

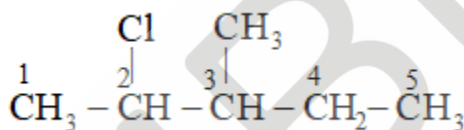
CBSE NCERT Solutions for Class 12 Chemistry Chapter 10**Back of Chapter Questions**

1. Write structure of the following compounds:

- (i) 2-chloro-3-methylpentane
- (ii) 1-chloro-4-ethylcyclohexane
- (iii) 4-tert, Butyl-3-iodoheptane
- (iv) 1,4-Dibromobut-2-ene
- (v) 1-Bromo-4-sec.butyl-2-methylbenzene

Solution:

- (i) 2-chloro-3-methyl pentane

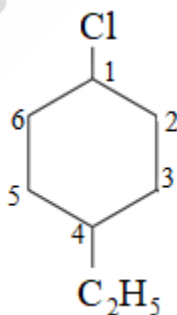


Parent-Carbon Chain = 5 membered (pent)

Prefix = Chloro (-Cl)

Substituent → methyl (-CH₃)

- (ii) 1-chloro-4-ethylcyclohexane



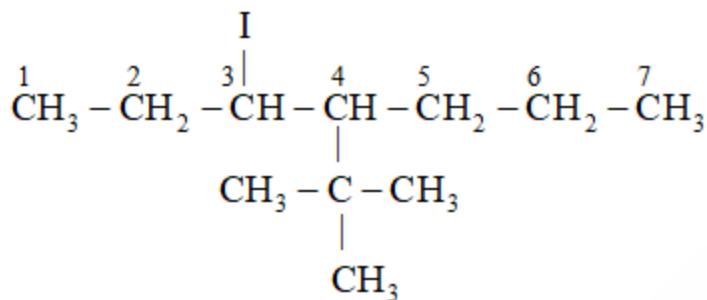
Parent-Carbon Chain = Cyclopent

Primary Prefix = Chloro (-Cl)

Substituent → ethyl (-C₂H₅)

Primary suffix = ane

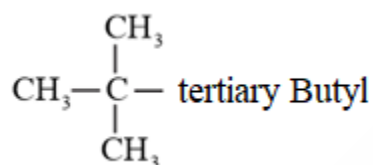
- (iii) 4-tert-Butyl-3-iodoheptane



Parent-Carbon Chain = 7 (hept)

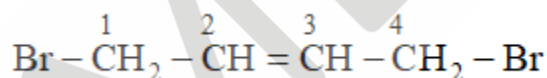
Primary Prefix = -I (Iodo)

Substituent →



Primary suffix = ane

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

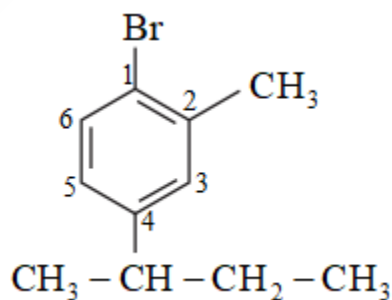


Primary Prefix = -Br (Bromo)

Parent-Carbon Chain = 4 (but)

Primary suffix = ene

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



Primary Prefix = -Br (Bromo)

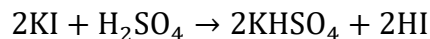
Substituent → -CH₃ (methyl) and CH₃ - CH - CH₂ - CH₃ (Secondary butyl)

Primary suffix = ane

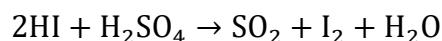
2. Why is sulphuric acid not used during the reaction of alcohols with KI?

Solution:

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



Since H_2SO_4 is an oxidising agent, it oxidises HI (produced in the reaction to I_2).



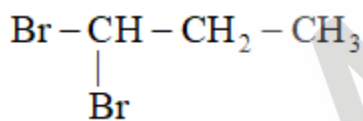
Thus, the reaction between alcohol and HI to form an alkyl iodide cannot occur. Hence, sulphuric acid is not used during the reaction of alcohols with KI. Instead, a non-oxidizing acid such as H_3PO_4 is used.

