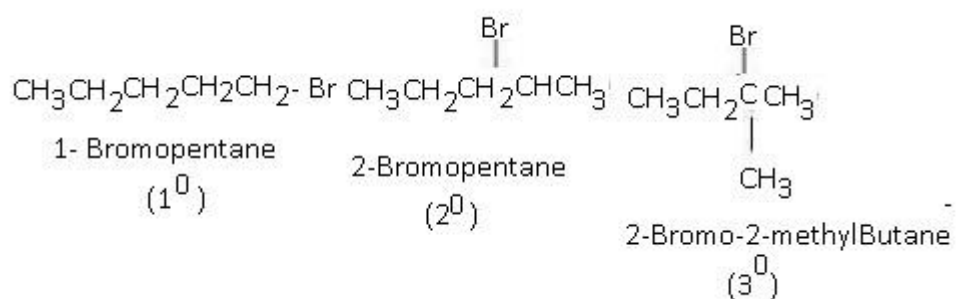
Question 10.16.

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)



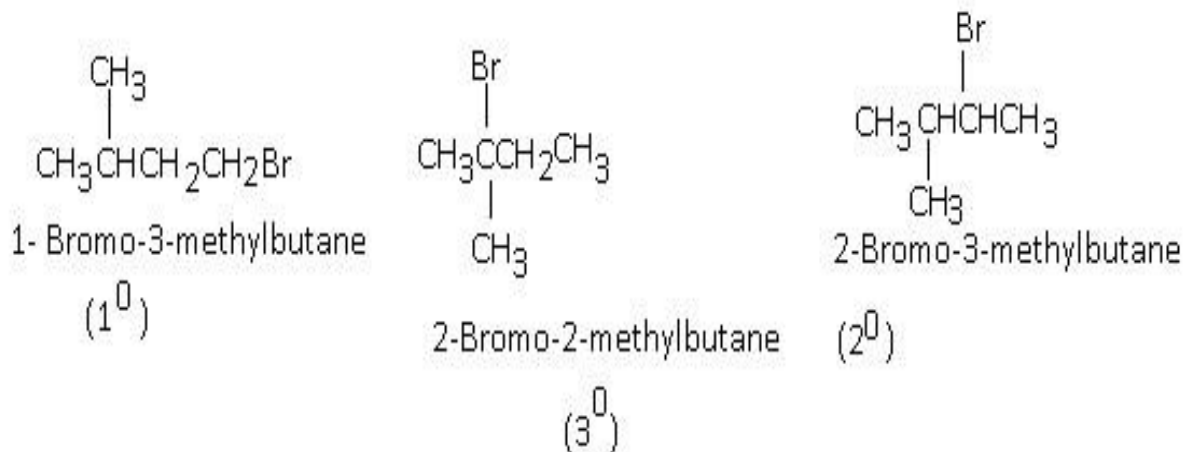
An S_N2 reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards S_N2 displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases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

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

Hence, the increasing order of reactivity towards S_N2 displacement is:

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

(ii)

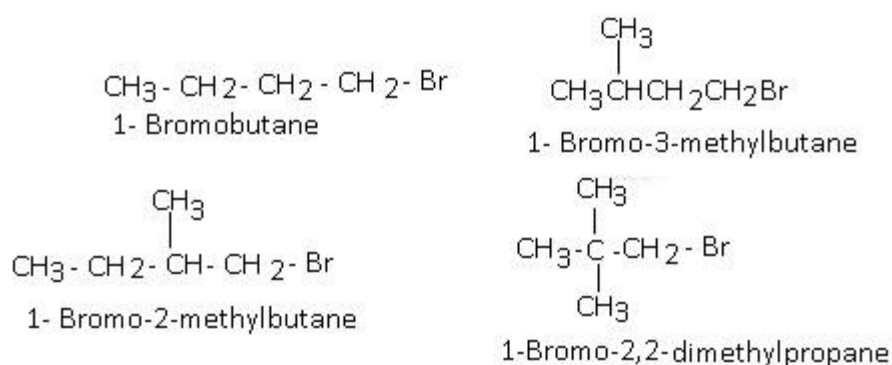


Since steric hindrance in alkyl halides increases in the order of $1^\circ < 2^\circ < 3^\circ$, the increasing order of reactivity towards S_N2 displacement is $3^\circ < 2^\circ < 1^\circ$.

