

# NCERT Solutions for Class XII Chemistry

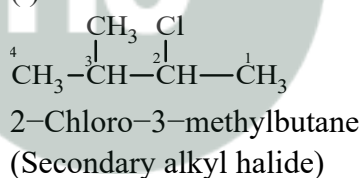
## CHAPTER -6

### NCERT Chemistry Class 12

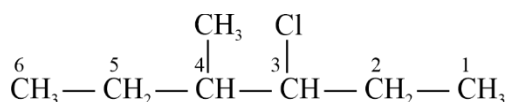
1. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

- (i)  $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_3$
- (ii)  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)\text{Cl}$
- (iii)  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$
- (iv)  $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{Br})\text{C}_6\text{H}_5$
- (v)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{Br})\text{CH}_3$
- (vi)  $\text{CH}_3\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Br}$
- (vii)  $\text{CH}_3\text{C}(\text{Cl})(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3$
- (viii)  $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$
- (ix)  $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$
- (x)  $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$
- (xi)  $m\text{-ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_3$
- (xii)  $o\text{-Br-C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

1.

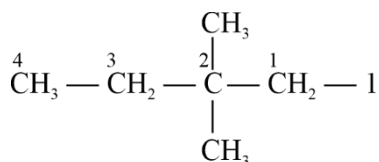


(ii)



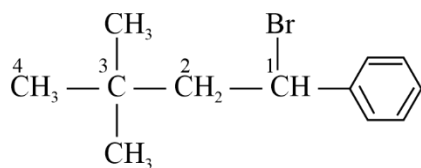
3-Chloro-4-methylhexane  
(Secondary alkyl halide)

(iii)



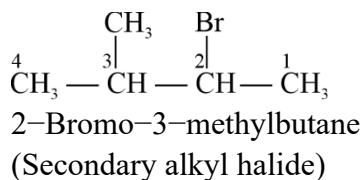
1-Iodo-2,2-dimethylbutane  
(Primary alkyl halide)

(iv)



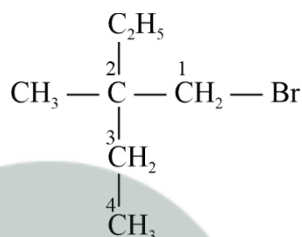
1-Bromo-3,3-dimethyl-1-phenylbutane  
(Secondary benzyl halide)

(v)



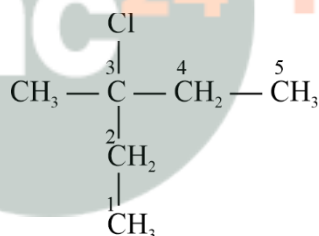
2-Bromo-3-methylbutane  
(Secondary alkyl halide)

(vi)



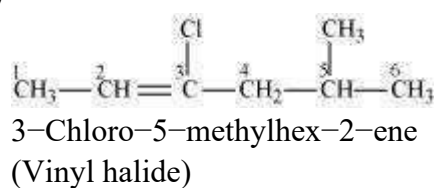
1-Bromo-2-ethyl-2-methylbutane  
(Primary alkyl halide)

(vii)



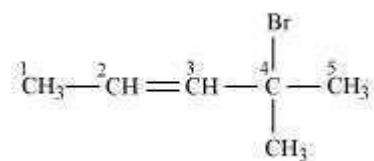
3-Chloro-3-methylpentane  
(Tertiary alkyl halide)

(viii)



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

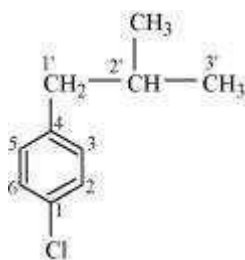
(ix)



4-Bromo-4-methylpent-2-ene

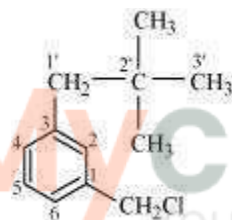
(Allyl halide)

(x)



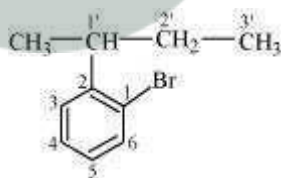
1-Chloro-4-(2-methylpropyl) benzene  
(Aryl halide)

(xi)



1-Chloromethyl-3-(2,2-dimethylpropyl) benzene  
(Primary benzyl halide)

(xii)

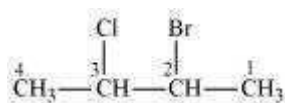


1-Bromo-2-(1-methylpropyl) benzene  
(Aryl halide)

2. Give the IUPAC names of the following compounds:

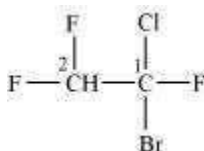
- (i)  $\text{CH}_3\text{CH}(\text{Cl})\text{CH}(\text{Br})\text{CH}_3$
- (ii)  $\text{CHF}_2\text{CBrClF}$
- (iii)  $\text{ClCH}_2\text{C} \equiv \text{CCH}_2\text{Br}$
- (iv)  $(\text{CCl}_3)_3\text{CCl}$
- (v)  $\text{CH}_3\text{C}(\text{p-ClC}_6\text{H}_4)_2\text{CH}(\text{Br})\text{CH}_3$
- (vi)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

2. (i)



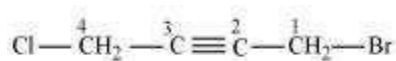
2-Bromo-3-chlorobutane

(ii)



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

(iii)



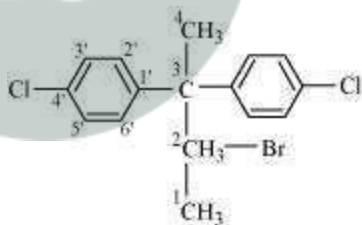
1-Bromo-4-chlorobut-2-yne

(iv)



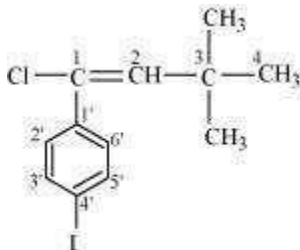
2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

(v)



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

(vi)



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

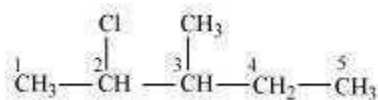
3. Write the structures of the following organic halogen compounds.

- (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

3.

