

## NCERT Solutions for Class 12 Chemistry Chapter 10 Haloalkanes and Haloarenes

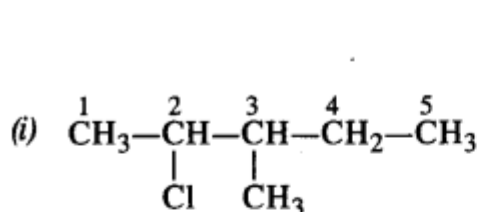
### NCERT IN-TEXT QUESTIONS

Question 1.

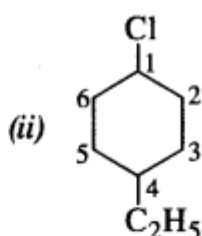
Write the structures of the following compounds : (C.B.S.E. Delhi 2010)

- (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. (C.B.S.E. Sample paper 2011)

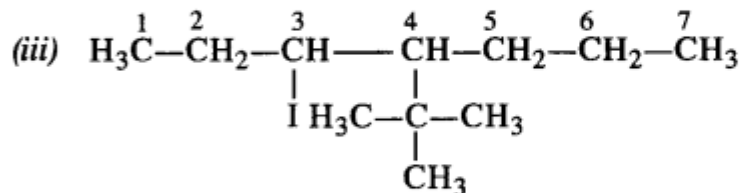
Answer:



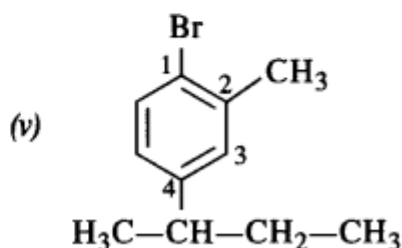
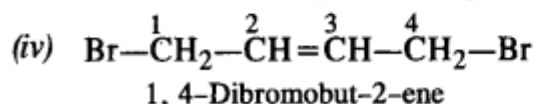
2-Chloro-3-methylpentane



1-Chloro-4-ethylcyclohexane



4-tert. butyl-3-iodoheptane



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

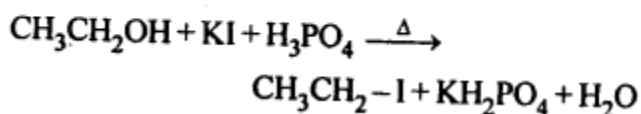
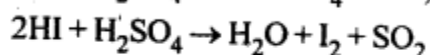
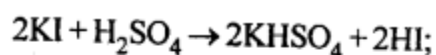
Question 2.

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

Answer:

$\text{H}_2\text{SO}_4$  is an oxidising agent. It oxidises HI produced during the reaction to  $\text{I}_2$  and thus prevents the reaction between an alcohol and HI to form alkyl iodide. To prevent this, a non-oxidising acid like

H<sub>3</sub>PO<sub>3</sub> is used.

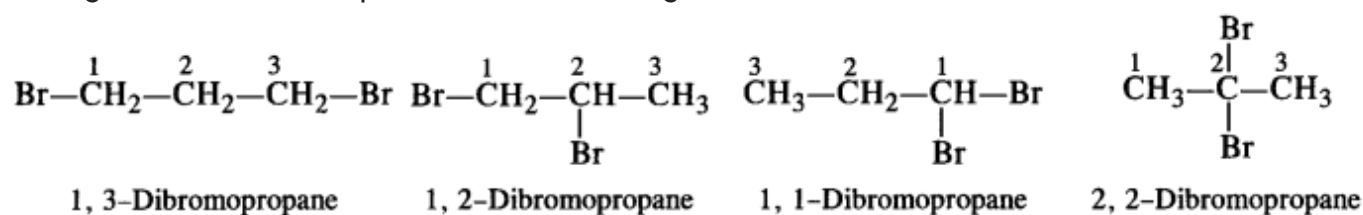


Question 3.

Write the structures of different dihalogen derivatives of propane.

Answer:

Propane (CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>) has two primary and one secondary hydrogen atoms present. Four isomeric dihalogen derivatives are possible. Let the halogen X be Br.



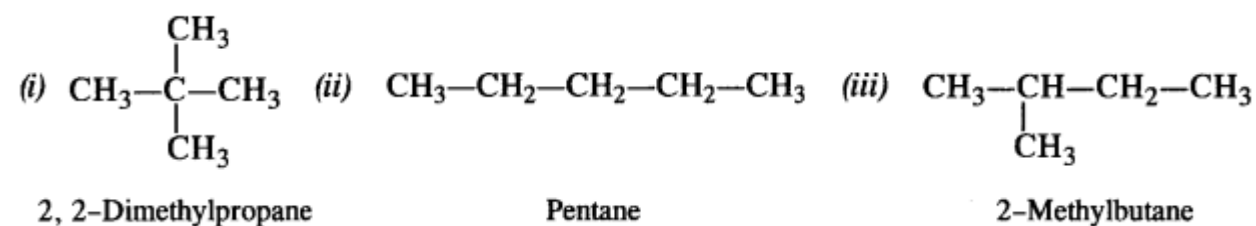
Question 4.

Among the isomeric alkanes of molecular formula C<sub>5</sub>H<sub>12</sub>, identify the one which on photochemical chlorination yields

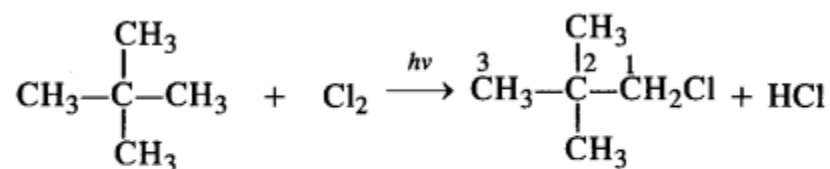
- (i) A single monochloride
- (ii) Three isomeric monochlorides
- (iii) Four isomeric monochlorides.

Answer:

The molecular formula C<sub>5</sub>H<sub>12</sub> represents three structural isomers which are chain isomers.



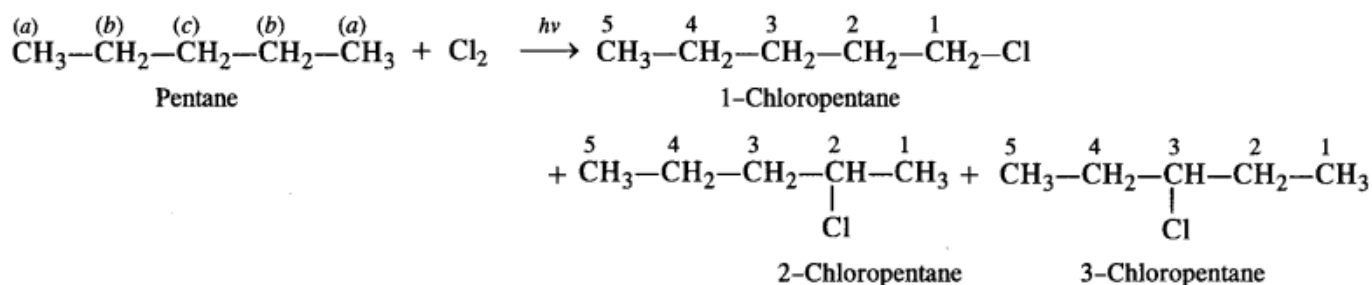
(i) The isomer is symmetrical with four primary (1°) carbon atoms and one quaternary (4°) carbon atom. Since all the hydrogen atoms are equivalent, it will yield only one monochloride upon photochlorination i.e., chlorination carried in the presence of ultra-violet light.



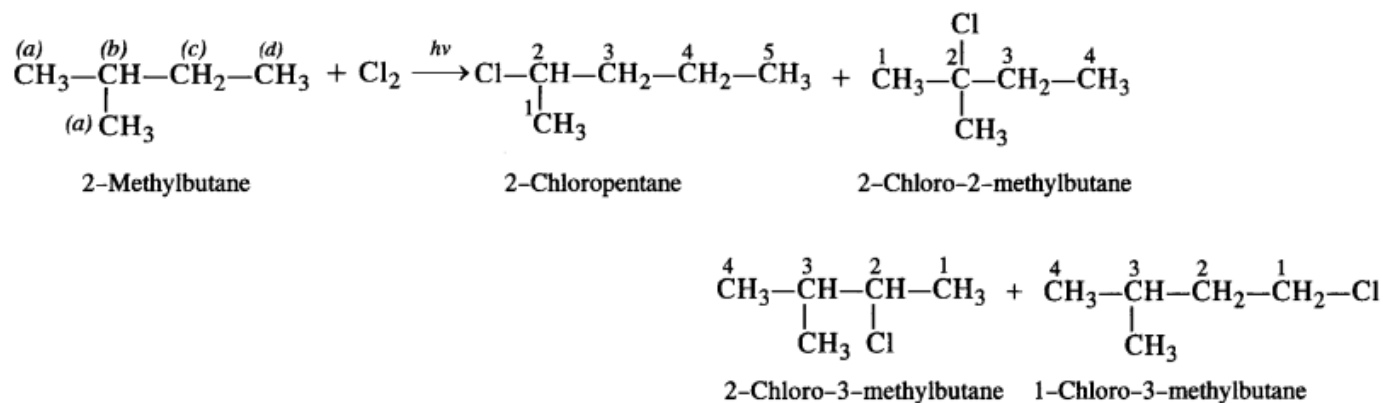
2, 2-Dimethylpropane

1-Chloro-2, 2-dimethylpropane

(ii) In the straight chain isomer pentane, there are three groups of equivalent hydrogen atoms. As a result, three isomeric monochlorides are possible.