Hence, the given set of compounds can be arranged in the increasing order of their reactivity towards S_N2 displacement as:

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

(iii)



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

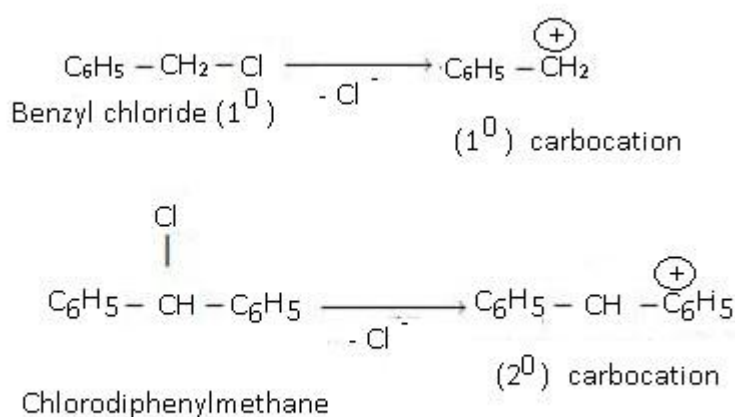
Question 10.17.

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

Answer:

Hydrolysis by KOH results in the formation of the carbocation. Those compounds which lead to the formation of stable carbocation are easily hydrolysed. $C_6H_5CH_2Cl$ leads to formation of 1° -carbocation, while $C_6H_5CHClC_6H_5$ forms 2° -carbocation, which is more stable than 1° -carbocation. Hence

$C_6H_5CHClC_6H_5$ is hydrolyzed more easily than $C_6H_5CH_2Cl$ by aqueous KOH.



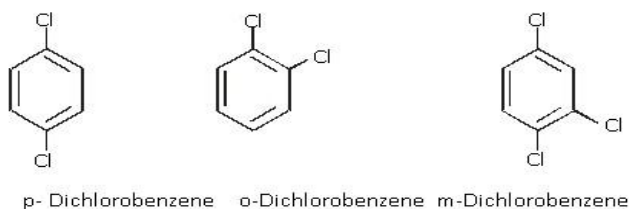
Question 10.18.

p-Dichlorobenzene has higher melting point and solubility than those of o- and m-isomers. Discuss.

Answer:

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.



Question 10.19.

How the following conversions can be carried out?

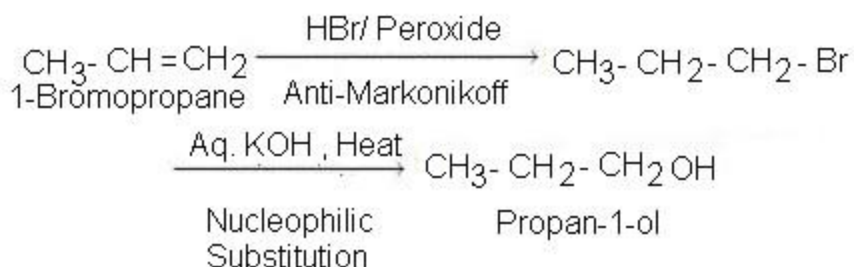
- (i) Propene to propan-1-ol
- (ii) Ethanol to but-1-yne
- (iii) 1-Bromopropane to 2-bromopropane
- (iv) Toluene to benzyl alcohol
- (v) Benzene to 4-bromonitrobenzene
- (vi) Benzyl alcohol to 2-phenylethanoic acid
- (vii) Ethanol to propanenitrile
- (viii) Aniline to chlorobenzene
- (ix) 2-Chlorobutane 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
- (xxi) tert-Butyl bromide to isobutyl bromide
- (xx) Aniline to phenylisocyanide.