(i)



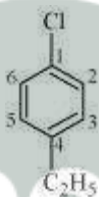
2-Chloro-3-methylpentane

(ii)



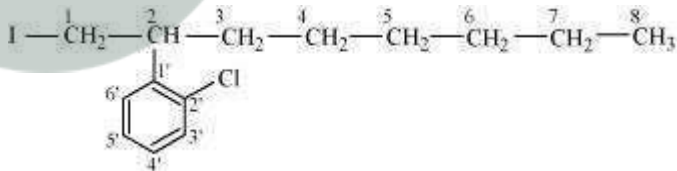
p-Bromochlorobenzene

(iii)



1-Chloro-4-ethylcyclohexane

(iv)



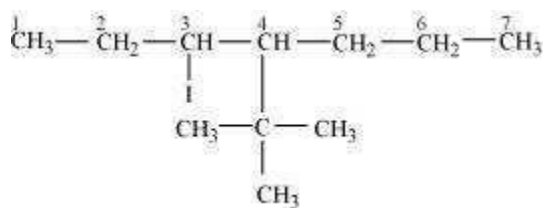
2-(2-Chlorophenyl)-1-iodooctane

(v)



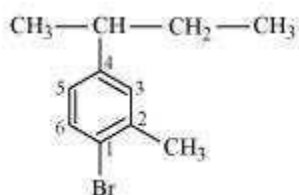
Perfluorobenzene

(vi)



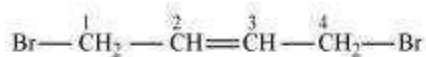
4-Tert-Butyl-3-iodoheptane

(vii)



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

(viii)



1,4-Dibromobut-2-ene

4. Which one of the following has the highest dipole moment?

(i)  $\text{CH}_2\text{Cl}_2$

(ii)  $\text{CHCl}_3$

(iii)  $\text{CCl}_4$

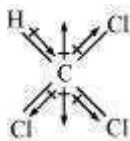
4. (i)



Dichloromethane ( $\text{CH}_2\text{Cl}_2$ )

$\mu = 1.60\text{D}$

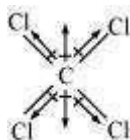
(ii)



Chloroform ( $\text{CHCl}_3$ )

$\mu = 1.08\text{D}$

(iii)



Carbon tetrachloride ( $\text{CCl}_4$ )

$\mu = 0\text{D}$

$\text{CCl}_4$  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 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,  $\text{CHCl}_3$  has a small dipole moment of 1.08 D.

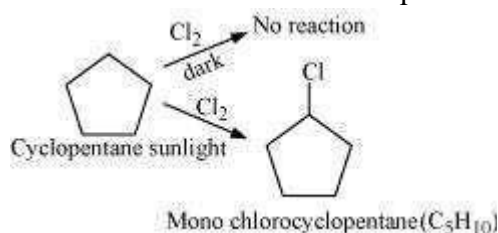
On the other hand, in case of  $\text{CH}_2\text{Cl}_2$ , the resultant of the dipole moments of two C–Cl bonds is strengthened by the resultant of the dipole moments of two C–H bonds. As a result,  $\text{CH}_2\text{Cl}_2$  has a higher dipole moment of 1.60 D than  $\text{CHCl}_3$  i.e.,  $\text{CH}_2\text{Cl}_2$  has the highest dipole moment. Hence, the given compounds can be arranged in the increasing order of their dipole moments as:  $\text{CCl}_4 < \text{CHCl}_3 < \text{CH}_2\text{Cl}_2$

5. A hydrocarbon  $\text{C}_5\text{H}_{10}$  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.
5. A hydrocarbon with the molecular formula,  $\text{C}_5\text{H}_{10}$  belongs to the group with a general molecular formula  $\text{C}_n\text{H}_{2n}$ . Therefore, it may either be an alkene or a cycloalkane. Since hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane. Further, the hydrocarbon gives a single monochloro compound,  $\text{C}_5\text{H}_9\text{Cl}$  by reacting with chlorine in bright sunlight. Since a single monochloro compound is formed, the hydrocarbon must contain H-atoms that are all equivalent. Also, as all H-atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.



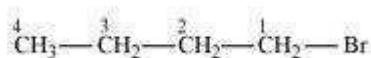
Cyclopentane ( $\text{C}_5\text{H}_{10}$ )

The reactions involved in the question are:



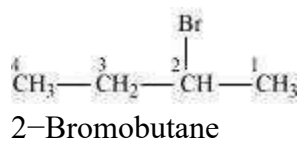
6. Write the isomers of the compound having formula  $\text{C}_4\text{H}_9\text{Br}$ .
6. There are four isomers of the compound having the formula  $\text{C}_4\text{H}_9\text{Br}$ . These isomers are given below.

(a)

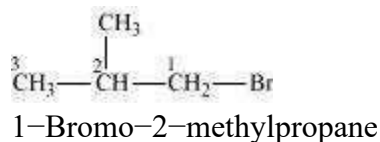


1-Bromobutane

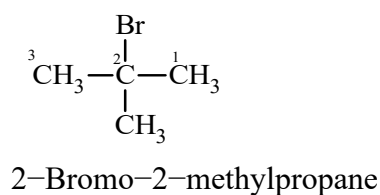
(b)



(c)



(d)



7. Write the equations for the preparation of 1-iodobutane from

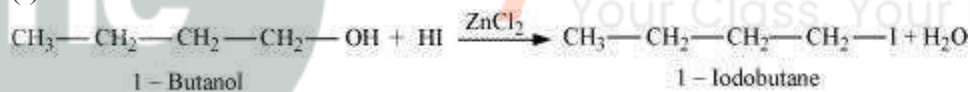
(i) 1-butanol

(ii) 1-chlorobutane

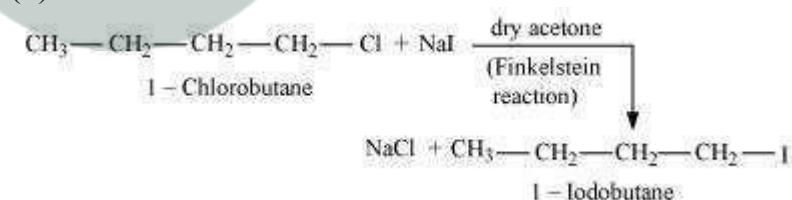
(iii) but-1-ene.

7.

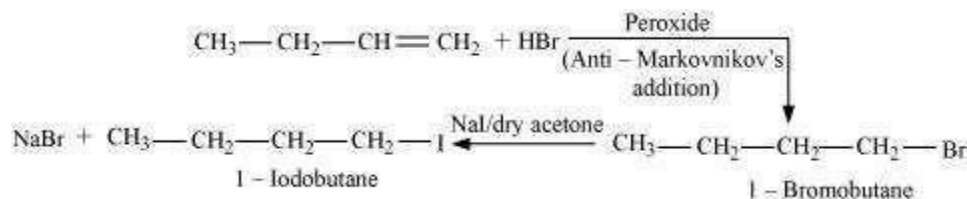
(i)



(ii)

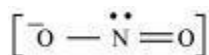


(iii)

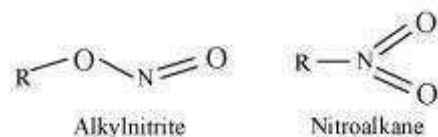


8. What are ambident nucleophiles? Explain with an example.

8. Ambident nucleophiles are nucleophiles having two nucleophilic sites. Thus, ambident nucleophiles have two sites through which they can attack. For example, nitrite ion is an ambident nucleophile.



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

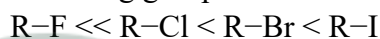


9. Which compound in each of the following pairs will react faster in  $\text{S}_\text{N}2$  reaction with  $\text{OH}^-$ ?

(i)  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$

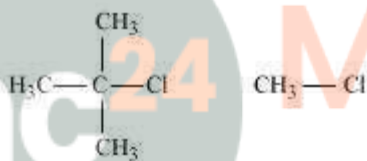
(ii)  $(\text{CH}_3)_3\text{CCl}$  or  $\text{CH}_3\text{Cl}$

9. (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,  $\text{CH}_3\text{I}$  will react faster than  $\text{CH}_3\text{Br}$  in  $\text{S}_\text{N}2$  reactions with  $\text{OH}^-$ .