3. Write structures of different dihalogen derivatives of propane.

Solution:

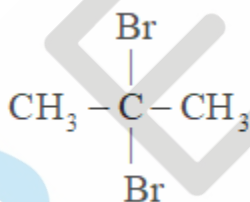
There are four different dihalogen derivatives of propane. The structure of these derivatives are shown below.

(i)



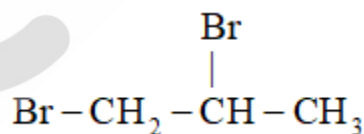
1,1-Dibromopropane

(ii)



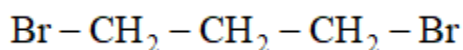
2,2-Dibromopropane

(iii)



1,2-Dibromopropane

(iv)



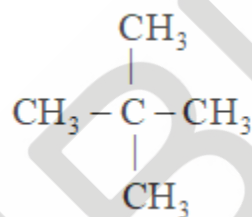
1,3-Dibromopropane

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

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

Solution:

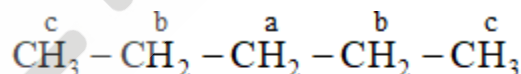
- (i) Only one type of hydrogen atom in the isomer of the alkane of the molecular formula C_5H_{12} should be there to have a single monochloride. This is because the replacement of any hydrogen atom leads to the formation of the same product. Thus the isomer is neopentane.



Neopentane

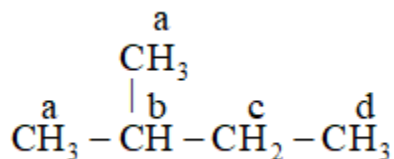
- (ii) The isomer of the alkane of the molecular formula C_5H_{12} should contain three different types of H-atoms to have three isomeric monochlorides.

Thus, the isomer is n-pentane. The three types of H atoms are labelled as a, b and c.

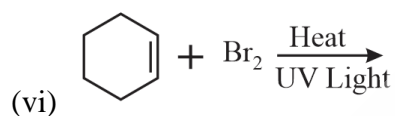
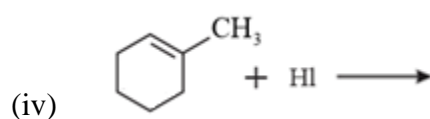
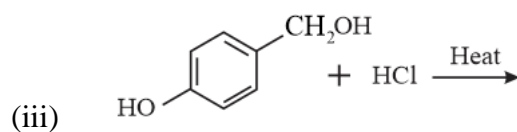
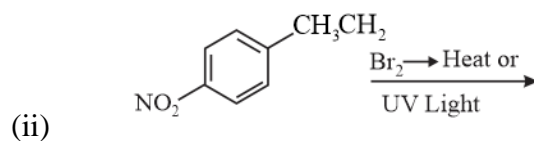
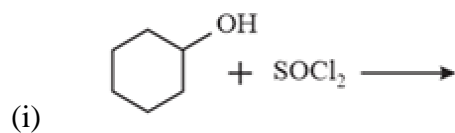
*n*-Pentane

- (iii) The isomer of the molecular formula C_5H_{12} should contain four different types of H-atoms to have four isomeric monochlorides.

Thus, the isomer is 2-methylbutane. The four types of H-atoms are labelled as a, b, c and d.