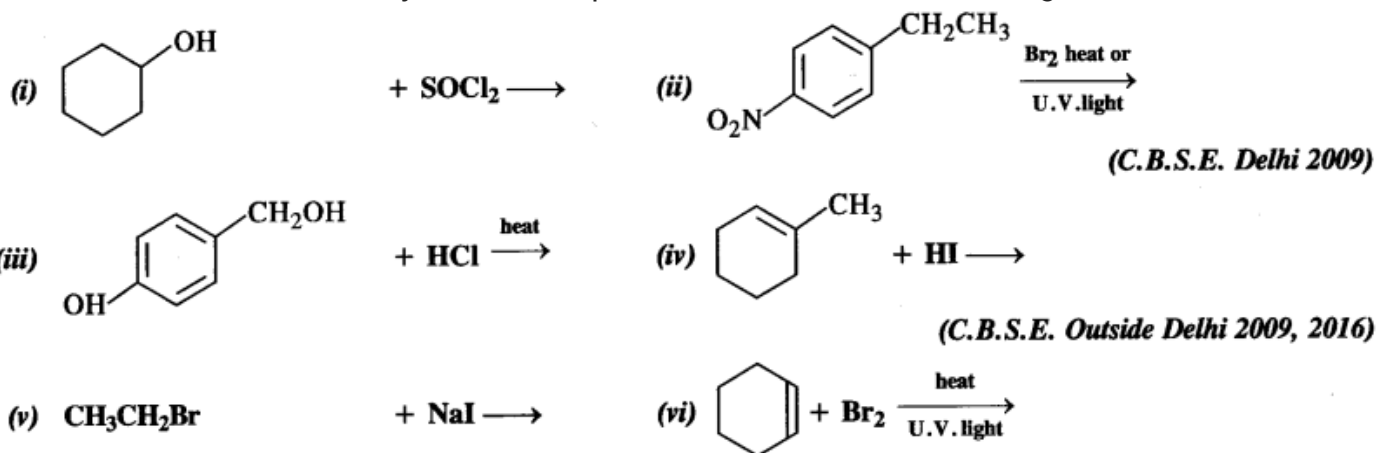


(iii) The branched chain isomer has four types of equivalent hydrogen atoms present. It will give four isomeric monochlorides upon chlorination.

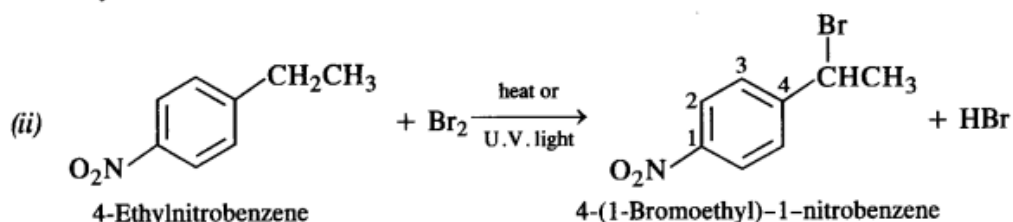
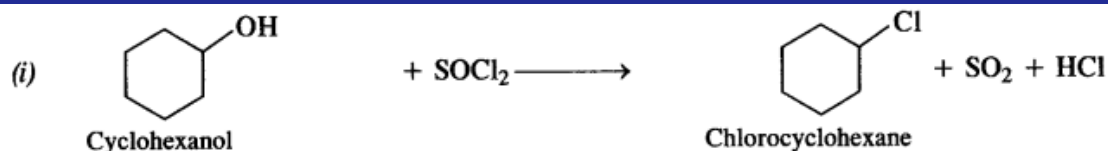


Question 5.

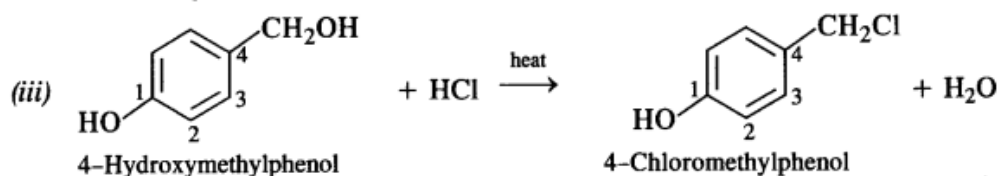
Draw the structures of the major monohaloproducs in each of the following reactions:



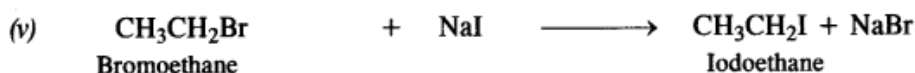
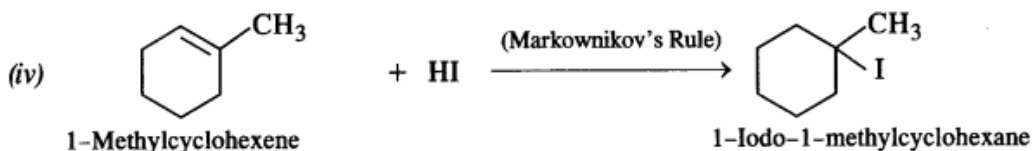
Answer:



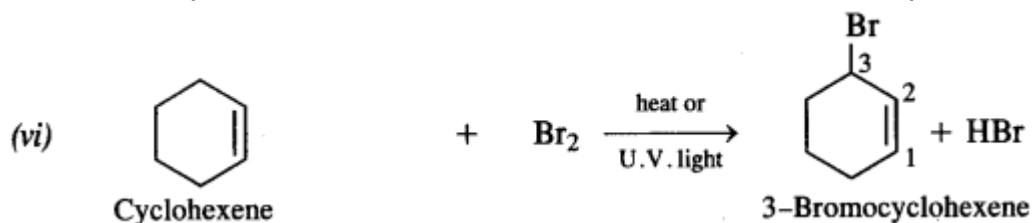
As the benzylic free radicals are more stable (secondary), therefore benzylic hydrogen is abstracted in this case.



Phenolic group is not replaced by Cl on reacting with HCl.



The reaction is carried in the presence of dry acetone upon heating. It is called Finkelstein reaction. In this reaction, I<sup>-</sup> ion being a stronger nucleophile displaces Br<sup>-</sup> ion. NaBr formed is insoluble in dry acetone whereas NaI dissolves. This shifts the equilibrium in the forward direction.



Under the reaction conditions allylic halogenation will take place. Addition of bromine can be possible in case the reaction is carried at room temperature.

Question 6.

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

The reason is:

(a) for same alkyl group, B.Pt increases with size of halogen atom.

(b) B.Pt increases as number of halogen atoms increase.

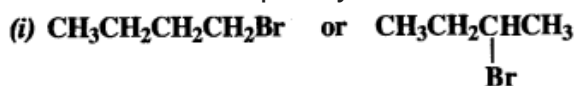
(ii) Isopropyl chloride < 1 - Chloropropane < 1 - Chlorobutane

Reason :

- (a) For same halogen, B.Pt. increases as size of alkyl group increases.  
 (b) B.Pt. decreases as branching increases.

Question 7.

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

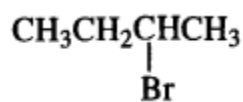


Answer:

If the leaving group is the same in different isomers of a particular molecular formula, the reactivity of the isomers towards  $S_N2$  mechanism decreases with the increase in steric hindrance. In the light of above, the reactivity order in different cases is :

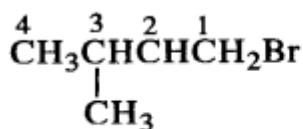
(i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  is a primary alkyl halide ( $1^\circ$ ). It is more reactive than the other isomer which is a secondary ( $2^\circ$ ) alkyl halide because less steric hindrance is caused by primary alkyl group as compared to secondary alkyl group.

(ii)

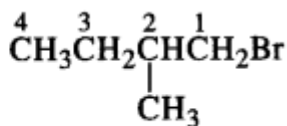


is a secondary alkyl halide ( $2^\circ$ ). It is more reactive than the other isomer which is a tertiary alkyl halide ( $3^\circ$ ). The explanation is the same.

(iii) Here both the isomers are primary alkyl halides ( $1^\circ$ ). However, the isomer with  $\text{CH}_3$  group at  $\text{C}_2$  atom exerts more steric hindrance to the attacking nucleophile at  $\text{C}_1$  atom as compared to the other isomer in which a  $\text{CH}_3$  group is attached to  $\text{C}_3$  atom. It is, therefore, less reactive.