(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  $\text{CH}_3\text{Cl}$ . Hence,  $\text{CH}_3\text{Cl}$  reacts faster than  $(\text{CH}_3)_3\text{CCl}$  in  $\text{S}_\text{N}2$  reaction with  $\text{OH}^-$ .

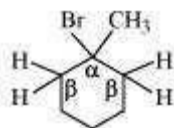
10. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane

(ii) 2-Chloro-2-methylbutane

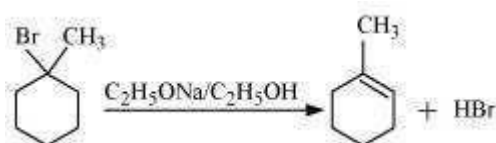
(iii) 2,2,3-Trimethyl-3-bromopentane.

10. (i)

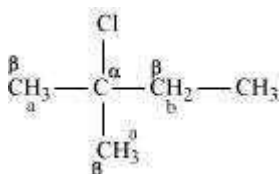


1-bromo-1-methylcyclohexane

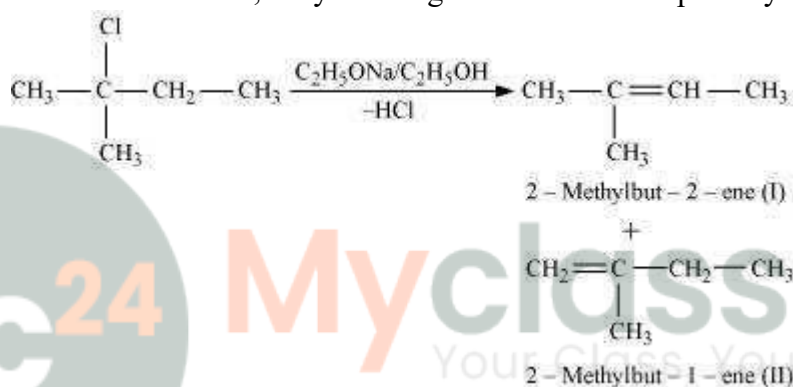
In the given compound, all  $\beta$ -hydrogen atoms are equivalent. Thus, dehydrohalogenation of this compound gives only one alkene.



(ii)

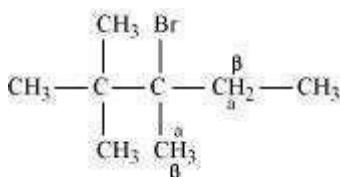


In the given compound, there are two different sets of equivalent  $\beta$ -hydrogen atoms labelled as a and b. Thus, dehydrohalogenation of the compound yields two alkenes.



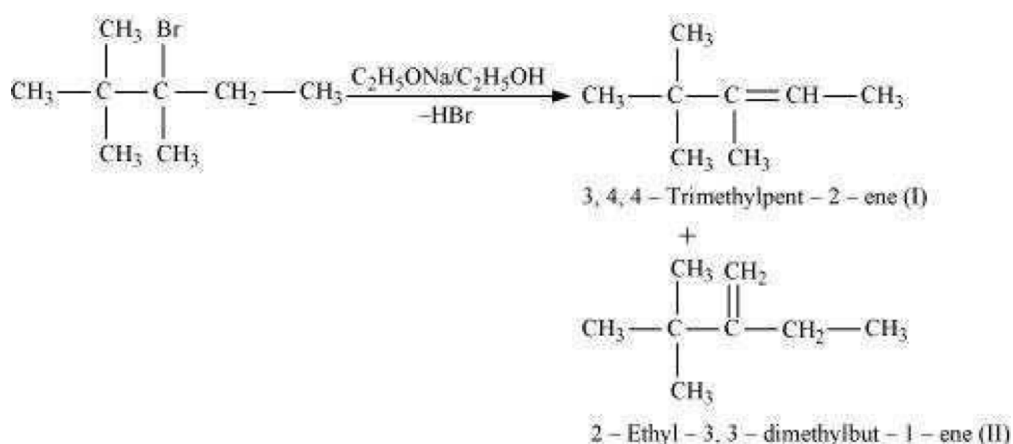
Saytzeff's rule implies that in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced. Therefore, alkene (I) i.e., 2-methylbut-2-ene is the major product in this reaction.

(iii)



2,2,3-Trimethyl-3-bromopentane

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

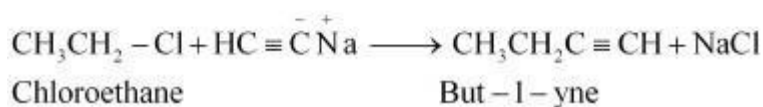
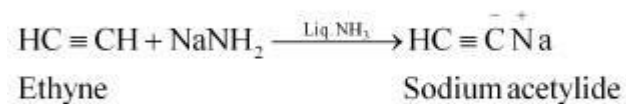
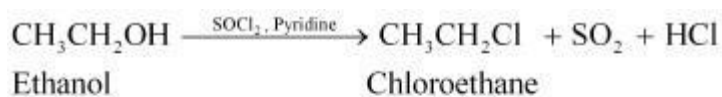


According to Saytzeff's rule, in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to the doubly bonded carbon atom is preferably formed. Hence, alkene (I) i.e., 3,4,4-trimethylpent-2-ene is the major product in this reaction.

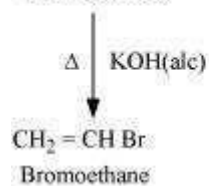
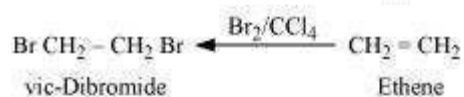
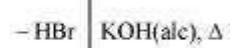
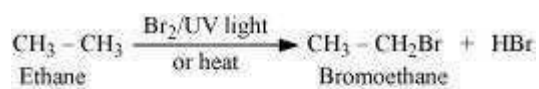
11. How will you bring about the following conversions?

- (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.

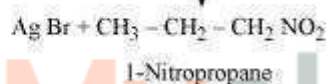
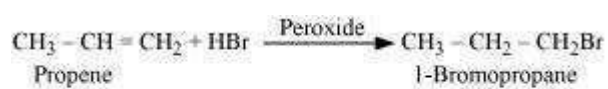
11. (i)



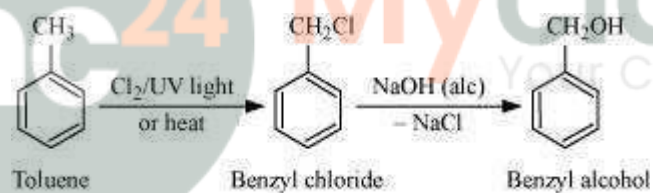
(ii)