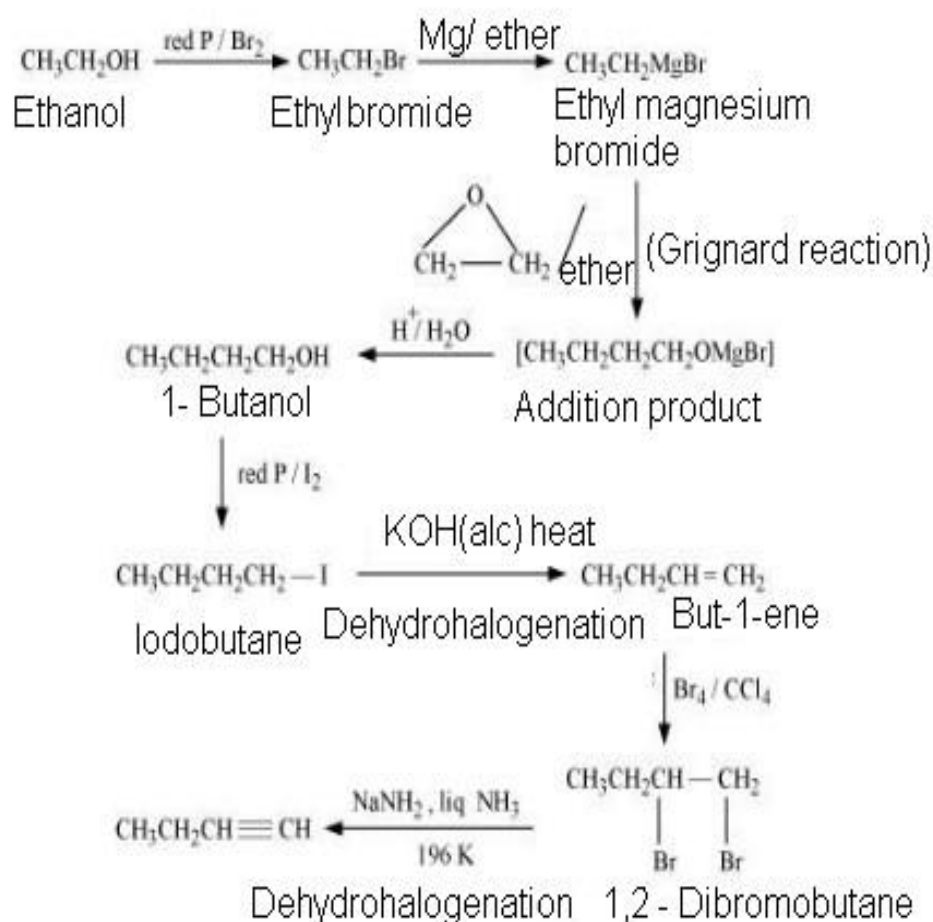
Answer:

(i) Propene to propan-1-ol

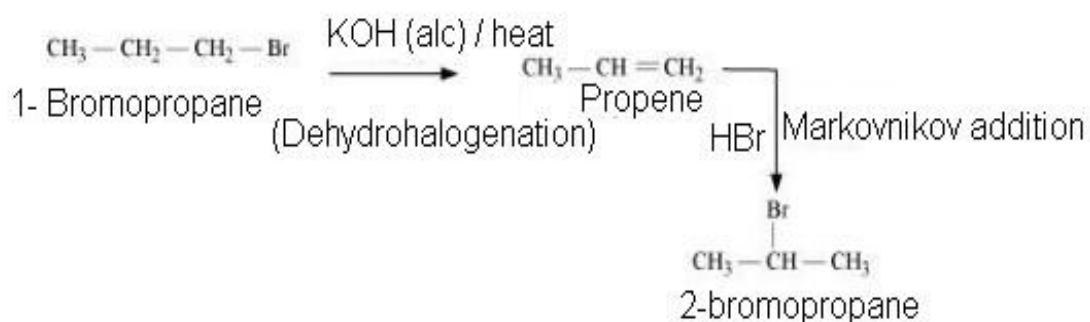
It is an AntiMarkovnikoff reaction in which under the presence of peroxide an alkene undergoes substitution, wherein the halo group is attached to that carbon which has least no. of alkyl groups attached to it.