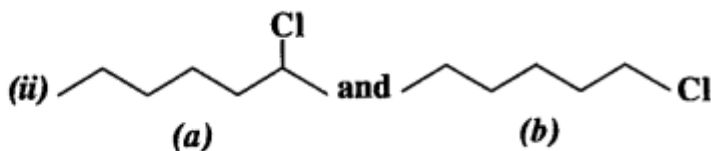
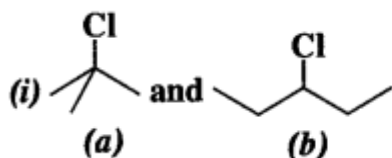
Less steric hindrance(I)



More steric hindrance(II)

Question 8.

In the following pairs of halogen compounds, which compound undergoes reaction faster?  
 (C.B.S.E. Delhi 2008, Outside Delhi 2010, 2013)



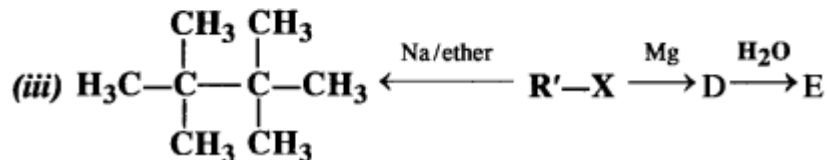
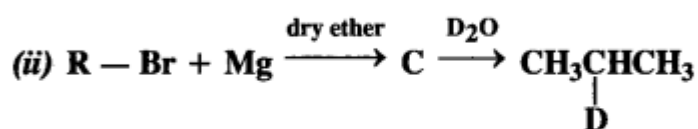
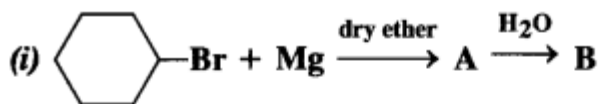
Answer:

The reactivity of a particular halogen compound towards  $S_N1$  reaction depends upon the stability of the carbocation formed as a result of ionisation. This is a slow step and is called rate determining step. The order of relative stabilities of different carbocations is in the order : tertiary > secondary > primary. In the light of this, the order of reactivity in the two cases is explained.

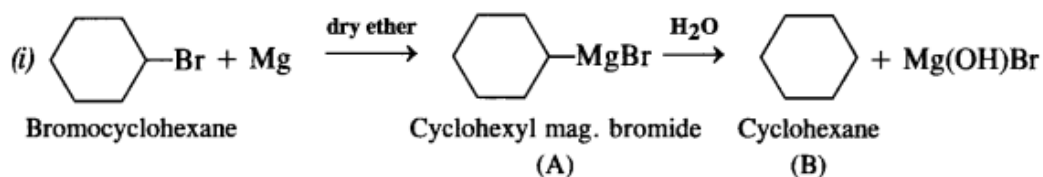
1. The isomer (a) is a tertiary alkyl chloride while the other isomer (b) is a secondary alkyl chloride. The isomer (a) is more reactive towards  $S_N1$  reaction since the tertiary carbocation formed in this case is more stable than the secondary carbocation which is likely to be formed in the other case.
2. The isomer (a) is a secondary alkyl chloride while the other isomer (b) is primary in nature. The secondary alkyl chloride (a) is expected to react faster since the secondary carbocation formed is more stable than the primary carbocation which is likely to be formed in the other case.

Question 9.

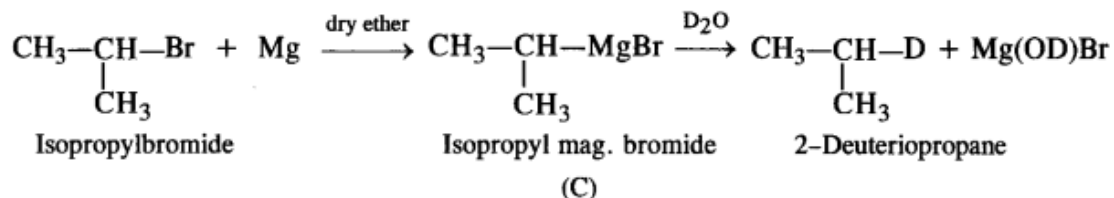
Identify A, B, C, D, E, R and R' in the following :



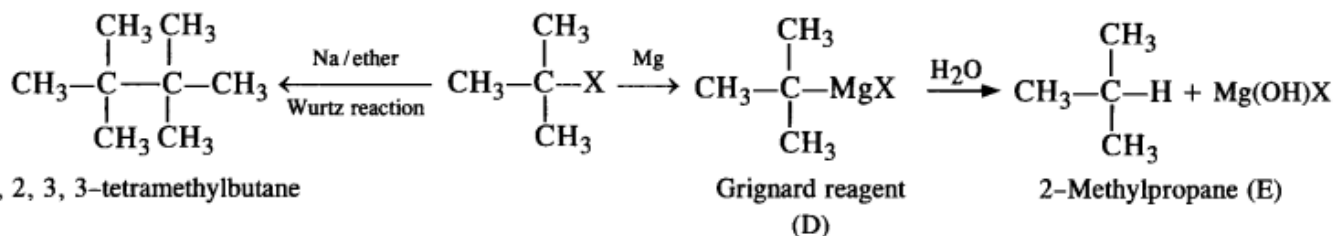
Answer:



(ii) In this reaction, the alkyl group R is  $(\text{CH}_3)_2\text{CH}-$ . The reaction proceeds as follows :



(iii) In this reaction, R' is  $(\text{CH}_3)_3\text{C}-$  group. The reaction proceeds as follows :



## NCERT EXERCISE

Question 1.

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

(i)  $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_3$  (C.B.S.E. Delhi 2013)

(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)  $\text{CH}_3\text{C}(\text{Cl})(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3$

(v)  $\text{CH}_3.\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Br}$

(vi)  $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$

(vii)  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Br}$

(viii)  $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$

(ix)  $m\text{-ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_3$

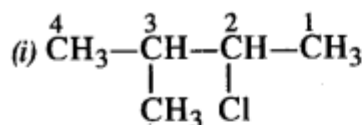
(x)  $o\text{-BrC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

(xi)  $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{Br})\text{C}_5\text{H}_5$

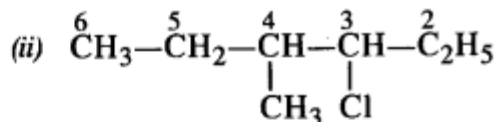
(xii)  $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$

Answer:

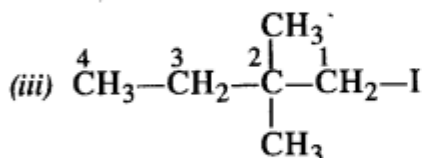




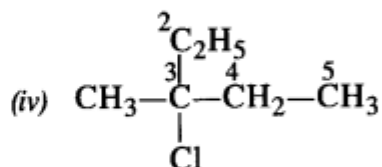
2-Chloro-3-methylbutane  
(2° alkyl halide)



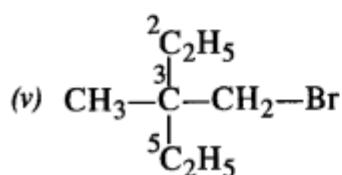
3-Chloro-4-methylhexane  
(2° alkyl halide)



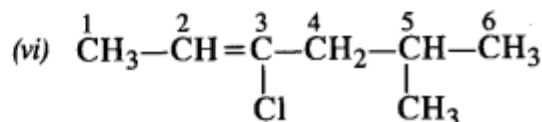
1-Iodo-2, 2-dimethylbutane  
(1° alkyl halide)



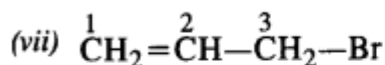
3-Chloro-3-methylpentane  
(3° alkyl halide)



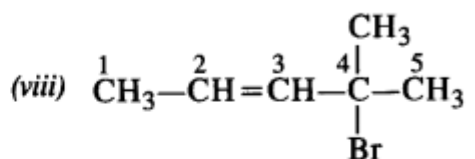
3-Bromomethyl-3-methylpentane  
(1° alkyl halide)



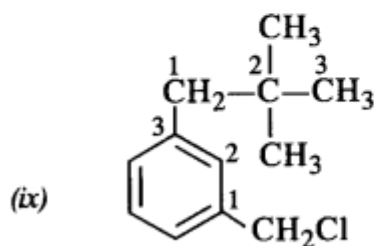
3-Chloro-5-methylhex-2-ene  
(Vinyl halide)



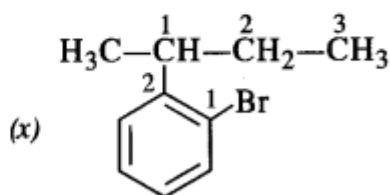
3-Bromoprop-1-ene  
(Allyl halide)



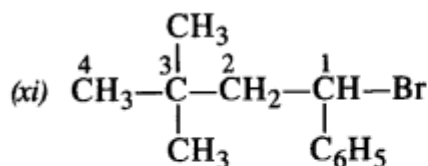
4-Bromo-4-methylpent-2-ene  
(Allyl halide)



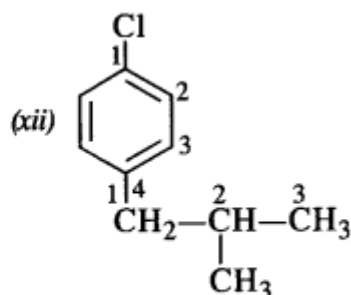
1-Chloromethyl-3-(2, 2-dimethylpropyl)  
benzene (Benzylic halide)