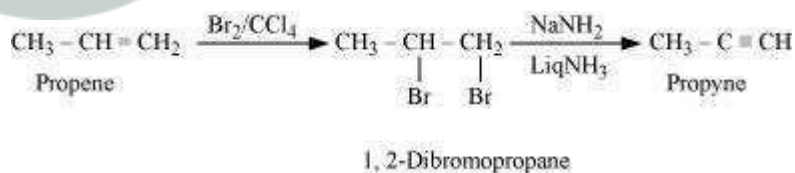
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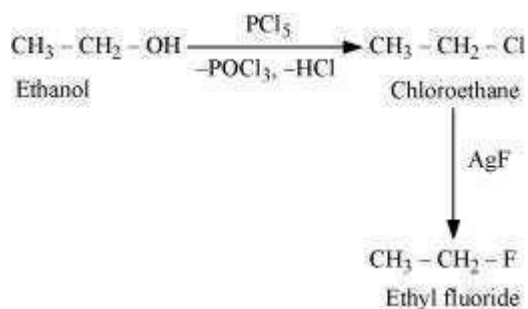
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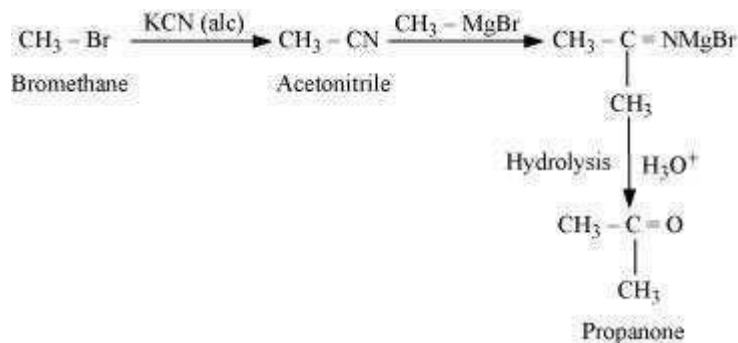
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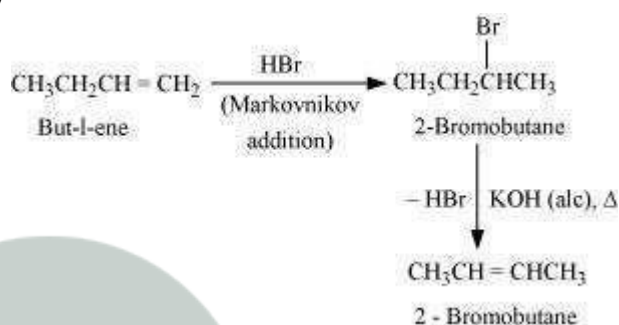
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(vii)



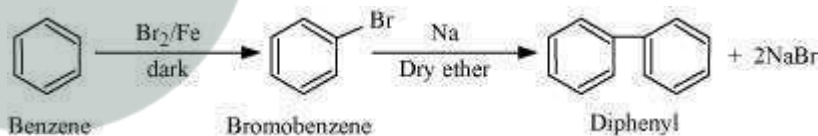
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(ix)



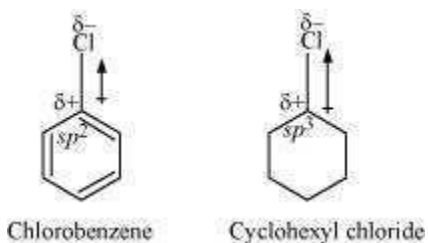
(x)



12. Explain why

- the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
- alkyl halides, though polar, are immiscible with water?
- Grignard reagents should be prepared under anhydrous conditions?

12. (i)

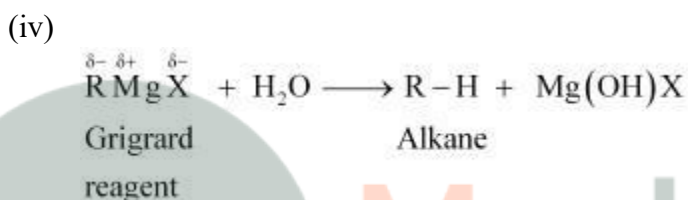


In chlorobenzene, the Cl-atom is linked to a  $sp^2$  hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to a  $sp^3$  hybridized carbon atom. Now,  $sp^2$  hybridized carbon has more s-character than  $sp^3$  hybridized carbon atom. Therefore, the former is more electronegative than 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.



(v) Therefore, Grignard reagents should be prepared under anhydrous conditions.

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

### 13. Uses of Freon – 12

Freon-12 (dichlorodifluoromethane,  $\text{CF}_2\text{Cl}_2$ ) 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

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

### Uses of carbontetrachloride ( $\text{CCl}_4$ )

- (i) It is used for manufacturing refrigerants and propellants for aerosol cans.
- (ii) It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.
- (iii) It is used as a solvent in the manufacture of pharmaceutical products.
- (iv) Until the mid 1960's, carbon tetrachloride was widely used as a cleaning fluid, a degreasing agent in industries, a spot reamer in homes, and a fire extinguisher.

### Uses of iodoform ( $\text{CHI}_3$ )

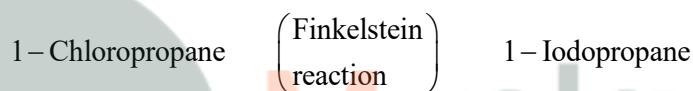
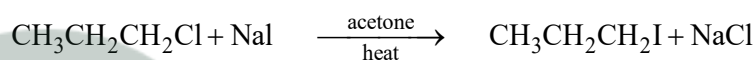
Iodoform was used earlier as an antiseptic, but now it has been replaced by other formulations-containing iodine-due to its objectionable smell. The antiseptic property of

iodoform is only due to the liberation of free iodine when it comes in contact with the skin.

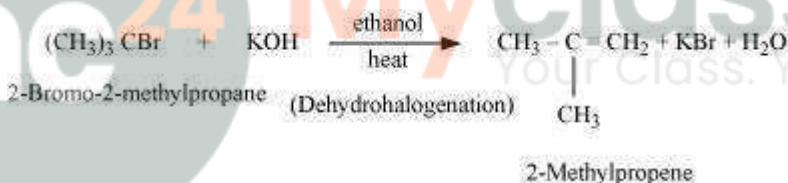
14. Write the structure of the major organic product in each of the following reactions:

- (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaI} \xrightarrow[\text{heat}]{\text{acetone}}$
- (ii)  $(\text{CH}_3)_3\text{CBr} + \text{KOH} \xrightarrow[\text{heat}]{\text{ethanol}}$
- (iii)  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3 + \text{NaOH} \xrightarrow{\text{water}}$
- (iv)  $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \xrightarrow{\text{aq. ethanol}}$
- (v)  $\text{C}_6\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{Cl} \longrightarrow$
- (vi)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \longrightarrow$
- (vii)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{Peroxide}}$
- (viii)  $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{HBr} \longrightarrow$

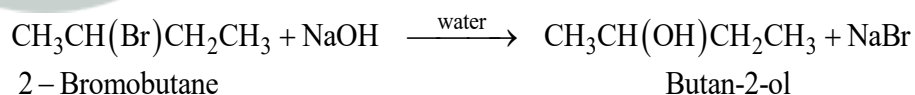
14. (i)