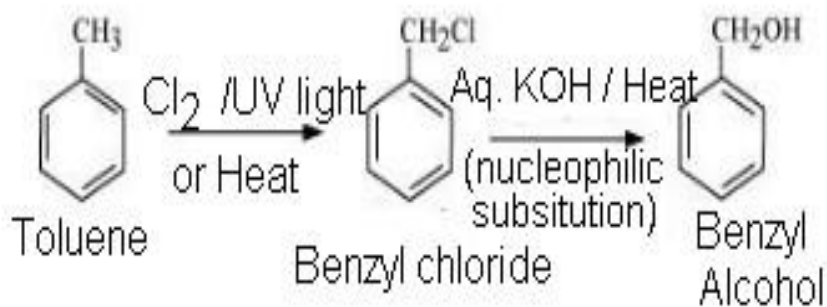
(ii) Ethanol to but-1-yne



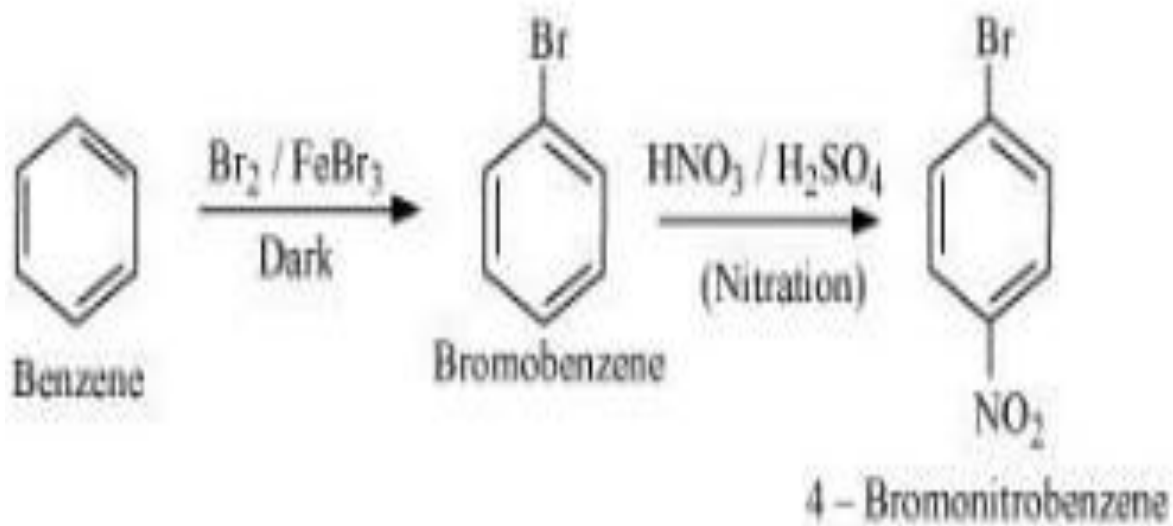
(iii)



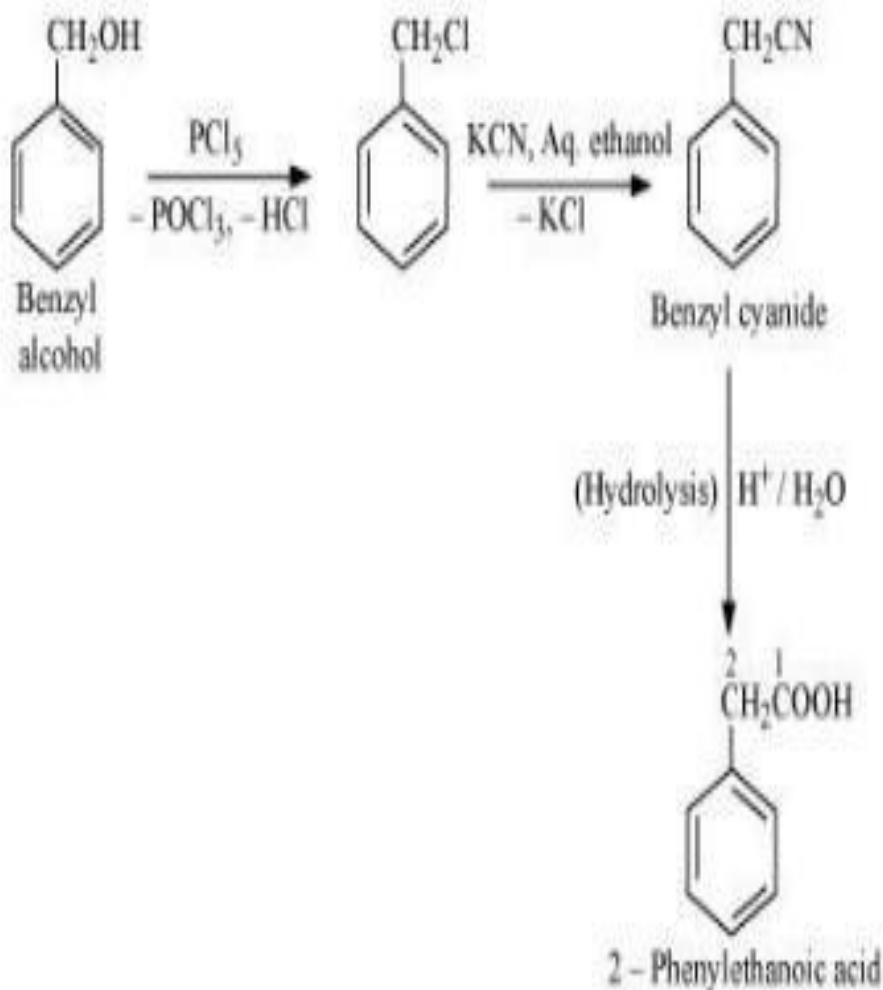
(iv)