1-Bromo-2-(1-methylpropyl)  
benzene (Aryl halide)



1-Bromo-3, 3-dimethyl-1-phenylbutane  
(Benzylic halide)



1-Chloro-4-(2-methylpropyl) benzene  
(Aryl halide)

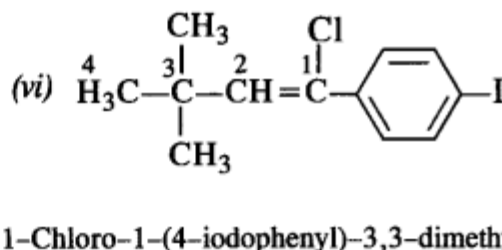
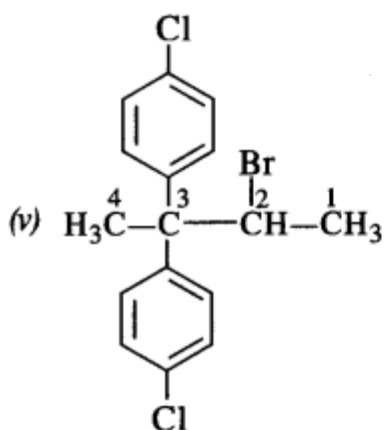
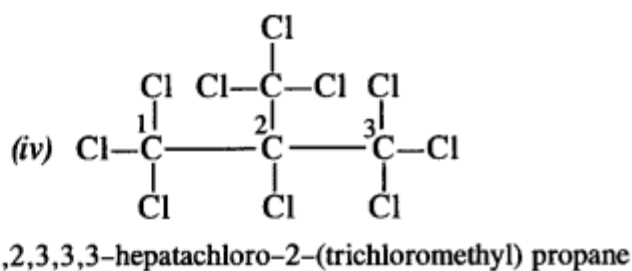
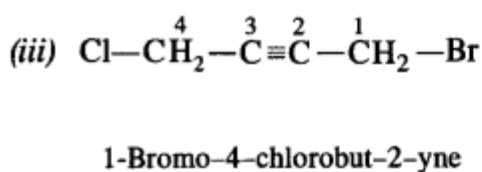
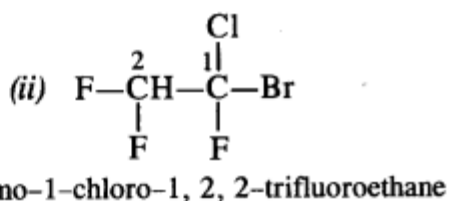
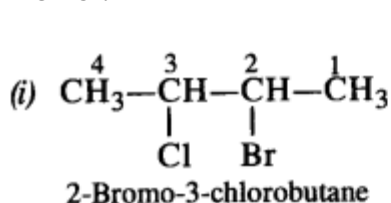


Question 2.

Give the IUPAC names of the following compounds :

- (i)  $\text{CH}_3\text{CH}(\text{Cl})\text{CH}(\text{Br})\text{CH}_3$                       (ii)  $\text{CHF}_2\text{CBrClF}$   
 (iii)  $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Br}$                       (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)  $(\text{CH}_3)_3\text{CCH}=\text{C}(\text{Cl})\text{C}_6\text{H}_4\text{I-p}$ .

Answer:



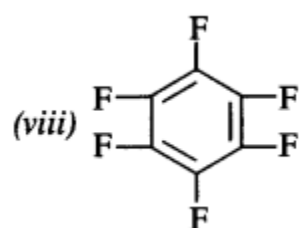
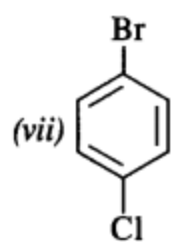
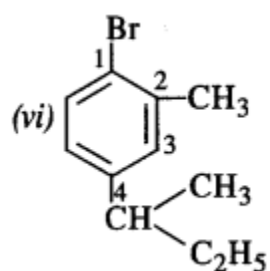
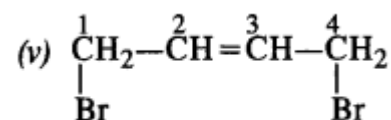
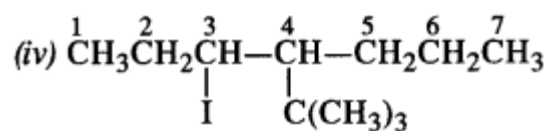
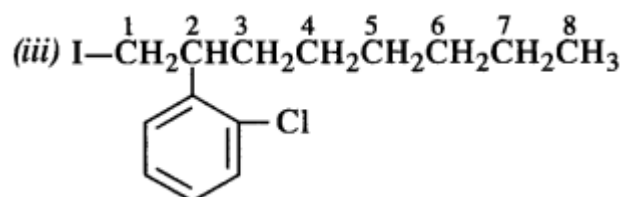
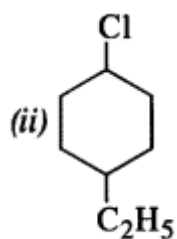
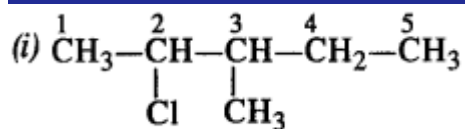
2-Bromo-3,3-bis(4-chlorophenyl) propane

Question 3.

Write the structures of the following compounds :

- (i) 2-Chloro-3-methylpentane  
 (ii) 1-Chloro-4-ethylcyclohexane.  
 (iii) 2-(2-Chlorophenyl)-1-iodooctane  
 (iv) 4-tert. butyl -3-iodooctane  
 (v) 1, 4-Dibromobut-2-ene  
 (vi) 1-Bromo-4-sec.butyl-2-methylbenzene.  
 (vii) p-Bromochlorobenzene  
 (viii) Perfluorobenzene

Answer:



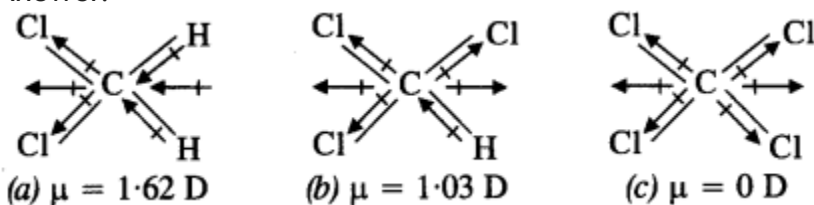
Question 4.

Which one of the following has highest dipole moment?

- (a)  $\text{CH}_2\text{Cl}_2$   
 (b)  $\text{CHCl}_3$

(c)  $\text{CCl}_4$

Answer:



$\text{CCl}_4$  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  $\text{CHCl}_3$ , the resultant dipole moments of two C-Cl bonds is opposed by the resultant dipole moments of one C-H and one C-Cl bond. Since the resultant of one C-H and one C-Cl bond is smaller than the resultant of the two C-Cl bonds dipole moments, the opposition is to a small extent. As a result  $\text{CHCl}_3$  has a small net dipole moment.

On the other hand, in case of  $\text{CH}_2\text{Cl}_2$  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,  $\text{CH}_2\text{Cl}_2$  has a higher dipole moment. Hence  $\text{CH}_2\text{Cl}_2$  has the highest dipole moments among the three compounds.

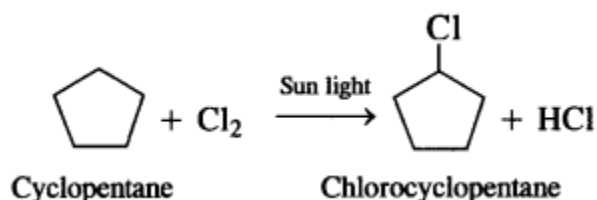
Hence, the given compounds can be arranged in the increasing order of their dipole moments as  $\text{CCl}_4 < \text{CHCl}_3 < \text{CH}_2\text{Cl}_2$

Question 5.

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

Answer:

A hydrocarbon with the molecular formula,  $\text{C}_5\text{H}_{10}$  belongs to the group with a general molecular form  $\text{C}_n\text{H}_{2n}$ . therefore, it may either be an alkene or a cycloalkane since hydrocarbon does not react with chlorine in the dark, it cannot be alkene. Further, the hydrocarbon gives a single monochloro compound,  $\text{C}_5\text{H}_9\text{Cl}$  by reacting with chlorine in bright sunshine since the formed compound is monochloro one all the C-H bonds should be equivalent. Hence the compound should be a cycloalkane. Hence the compound is  $\text{C}_5\text{H}_{10}$  (cyclopentane).

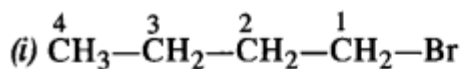


Question 6.

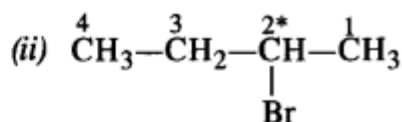
Write the isomers of the compound having the formula  $\text{C}_4\text{H}_9\text{Br}$ . (**Haryana Board 2013**)

Answer:

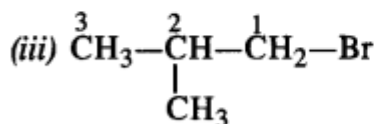
The compound has the following structural isomers.