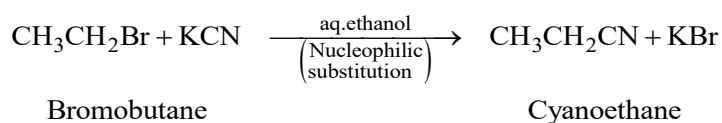
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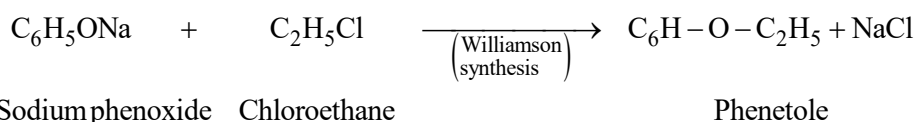
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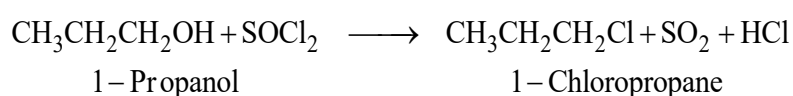
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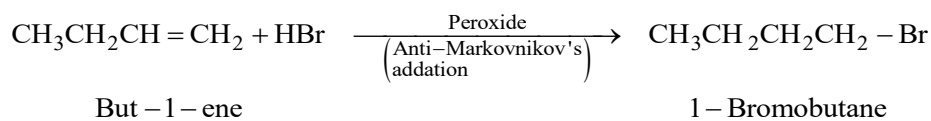
(v)



(vi)



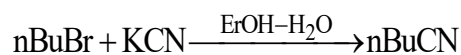
(vii)



(viii)



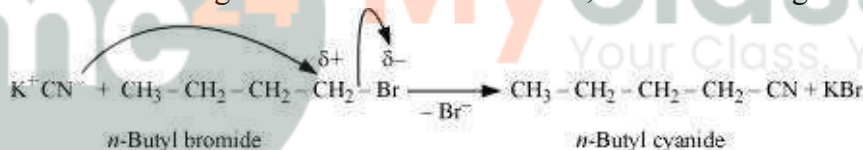
15. Write the mechanism of the following reaction:



15. The given reaction is:



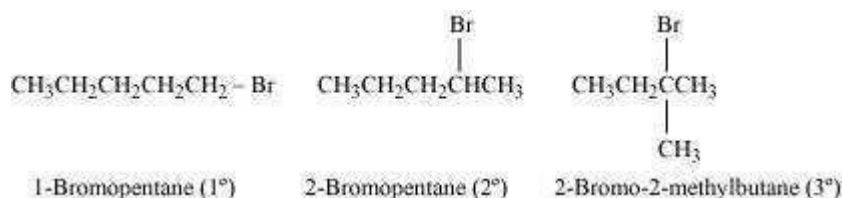
The given reaction is an  $\text{S}_\text{N}2$  reaction. In this reaction,  $\text{CN}^-$  acts as the nucleophile and attacks the carbon atom to which Br is attached.  $\text{CN}^-$  ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



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

- (i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
- (ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane
- (iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

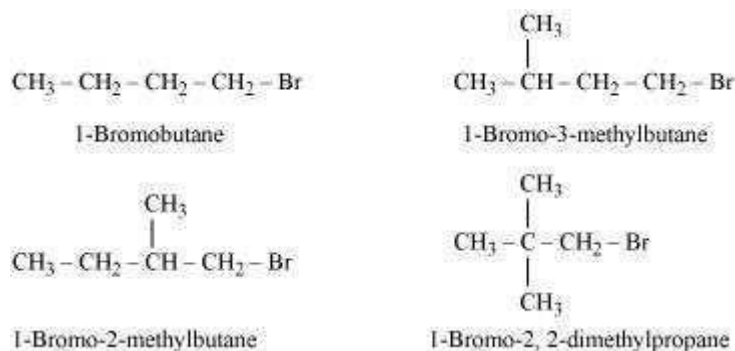
16. (i)



An  $\text{S}_\text{N}2$  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  $\text{S}_\text{N}2$  displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases in the following order.

1-Bromopentane < 2-bromopentane < 2-Bromo-2-methylbutane  
Hence, the increasing order of reactivity towards  $S_N^2$  displacement is:  
2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

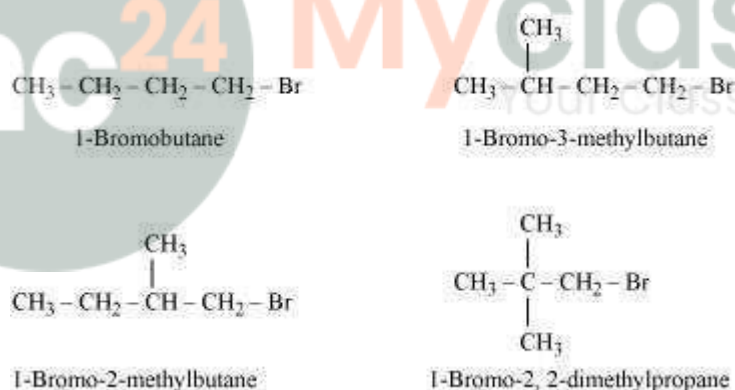
(ii)



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  $S_N^2$  displacement as:

2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane  
[2-Bromo-3-methylbutane is incorrectly given in NCERT]

(iii)

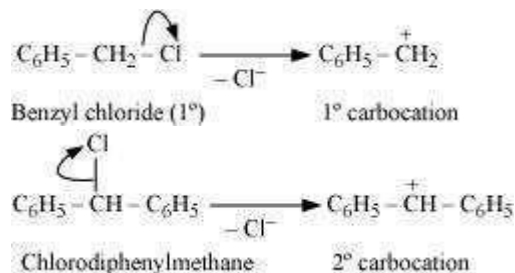


The steric hindrance to the nucleophile in the  $S_N2$  mechanism increases with a decrease in the distance of the substituents from the atom containing the leaving group. Further, the steric hindrance increases with an increase in the number of substituents. Therefore, the increasing order of steric 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

17. Out of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  and  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ , which is more easily hydrolysed by aqueous KOH?

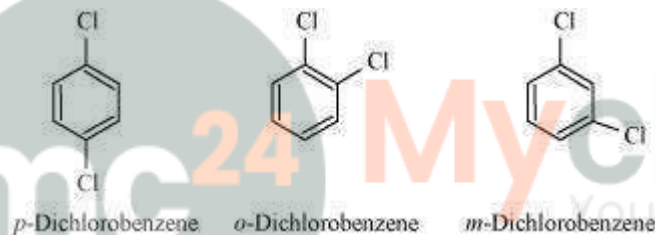
17.



Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. Now,  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  forms  $1^\circ$ -carbocation, while  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$  forms  $2^\circ$ -carbocation, which is more stable than  $1^\circ$ -carbocation. Hence,  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$  is hydrolyzed more easily than  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  by aqueous KOH.

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

18.