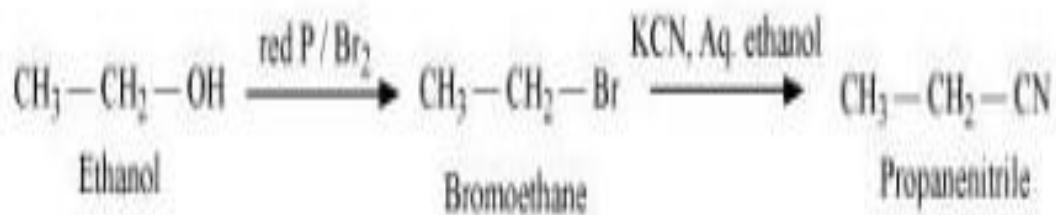
(v)



(vi)



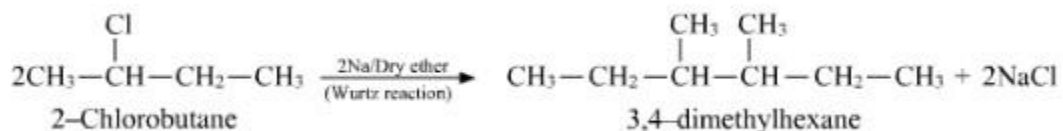
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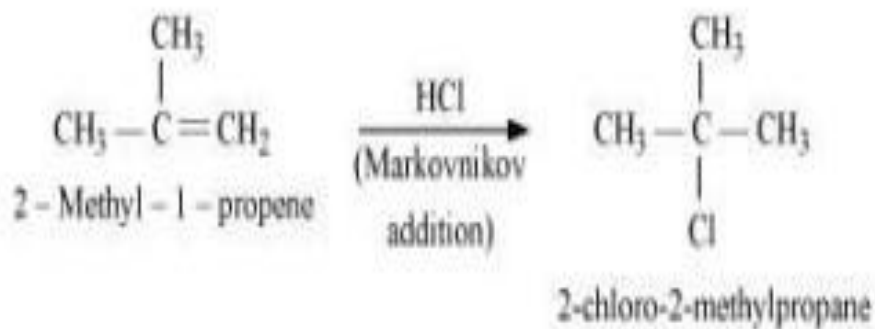
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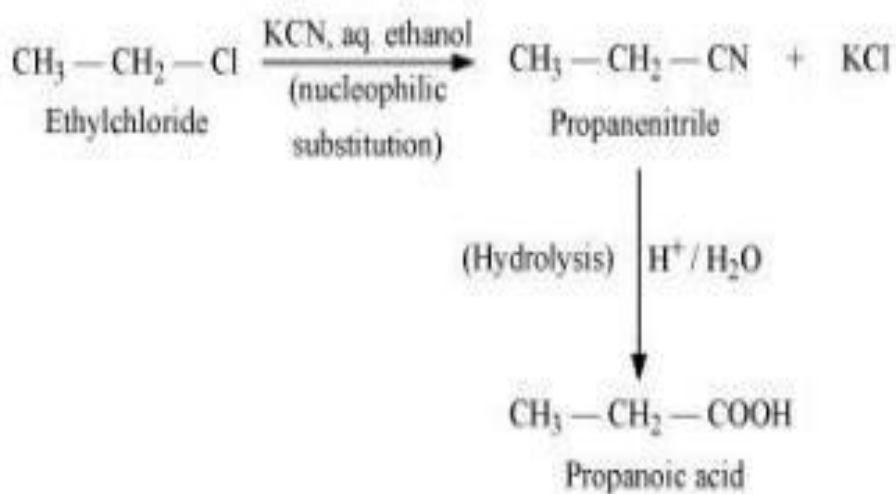
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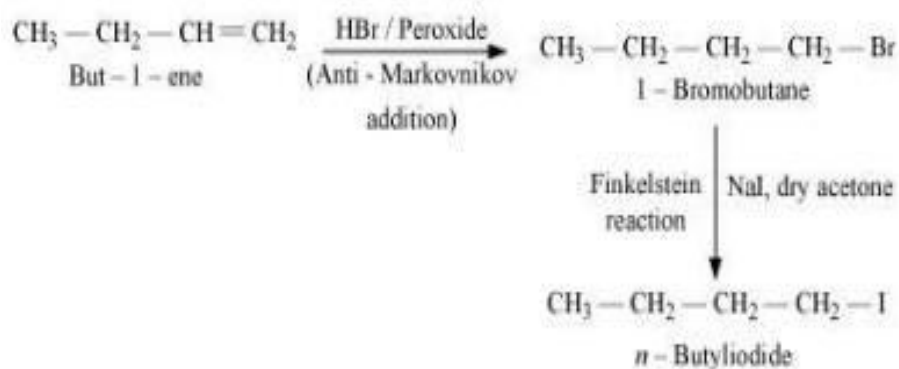
(x)