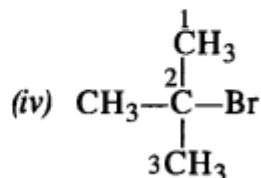
1-Bromobutane



2-Bromobutane



1-Bromo-2-methylpropane



2-Bromo-2-methylpropane

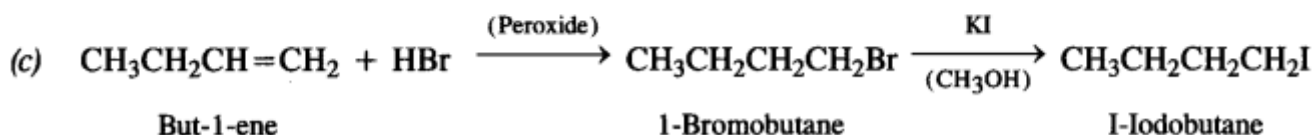
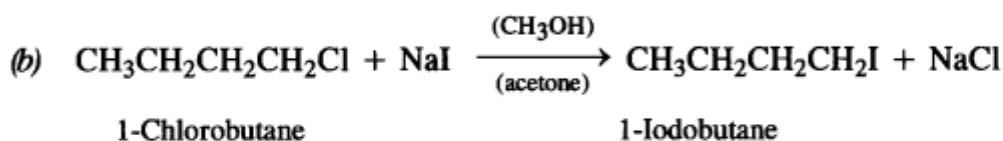
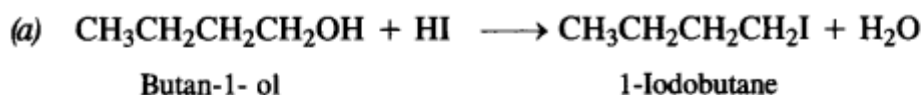
2-Bromobutane has a chiral carbon and it is expected to exhibit optical isomerism.

Question 7.

Write equations for the preparation of 1-Iodobutane from :

- (a) Butan-1-ol
- (b) 1-Chlorobutane
- (c) But-1-ene.

Answer:

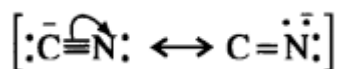


Question 8.

What are ambident nucleophiles? Explain with an example.

Answer:

Nucleophiles which can attack through two different sites are called ambident nucleophiles. For example, cyanide ion exists as a hybrid of the following two structures. It can attack either



through carbon to form cyanides (or nitriles) or through nitrogen to form isocyanides (or carbyl amines). For more details, consult section 11.7.

Question 9.

Which compound in the following pairs will react faster in the S<sub>N</sub>2 reaction?

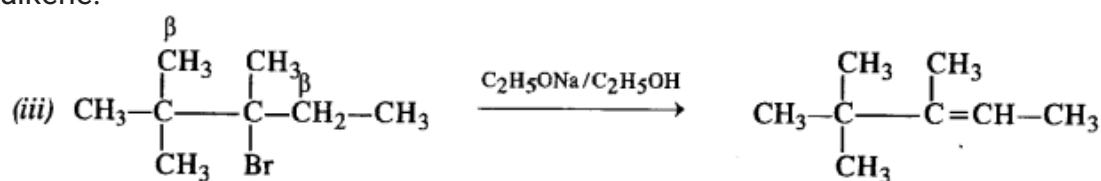
- (1) CH<sub>3</sub>Br or CH<sub>3</sub>I
- (1) (CH<sub>3</sub>)<sub>3</sub>CCl or CH<sub>3</sub>Cl (C.B.S.E. 2008)

Answer:

1. In the S<sub>N</sub>2 mechanism the reactivity of halides for the same alkyl group increase in order. This happens because as the size increases the halide ion becomes a better leaving group.

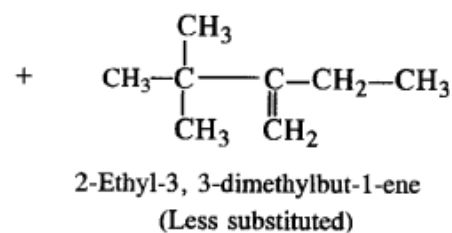


alkene.



3-Bromo-2, 2, 3-trimethylpentane

3, 4, 4-Trimethylpent-2-ene  
(More substituted)

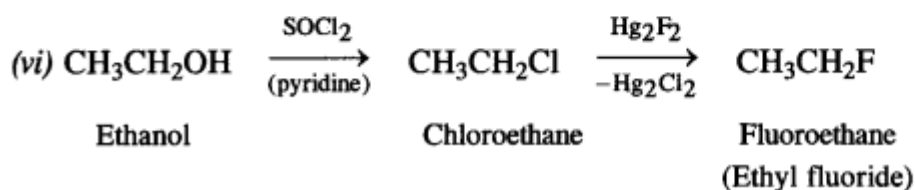
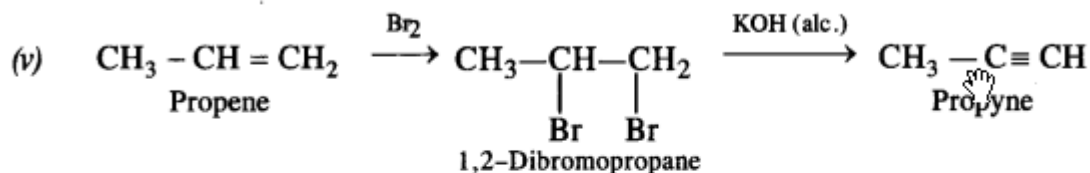
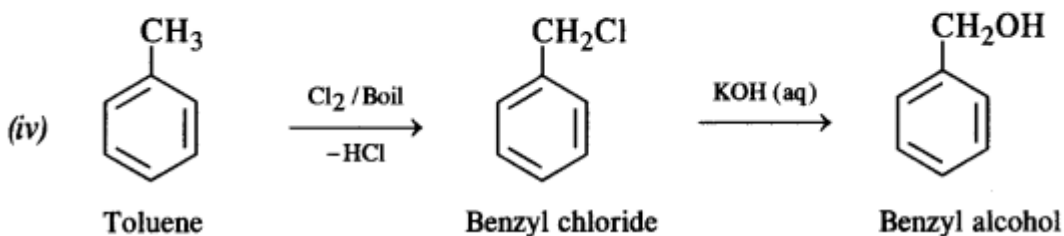
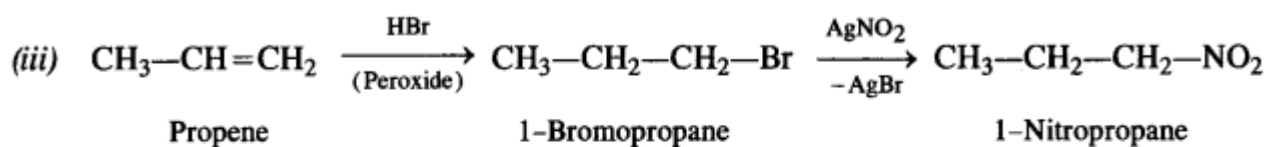
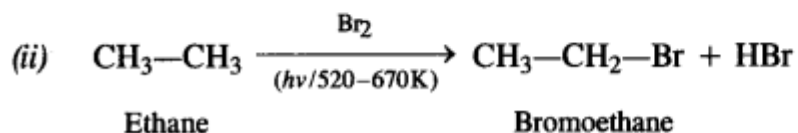
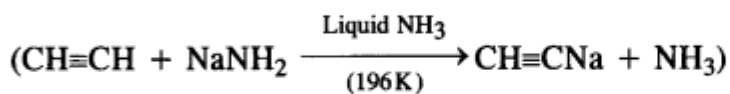
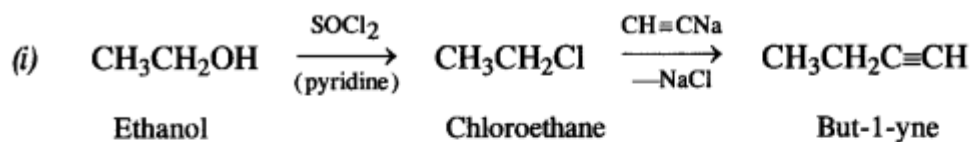


Question 11.