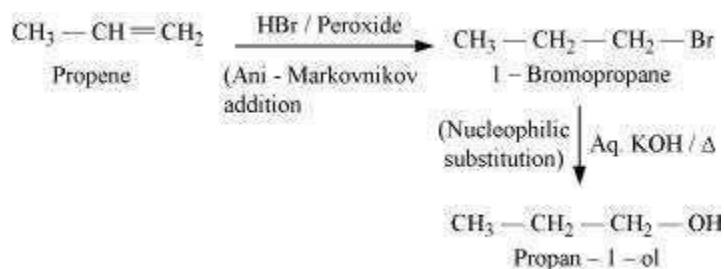
p-Dichlorobenzene is more symmetrical than o- and m-isomers. For this reason, it fits more closely than o- and m-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of p-dichlorobenzene. As a result, p-dichlorobenzene has a higher melting point and lower solubility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

19. How the following conversions can be carried out?

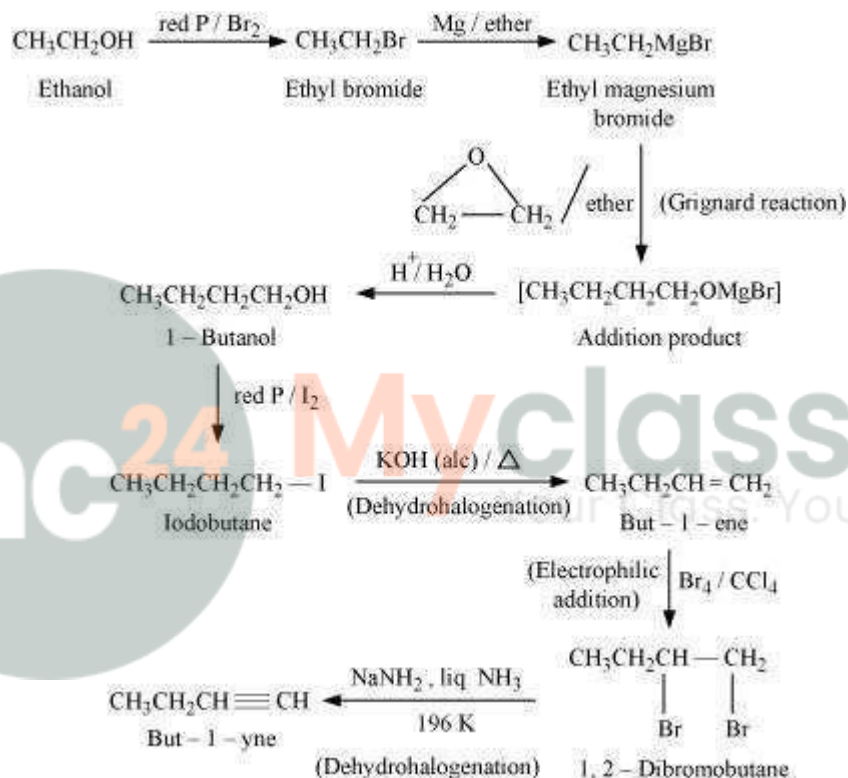
- |                                            |                                                    |
|--------------------------------------------|----------------------------------------------------|
| (i) Propene to propan-1-ol                 | (ii) Ethanol to but-1-yne                          |
| (iii) 1-Bromopropane to 2-bromopropane     | (iv) Toluene to benzyl alcohol                     |
| (v) Benzene to 4-bromonitrobenzene         | (vi) Benzyl alcohol to 2-phenylethanoic acid       |
| (vii) Ethanol to propanenitrile            | (viii) Aniline to chlorobenzene                    |
| (ix) 2-Chlorobutane to 3, 4-dimethylhexane | (x) 2-Methyl-1-propene to 2-chloro-2-methylpropane |
| (xi) Ethyl chloride to propanoic acid      | (xii) But-1-ene to n-butyliodide                   |
| (xiii) 2-Chloropropane to 1-propanol       | (xiv) Isopropyl alcohol to iodoform                |
| (xv) Chlorobenzene to p-nitrophenol        | (xvi) 2-Bromopropane to 1-bromopropane             |
| (xvii) Chloroethane to butane              | (xviii) Benzene to diphenyl                        |

(xix) tert-Butyl bromide to isobutyl bromide    (xx) Aniline to phenylisocyanide

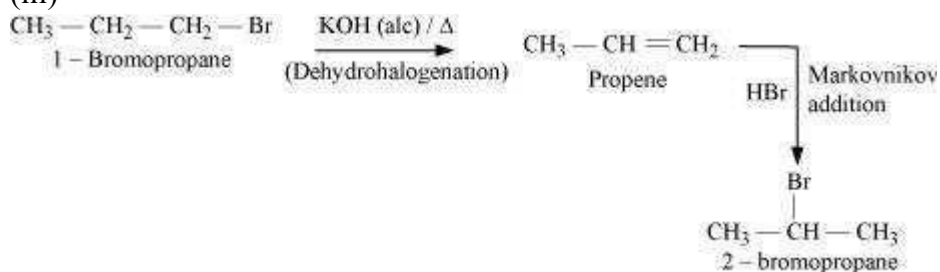
19. (i)



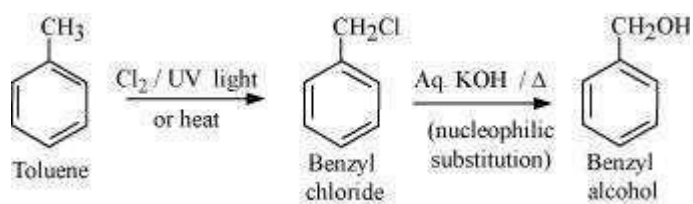
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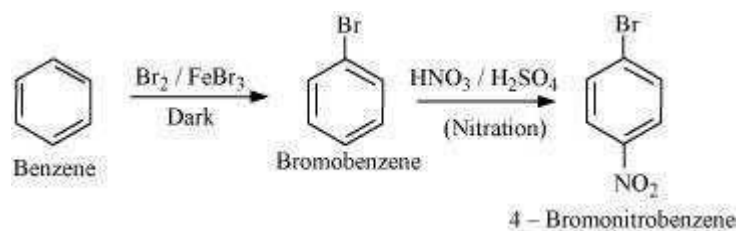
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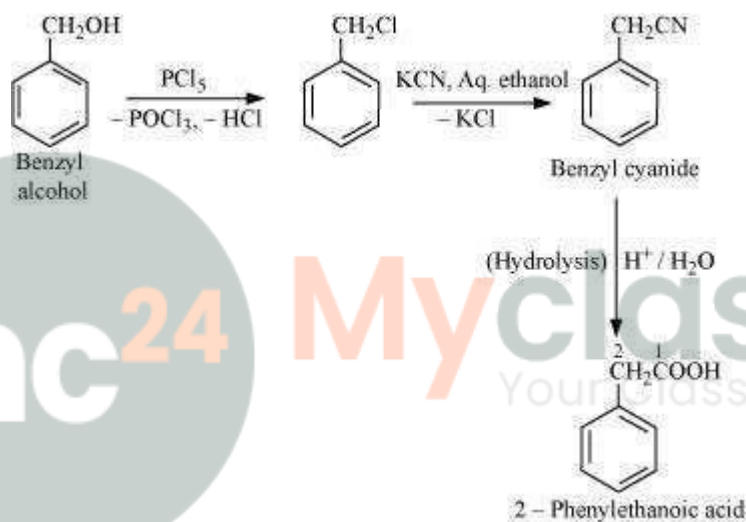
(iv)