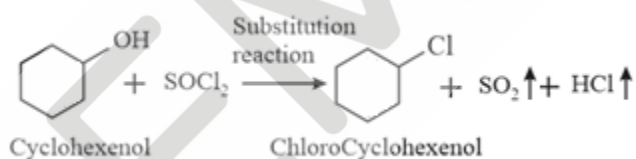


5. Draw the structures of major monohalo products in each of the following reactions:

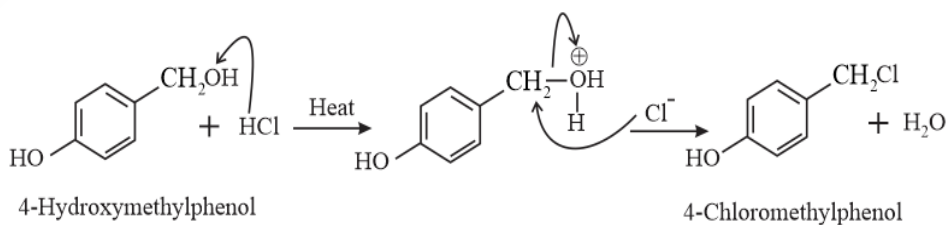
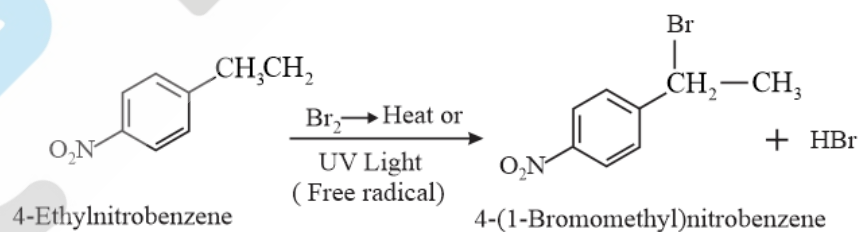


Solution:

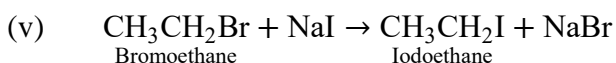
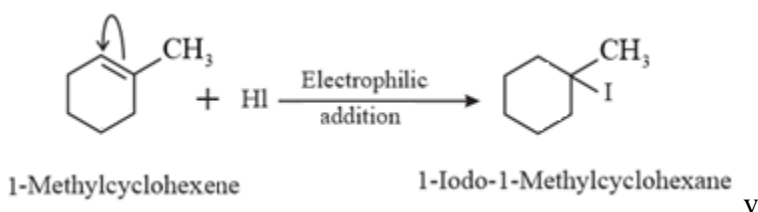
(i)



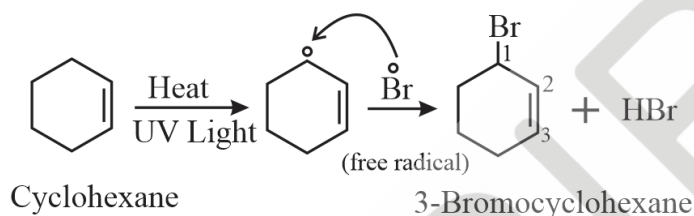
(ii)



(iv)



(vi)

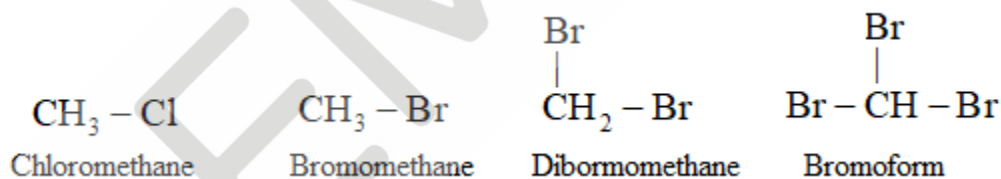


6. Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

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

Solution:



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

Since the atomic mass of Bromine ($-\text{Br}$) is greater than that of Chlorine ($-\text{Cl}$), the boiling point of bromomethane ($-\text{CH}_3\text{Br}$) is higher than that of chloromethane (CH_3Cl) due to Vander wall forces.

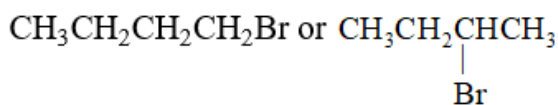
Also, for alkyl halides having the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of dibromomethane (CH_2Br_2) is higher than that of chloromethane (CH_3Cl) and bromomethane (CH_3Br), but lower than that of bromoform (CHBr_3).