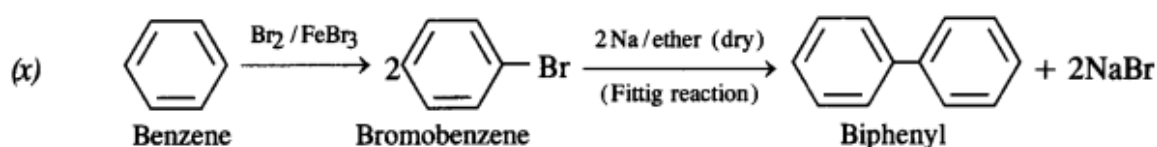
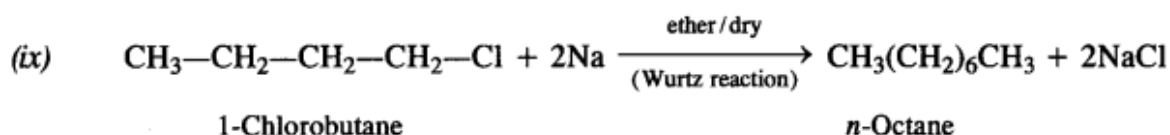
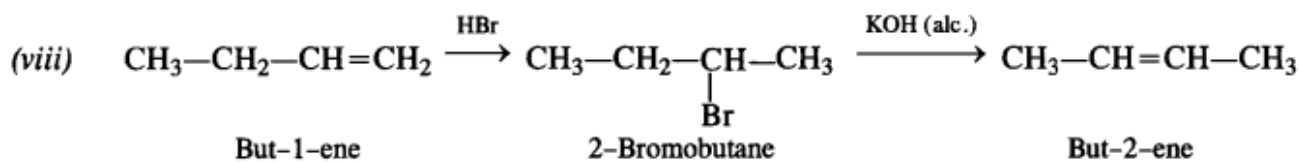
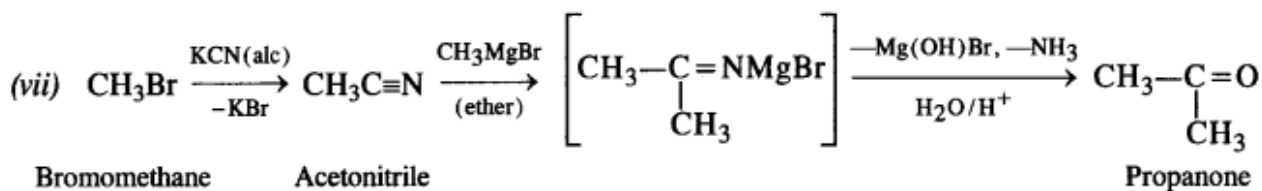
How will you bring about the following conversions? (Haryana Board 2011)

- (i) Ethanol to but-1-yne
- (ii) Ethane to bromoethane
- (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:







Question 12.

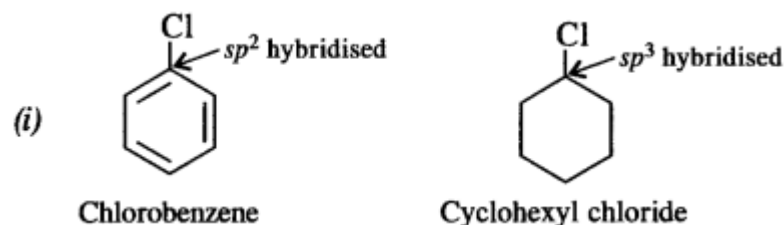
Explain why:

(i) Dipole moment of chlorobenzene is lower than that of cyclohexyl chloride (C.B.S.E 2016)

(ii) Alkyl halides though polar, are immiscible with water.

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

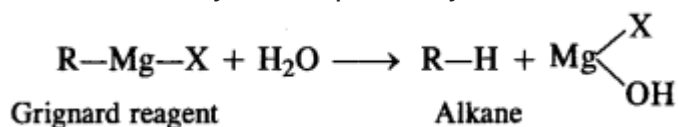
Answer:



The polarity of C-Cl bond in chlorobenzene is less than that of same bond in cyclohexyl chloride because of carbon atom involved in chlorobenzene is more electronegative (greater s-character) as compared to the carbon atom in case of cyclohexyl chloride (lesser s-character). Therefore, the dipole moment of chlorobenzene is less with respect to cyclohexyl chloride.

(ii) In water, H<sub>2</sub>O molecules are linked to each other by intermolecular hydrogen bonding. Although alkyl halides also contain polar C-X bonds, they cannot break the hydrogen bonding in H<sub>2</sub>O molecules. This means that there is hardly any scope for the association between molecules of alkyl halides and water. They, therefore, exist as separate layers and are immiscible with each other. For more details, consult section 11.6.

(iii) Grignard reagents (R-Mg-X) should be prepared under anhydrous conditions because these are readily decomposed by water to form alkanes.

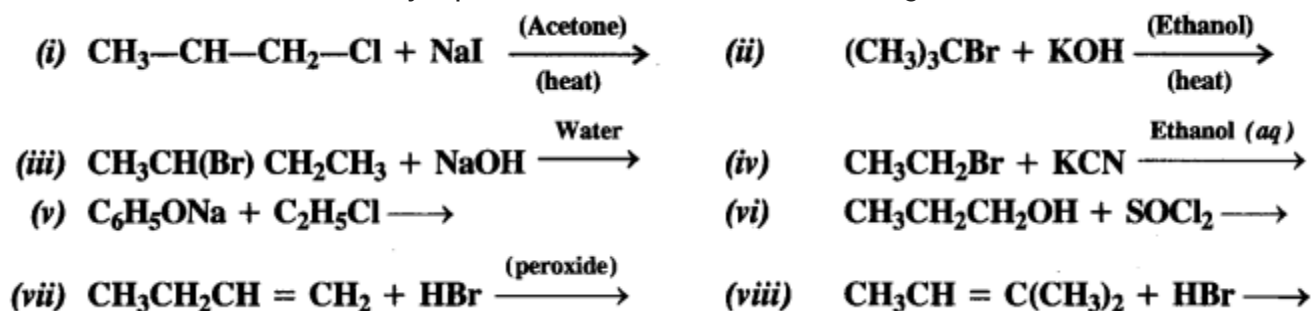


That is why ether used as solvent in the preparation of Grignard reagent is completely anhydrous in nature.

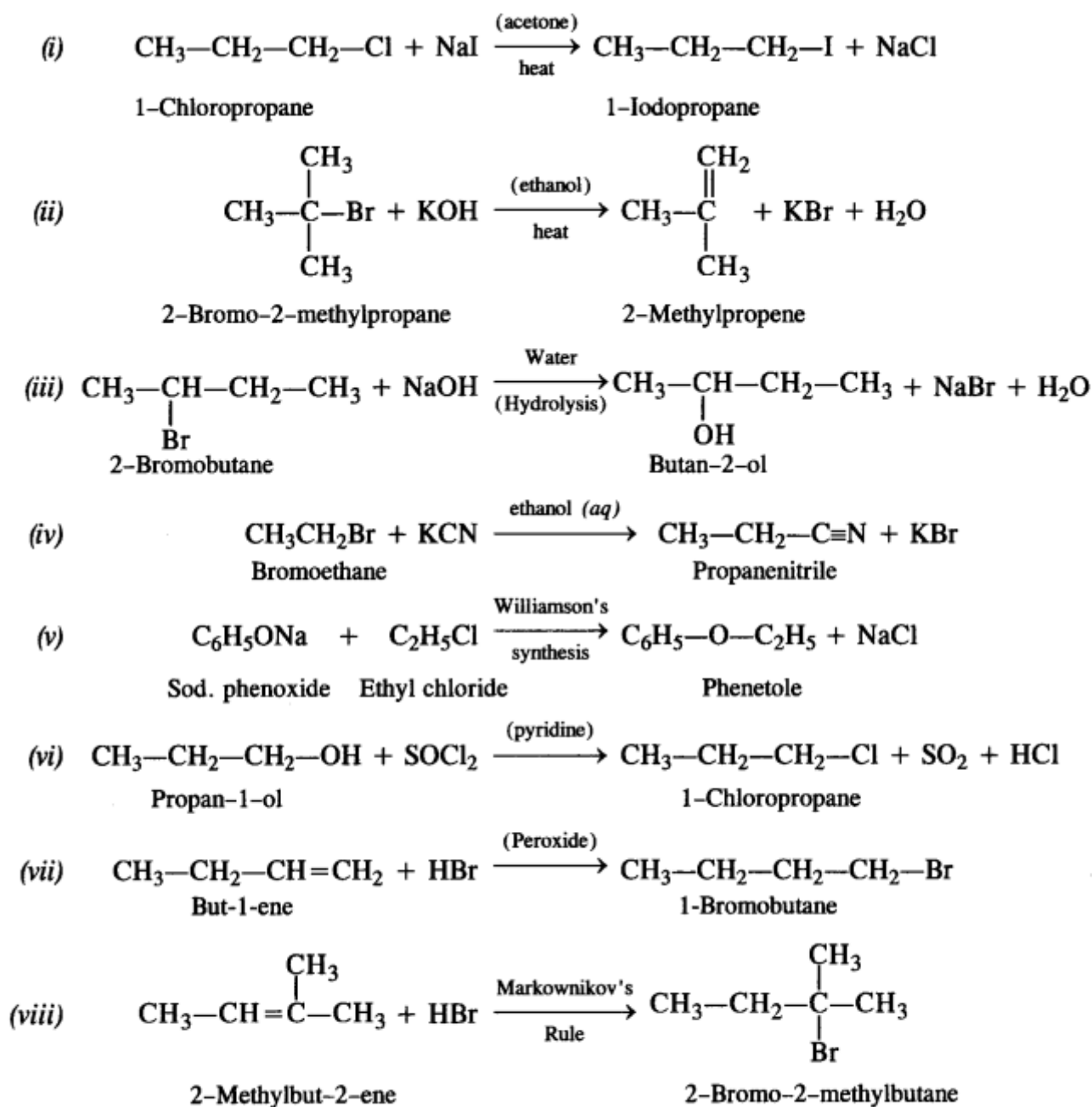


Question 14.