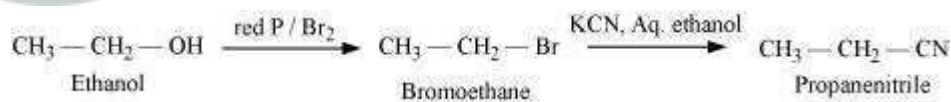
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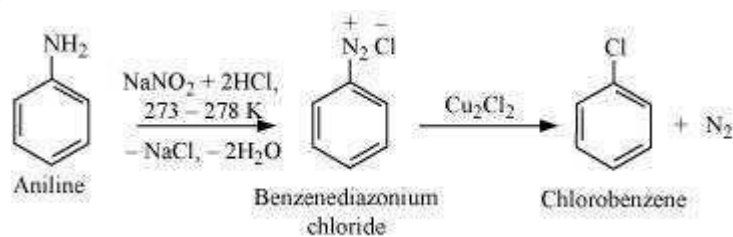
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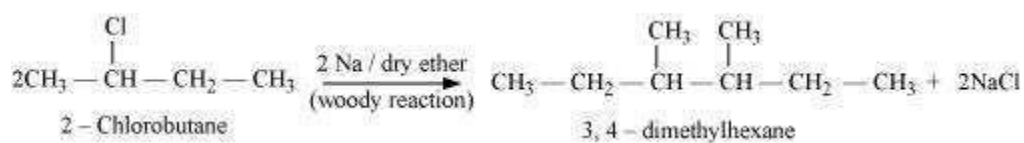
(vii)



(viii)



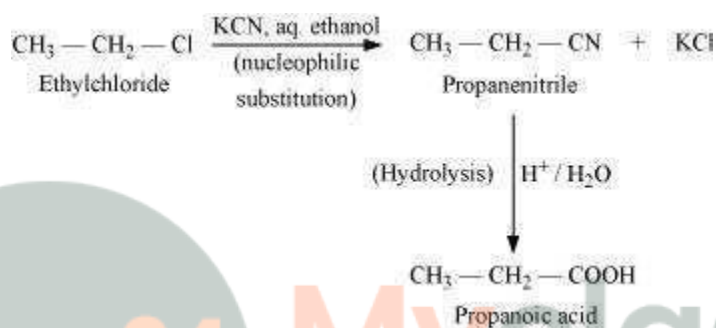
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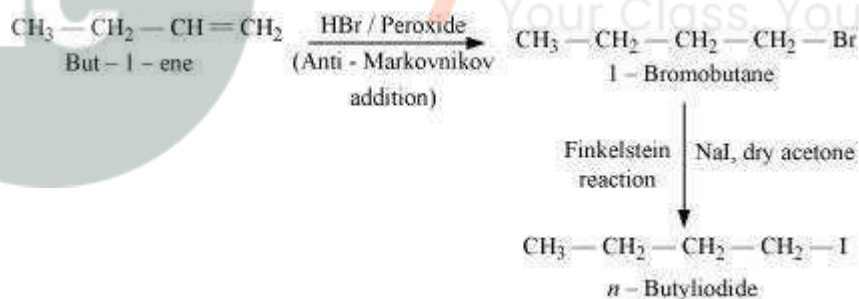
(x)



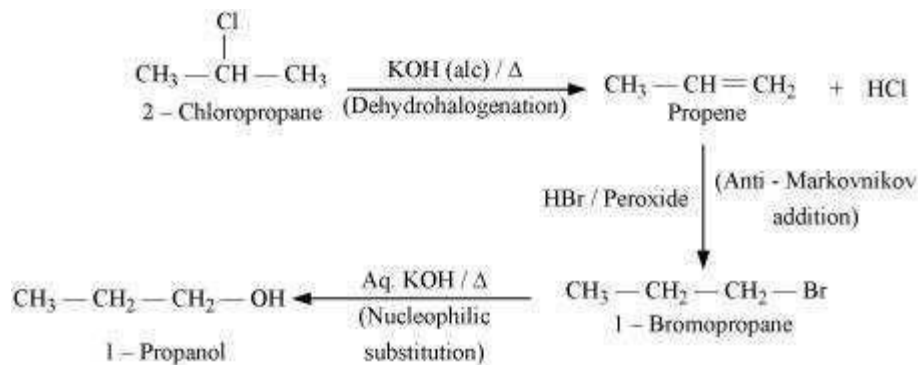
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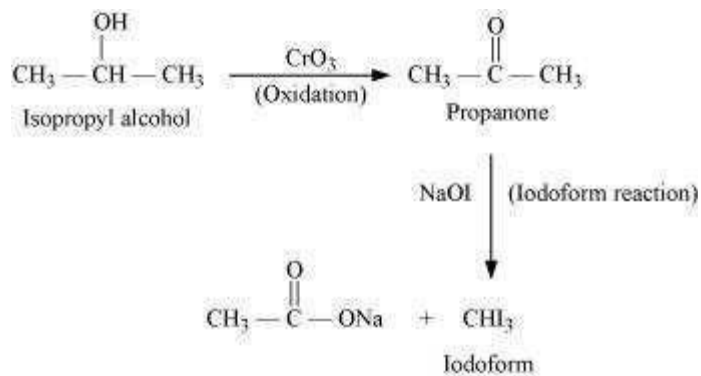
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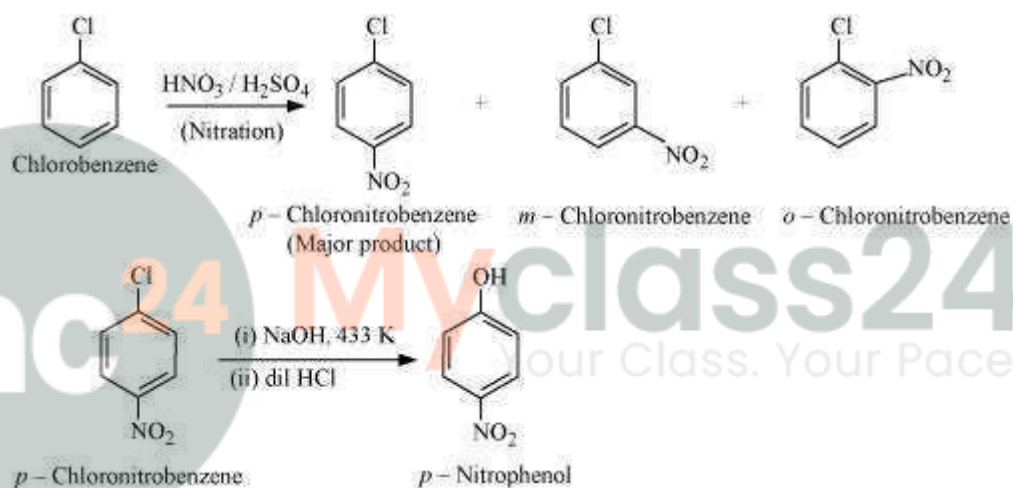
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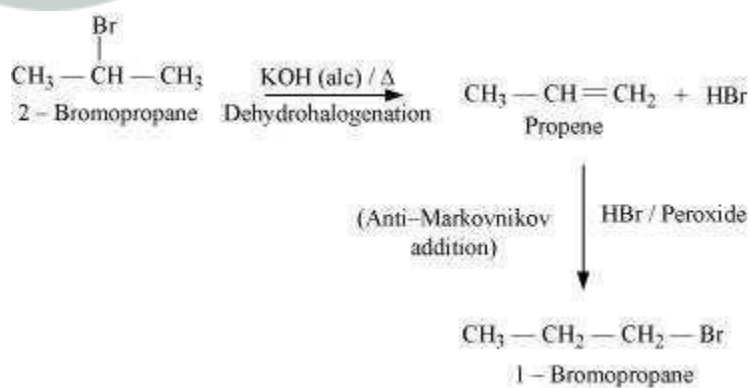
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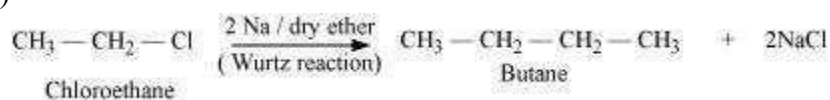
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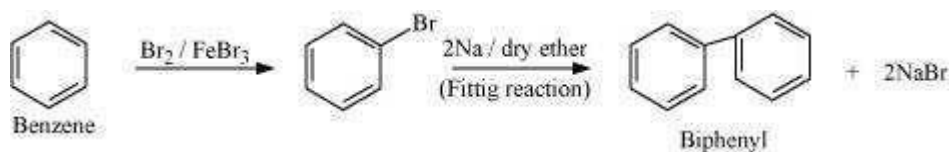
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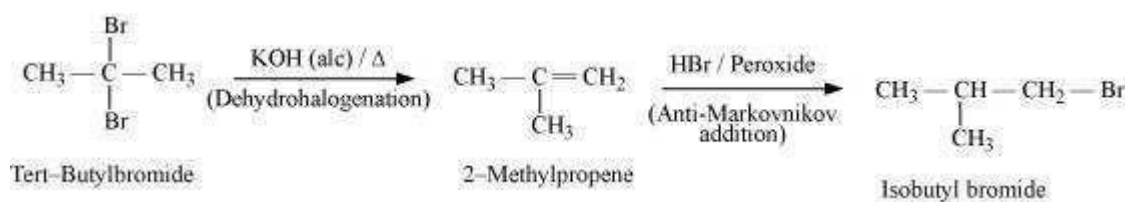
(xvii)