Therefore, the given compounds can be arranged in the order of their increasing boiling points as

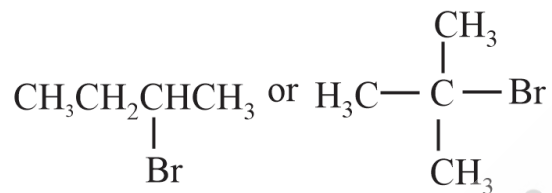
chloromethane (CH_3Cl) < bromomethane (CH_3Br) < Dibromomethane (CH_2Br_2) < bromoform (CHBr_3)

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

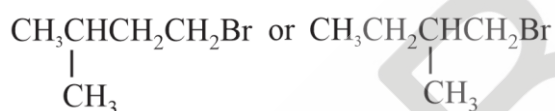
(i)



(ii)

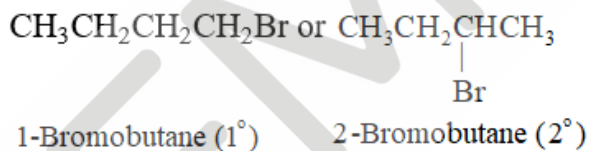


(iii)



Solution:

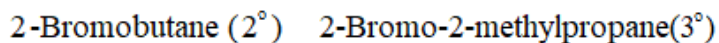
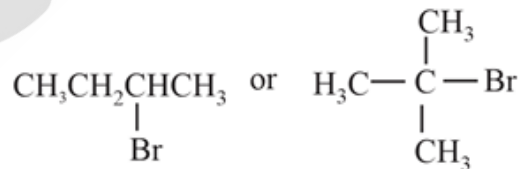
(i)



$$\text{Rate of } S_N2 \propto \frac{1}{\text{steric hindrance}}$$

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

(ii)



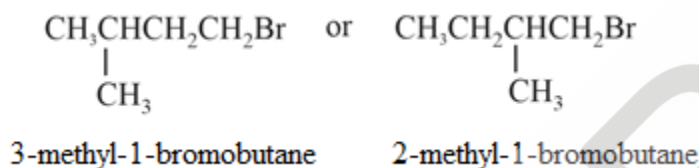
$$\text{Rate of } S_N2 \propto \frac{1}{\text{steric hindrance}}$$

2-bromobutane is 2° alkyl halide whereas 2-bromo-2-methylpropane is 3° alkyl halide.

Thus, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide for hindering the approaching nucleophile.

Therefore, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.

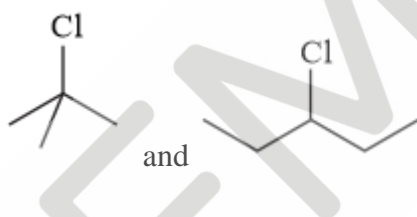
(iii)



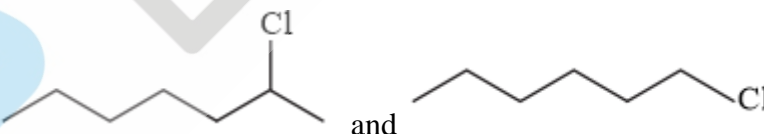
2-methyl-1-bromobutane is β substituted methyl group. So, it is more hindered as compared to 3-methyl-1-bromobutane. Therefore, S_N2 reaction rate will be higher in 3-methyl-1-bromobutane.

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

(i)

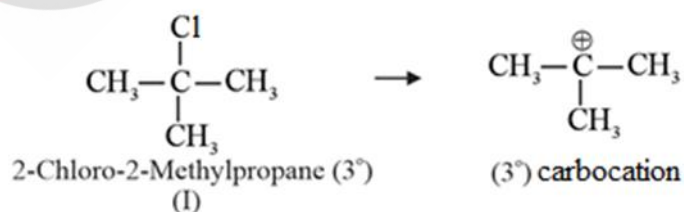


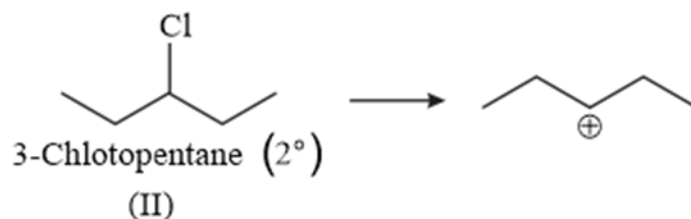
(ii)



Solution:

(i)