Write the structures of the major products in each of the following reactions :

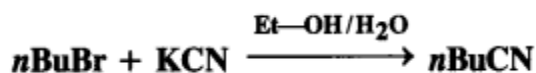


Answer:



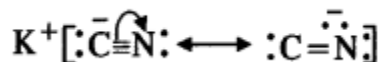
Question 15.

Explain the following reaction : (C.B.S.E. Delhi 2009 Comptt.)

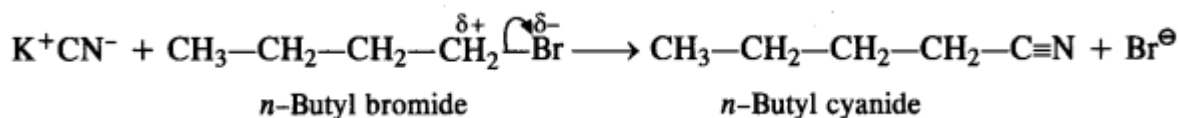


Answer:

KCN is a resonance hybrid of two contributing structures :



This shows that the cyanide ion is an ambident nucleophile and the nucleophile attack is possible either through carbon atom or nitrogen atom resulting in cyanides and isocyanides respectively. In this case, in the presence of polar solvent, KCN readily ionises to furnish ions. The nucleophile attack takes place predominantly through a carbon atom and not through nitrogen atom as C-C bond is more stable than C-N bond.



Question 16.

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

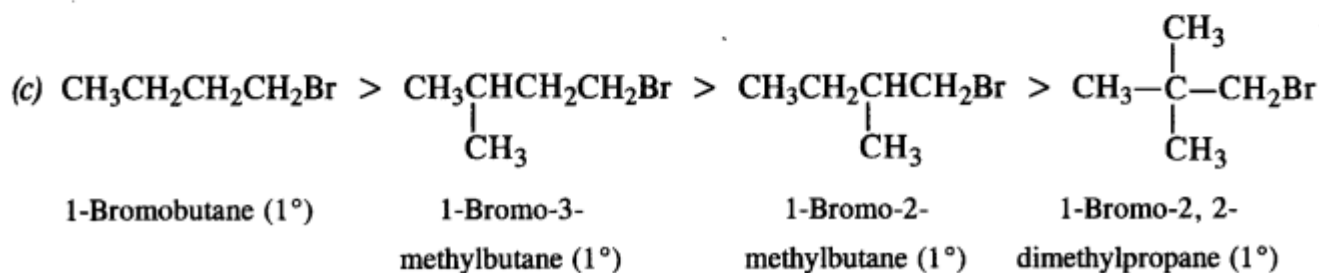
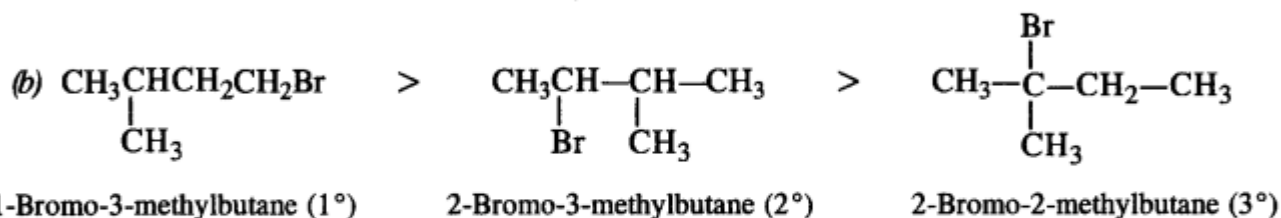
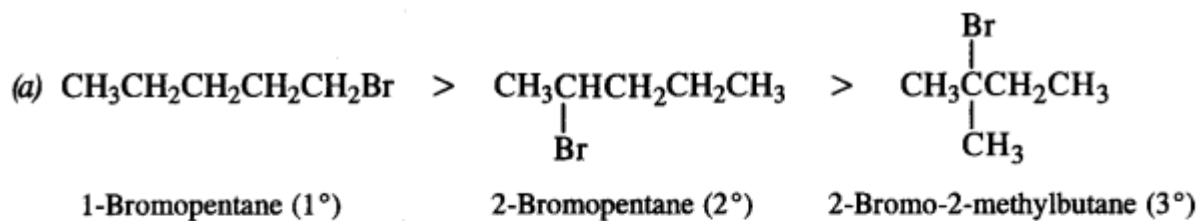
(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(b) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

(c) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane. (C.B.S.E. Outside Delhi 2011)

Answer:

The reactivity of a particular haloalkane towards  $\text{S}_{\text{N}}2$  reaction is inversely proportional to the steric hindrance around the carbon atom involved in C-X bond. More the steric hindrance, lesser will be the reactivity. In the light of this, the decreasing order of reactivity in all the three cases is as follows :



### Question 17.

Out of  $C_6H_5CH_2Cl$  and  $C_6H_5CH(Cl)C_6H_5$  which is more easily hydrolysed by aqueous KOH?

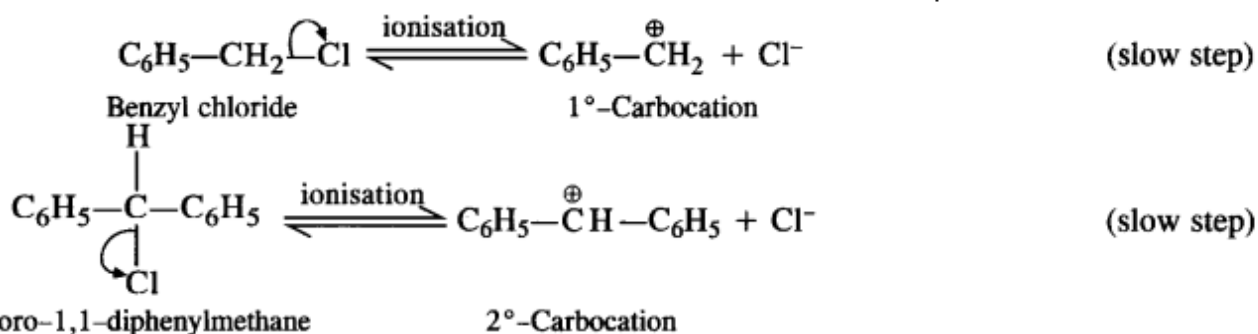
Answer:

The compound  $C_6H_5CH_2Cl$  is a primary alkyl halide while  $C_6H_5CH(Cl)C_6H_5$  is secondary in nature. The hydrolysis of both these compounds with aqueous KOH (polar) is likely to proceed by  $S_N1$  mechanism due to the following reasons.

(a) The carbocations formed in both the cases as a result of ionisation are resonance stabilised due to the presence of phenyl groups at the  $\alpha$ -position(s).

(b) As water is a polar solvent, it is expected to favour ionisation of the two halogen-substituted compounds leading to  $S_N1$  mechanism.

The carbocations that are formed as a result of ionisation in the slow steps are shown :



The ease of hydrolysis depends upon the relative stability of the carbocation/s that are formed in two cases. The secondary carbocation is more stable since the positive charge on the carbocation is delocalised on two phenyl groups that are present at the  $\alpha$ -positions. On the other hand, there is only one phenyl group in primary carbocation available for charge delocalisation.

Thus, we may conclude that  $C_6H_5CHClC_6H_5$  is more easily hydrolysed by aqueous KOH as compared to  $C_6H_5CH_2Cl$ .

### Question 18.

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

Answer:

p-dichlorobenzene has a higher melting point than its o-isomer due to the symmetry of the p-isomer that fits in the crystal lattice better than the o- or m-isomer. Therefore, it has stronger intermolecular forces of attraction than o- and m-isomers, and thus greater energy are required to break crystal lattice to melt or dissolve the p-isomer than the corresponding o- and m-isomers. In other words, the melting point of the p-isomer is higher and its solubility is lower than corresponding m- and o-isomers.

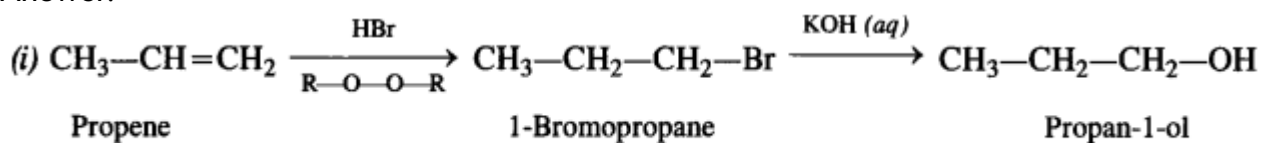
### Question 19.

How the following conversions can be carried out?