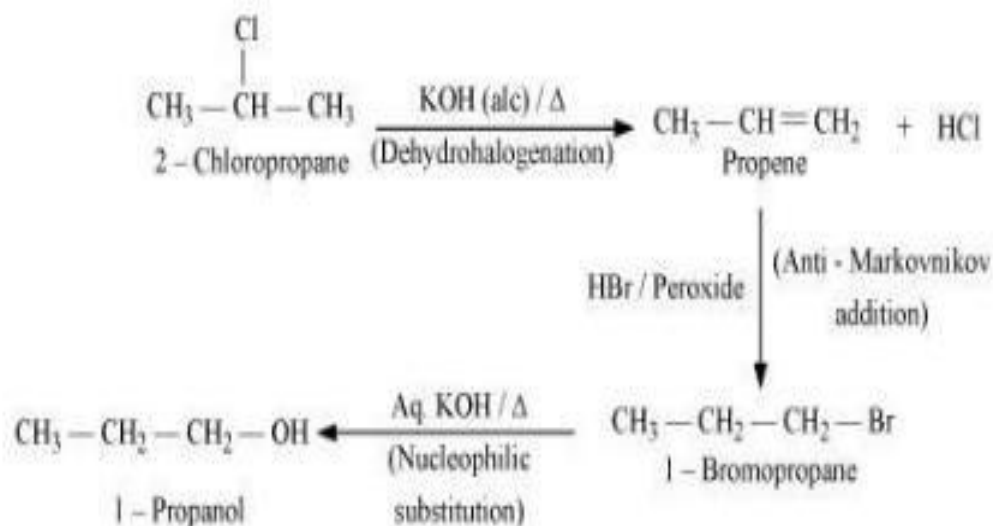
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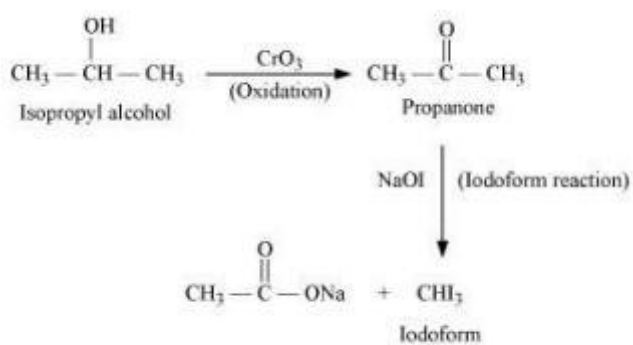
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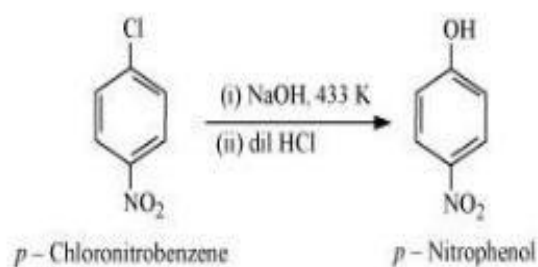
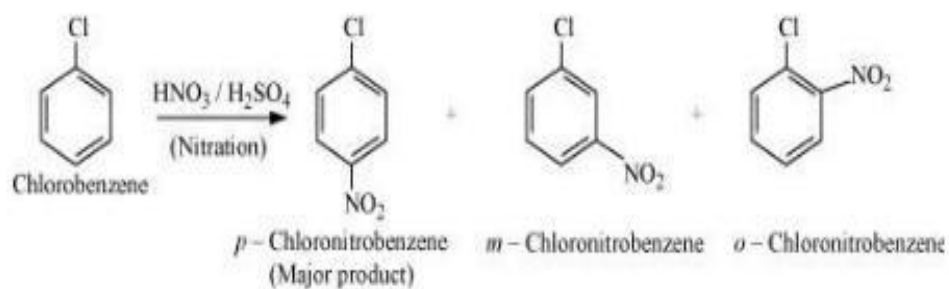
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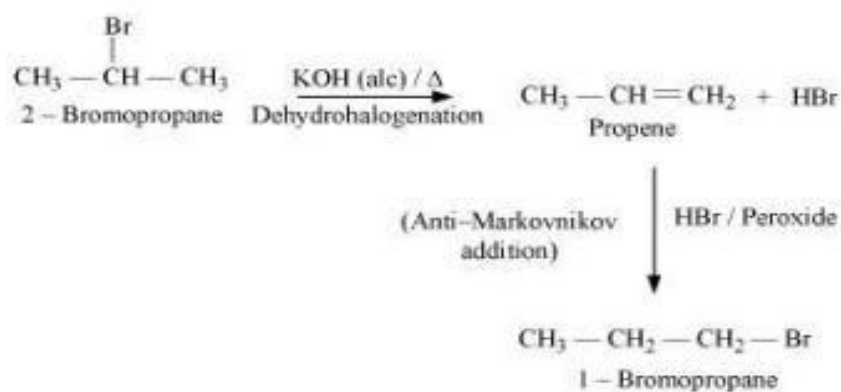
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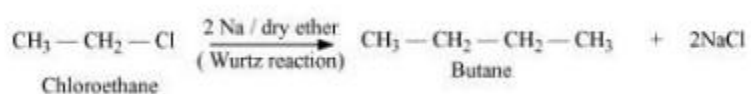
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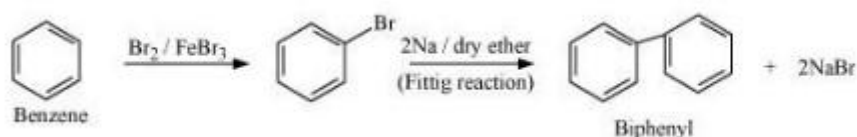
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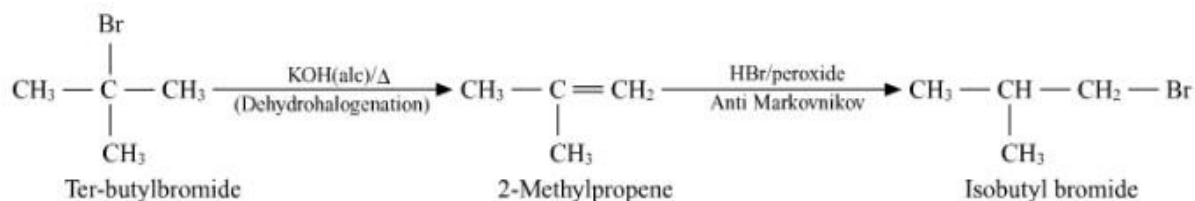
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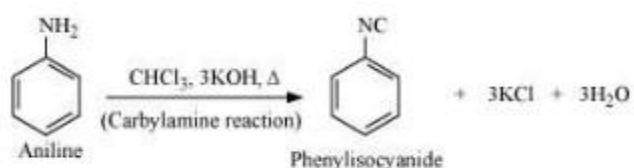
(xviii)