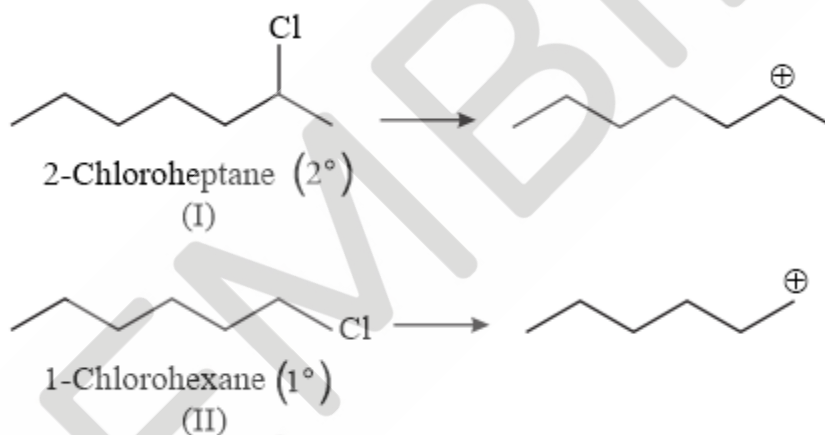






S_N1 reaction proceeds via the formation of carbocation. The alkyl halide (i) is 3° while (ii) is 2° . Therefore, (I) forms 3° carbocation while (II) forms 2° Carbocation. Greater the stability of the carbocation, faster is the rate of S_N1 reaction. 3° carbocation is more stable due to 9 hyperconjugation and more +I effect of 3 – CH_3 group 2° carbocation formed has 4 hyperconjugation and 2 – C_2H_5 (+I group). So, it is less stable.

Therefore, (I), i.e. 2-chloro-2-methylpropane, undergoes faster S_N1 reaction than (ii) i.e., 3-chloropentane.

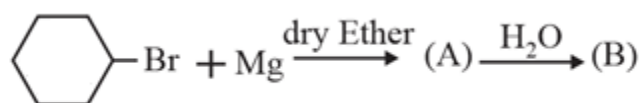
(ii)

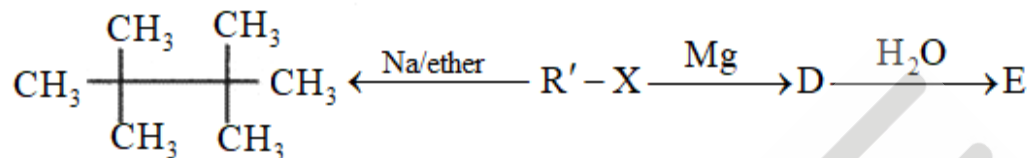
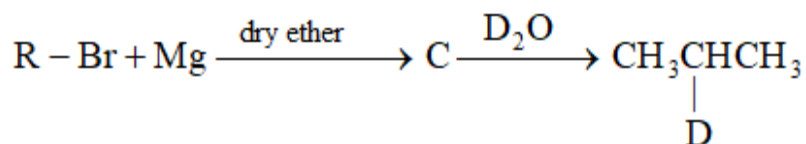


The alkyl halide (i) is 2° while (ii) is 1° , 2° carbocation is more stable than 1°

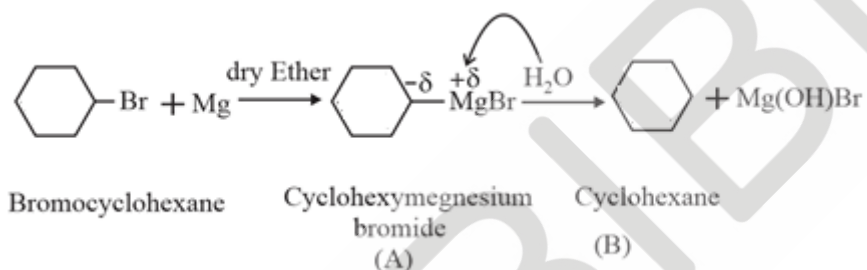
carbocation because in 2° carbocation  4 hyperconjugations are taking place and +I effect of 2 – C_2H_5 group while in  2 hyperconjugations are taking place & +I effect of – C_5H_{11} group. Therefore (I), 2-chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