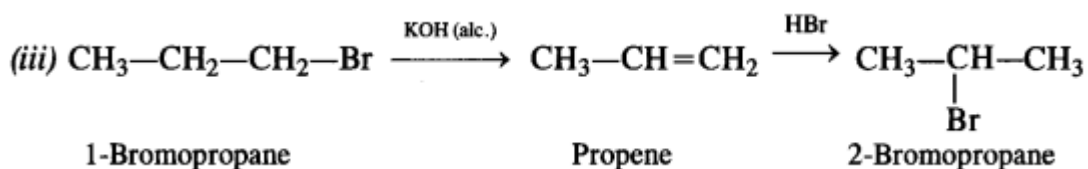
- (i) Propene to propan-1-ol
- (ii) Ethanol to but-1-yne
- (iii) 1-Bromopropane to 2-bromopropane
- (iv) Toluene to benzyl alcohol
- (v) Benzene to 4-bromonitrobenzene
- (vi) Benzyl alcohol to 2-phenyl ethanoic acid
- (vii) Ethanol to propane nitrite
- (viii) Aniline to chlorobenzene
- (ix) 2-Chlorobutane to 3, 4 - dimethyl hexane
- (x) 2-Methylpropene to 2-chloro-2-methylpropane

- (xi) Ethyl chloride to propanoic acid
- (xii) But-1-ene to n-butyl iodide
- (xiii) 2-Chloropropane to propan-1-ol
- (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 phenyl isocyanide.

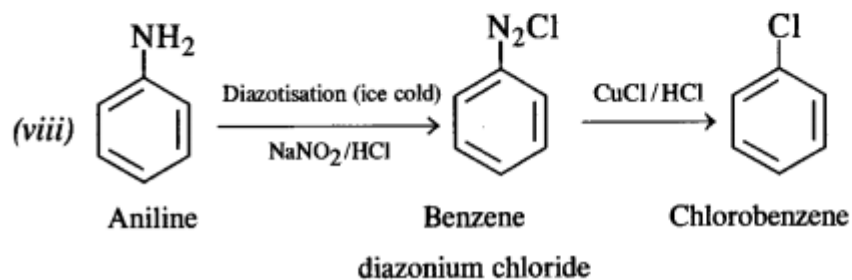
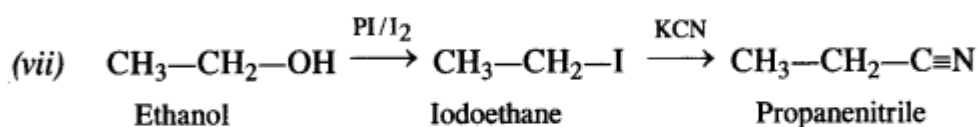
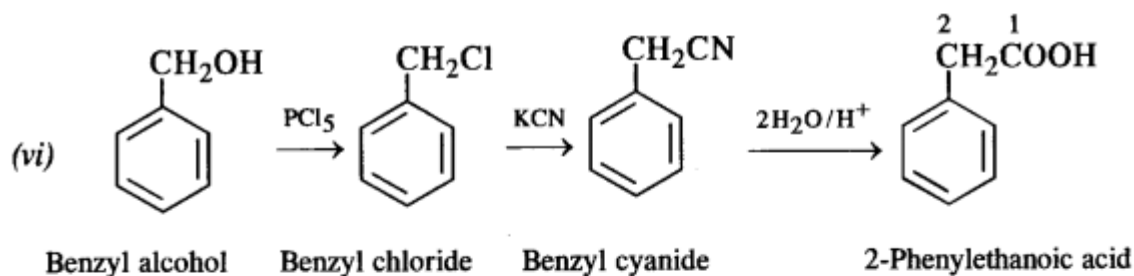
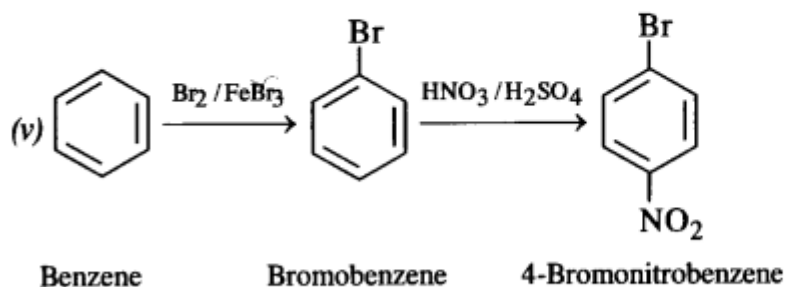
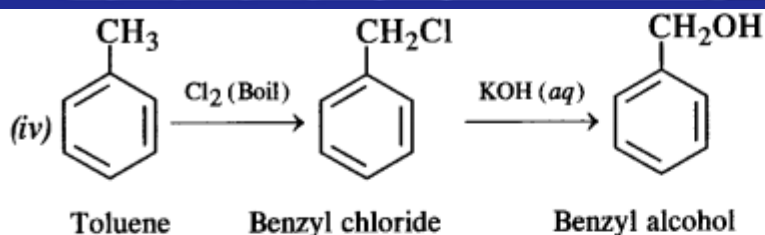
Answer:



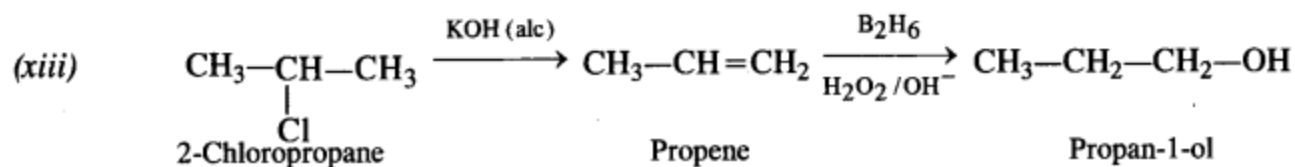
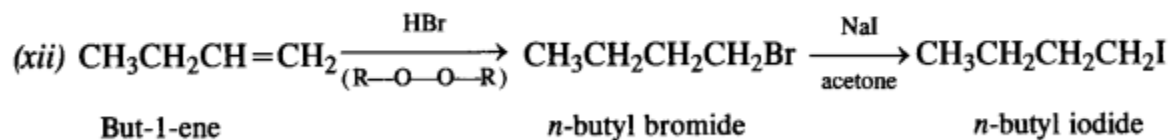
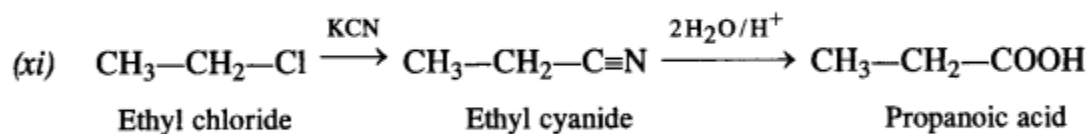
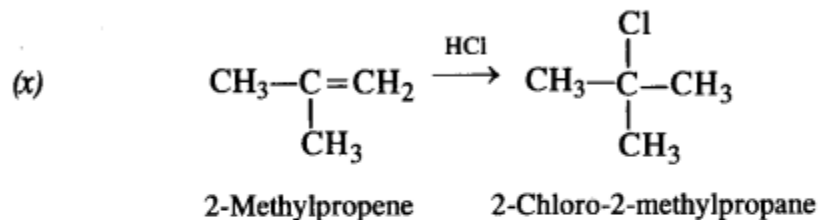
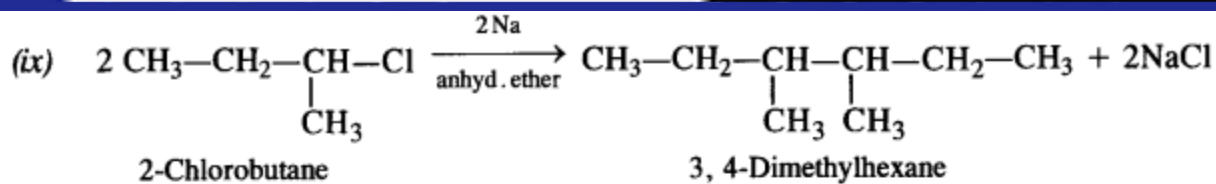
(ii) For answer, consult answer to Q. No. 11.





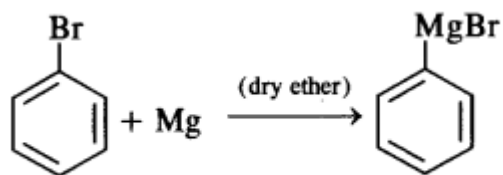










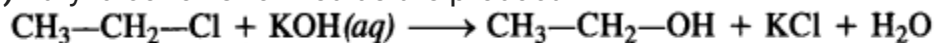


**Bromobenzene**

**Phenyl mag. bromide**

(iii) Chlorobenzene will not get hydrolysed on boiling with NaOH. No product will be formed.

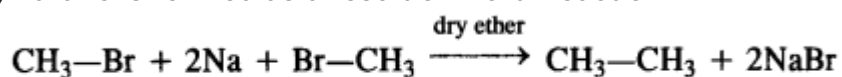
(iv) Ethyl alcohol is formed as the product



**Ethyl chloride**

**Ethyl alcohol**

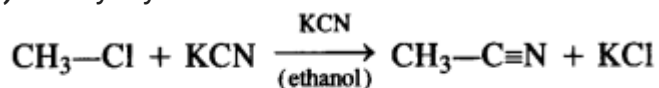
(v) Ethane is formed as a result of Wurtz reaction



**Methyl bromide**

**Ethane**

(vi) Methyl cyanide is formed.



**Methyl chloride**

**Acetonitrile  
(Methyl cyanide)**