(xix)



(xx)



Question 10.20.

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.

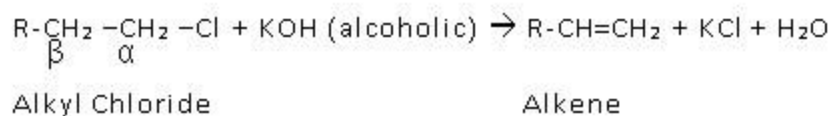
Answer:

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.



Alkyl Chloride Alcohol

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



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 hydrogen from the β -carbon.

Question 10.21.

Primary alkyl halide $\text{C}_4\text{H}_9\text{Br}$

(a) reacted with alcoholic KOH to give compound

(b) is reacted with HBr to give

(c) which is an isomer of (a).

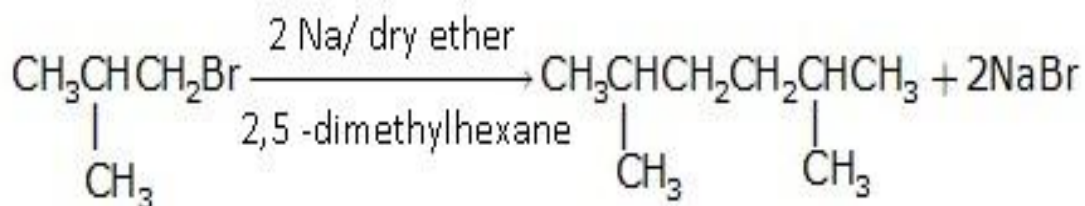
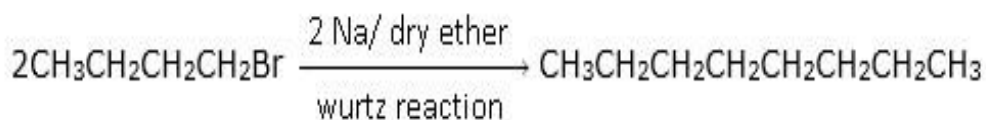
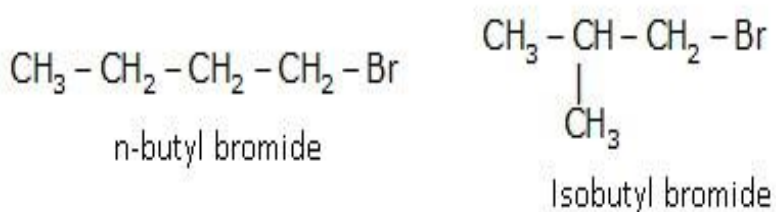
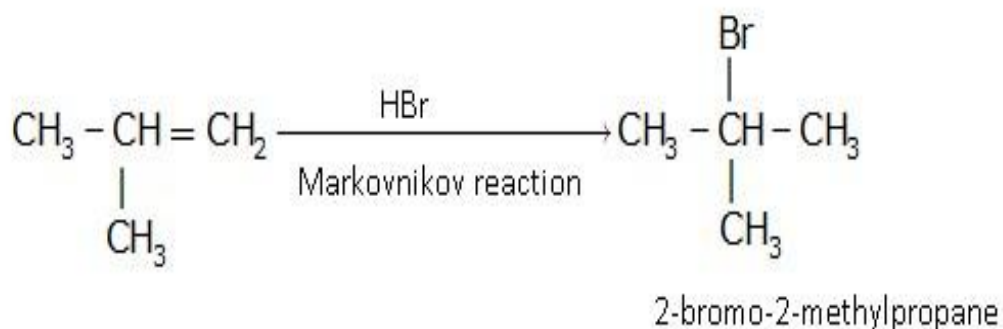
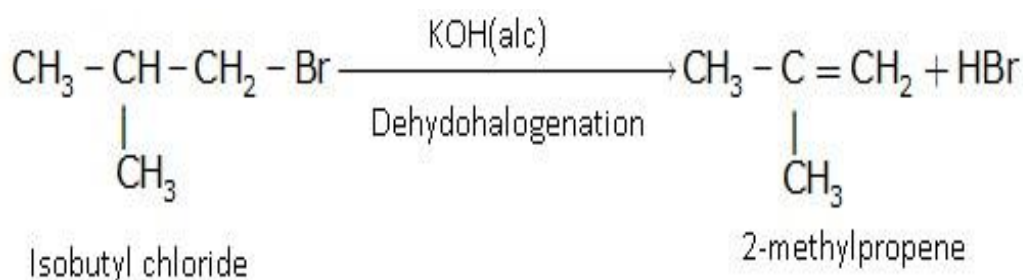
When (a) is reacted with sodium metal it gives compound