9. Identify A, B, C, D, E, R and R^1 in the following:

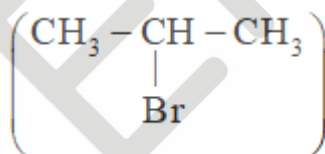
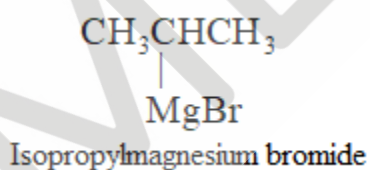




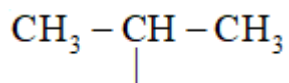
Solution:



Since Deuterium of D_2O gets attached Grignard reagent to the carbon atom to which $MgBr$ is attached, Hence C is

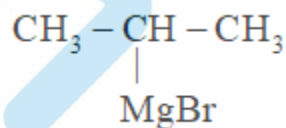


the

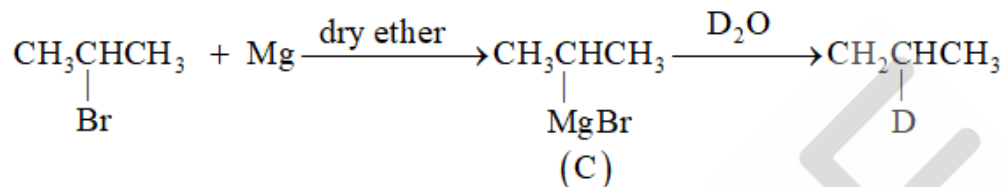
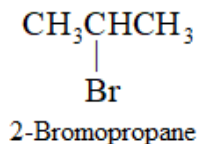


compound

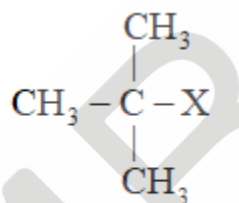
Therefore,



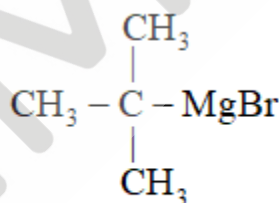
will form when Mg react with alkyl halide. Hence R is



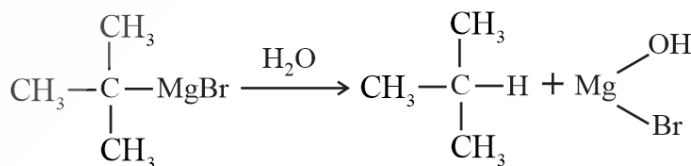
When an alkyl halide is treated with Na in the presence of dry ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as the product. This reaction is known as Wurtz reaction. Therefore, the halide, $\text{R}^1 - \text{X}$, is