(xviii)



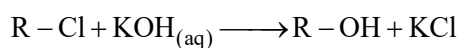
(xix)



(xx)



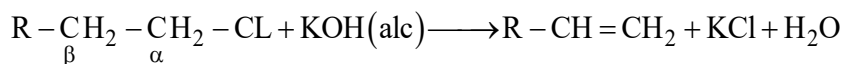
20. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.
20. In an aqueous solution, KOH almost completely ionizes to give OH<sup>-</sup> ions. OH<sup>-</sup> ion is a strong nucleophile, which 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<sup>-</sup>) ion, which is a strong base. Thus, it can abstract a hydrogen from the β-carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.

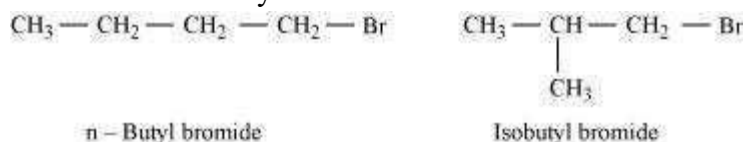


Alkyl chloride

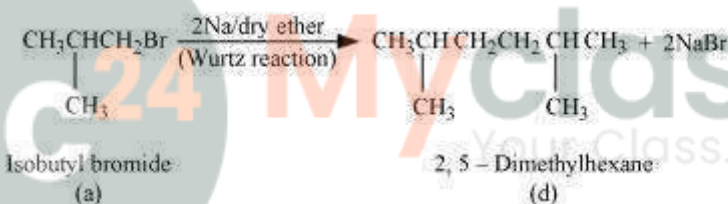
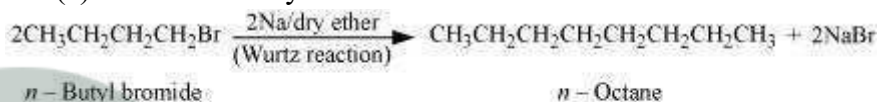
Alkene

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

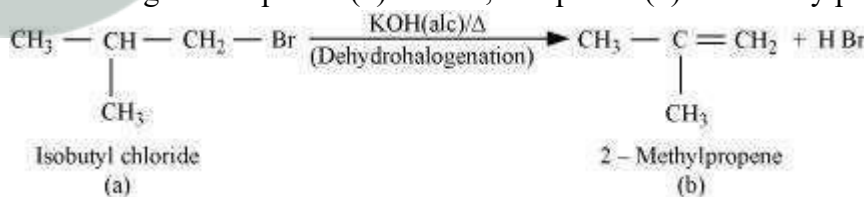
21. Primary alkyl halide  $C_4H_9Br$  (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d),  $C_8H_{18}$  which is different from the compound formed when n-butyl bromide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



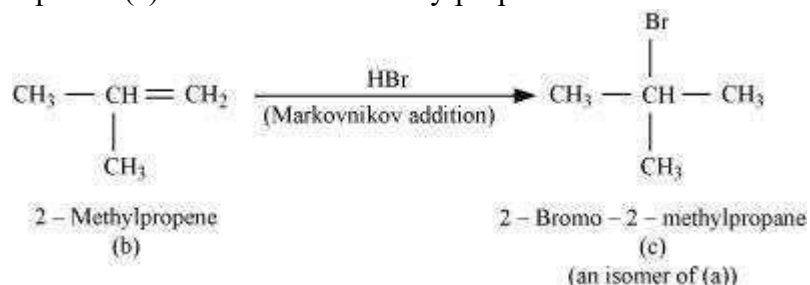
Therefore, compound (a) is either n-butyl bromide or isobutyl bromide. Now, compound (a) reacts with Na metal to give compound (b) of molecular formula,  $C_8H_{18}$ , which is different from the compound formed when n-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.



Thus, compound (d) is 2, 5-dimethylhexane. It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2-methylpropene.



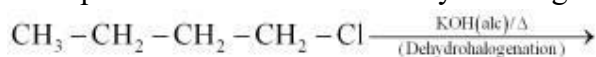
Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2-bromo-2-methylpropane.



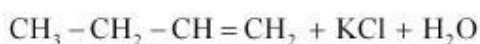
22. What happens when

- (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.

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



n-Butyl chloride

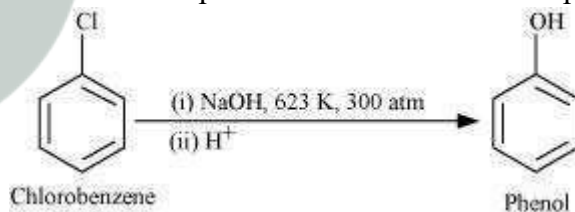


But-1-ene

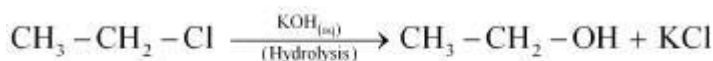
- (ii) When bromobenzene is treated with Mg in the presence of dry ether, phenyl magnesium bromide is formed.



- (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.



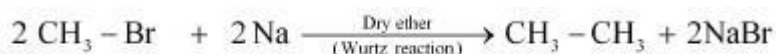
- (iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.



Ethyl chloride

Ethanol

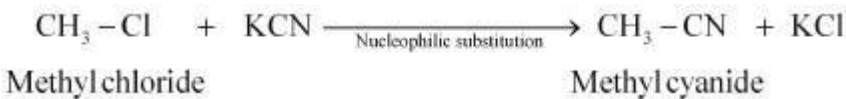
- (v) When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction.



Methyl bromide

Ethane

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



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