(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, $\text{C}_4\text{H}_9\text{Br}$. They are n-butyl 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, C₈H₁₈, 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.

Question 10.22.

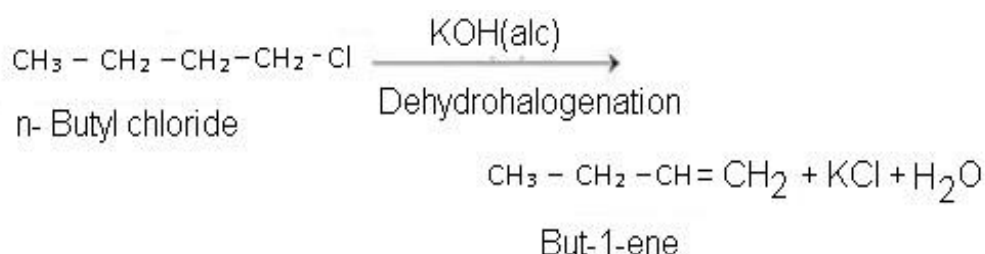
What happens when:-

- (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??

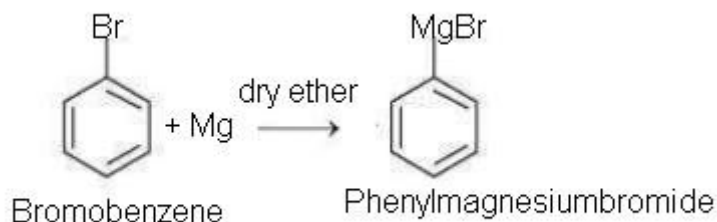
Answer:

(i) When n–butyl chloride is treated with alcoholic KOH, the formation of but–1–ene takes place.

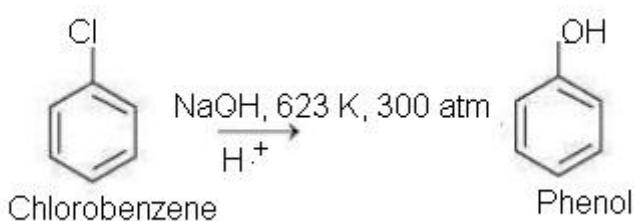
This reaction is a dehydrohalogenation reaction.



(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.



Ethyl chloride 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.

(In presence of Dry ether and Wurtz reaction)



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