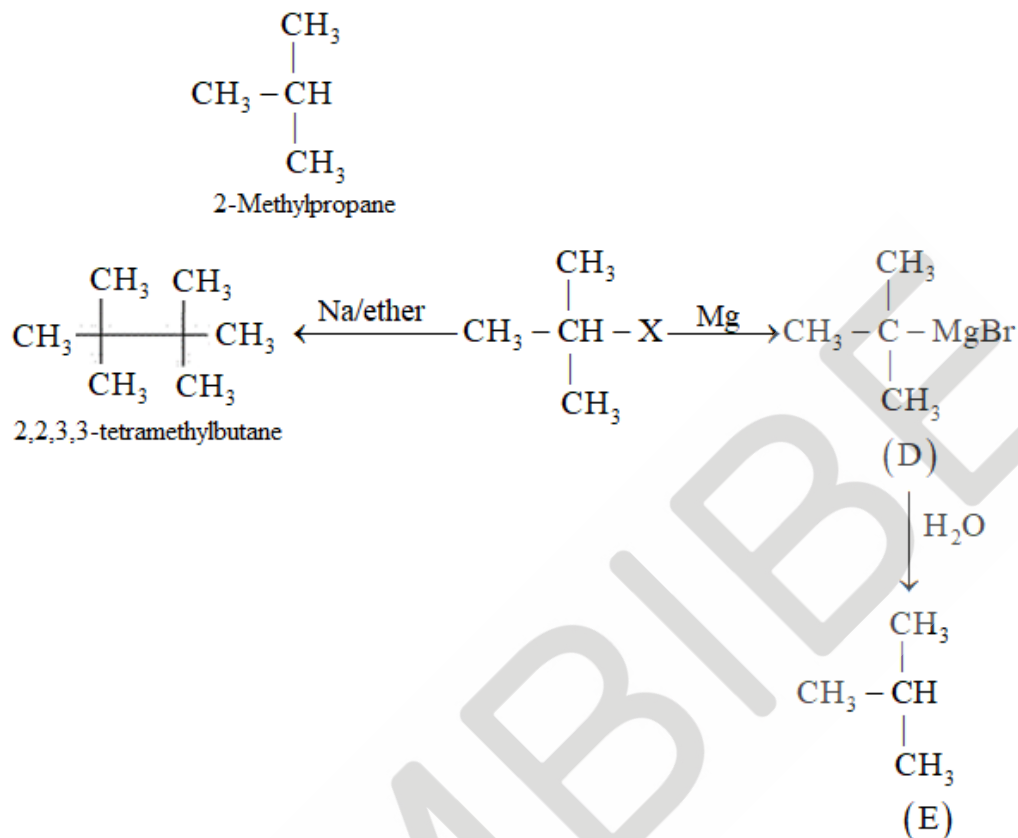
tert-Butylhalide



tert-Butylmagnesiumbromide



And, compound E is

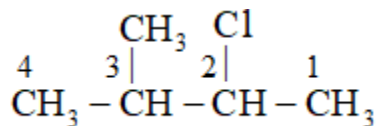
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1. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:

- (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) $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$
- (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) $o - \text{Br} - \text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

Solution:

(i)

Substituent = $-\text{CH}_3$ (Methyl)Secondary prefix = $-\text{Cl}$ (Chloro)

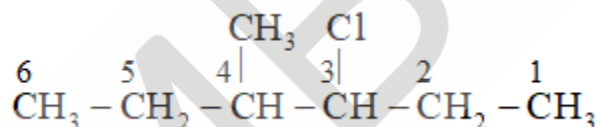
(Word root) Parent Carbon chain = 4 (but)

Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

IUPAC name is 2 -Chloro-3 -methylbutane (secondary alkyl halide).

(ii)

Substituent = $-\text{CH}_3$ (Methyl)Secondary prefix = $-\text{Cl}$ (Chloro)

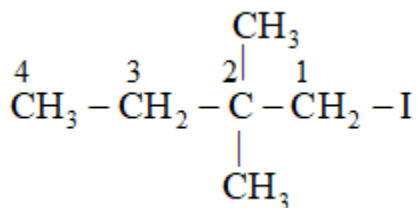
(Word root) Parent Carbon chain = 6 (hex)

Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

IUPAC name is 3 -chloro-4 -methyhexane (secondary alkyl halide).

(iii)

Substitute = $-\text{CH}_3$ (Methyl)Secondary prefix = $-\text{I}$ (Iodo)

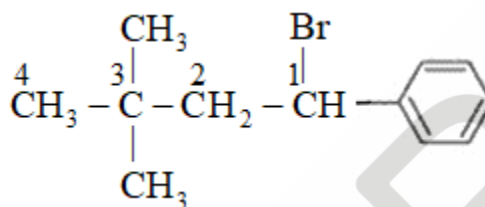
(Word root) Parent Carbon chain = 4 (but)

Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

IUPAC name is 1 – Iodo – 2,2 – dimethylbutane (primary alkyl halide).

(iv)



Substitute = $-\text{CH}_3$ (Methyl)

Secondary prefix = $-\text{Br}$ (Bromo)

(Word root) Parent Carbon chain = 4 (but)

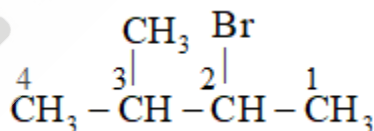
Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

1 – Bromo – 3,3 – dimethyl – 1 – phenylbutane

(secondary benzyl halide)

(v)



Substitute = $-\text{CH}_3$ (Methyl)

Secondary prefix = $-\text{Br}$ (Bromo)

(Word root) Parent Carbon chain = 4 (but)

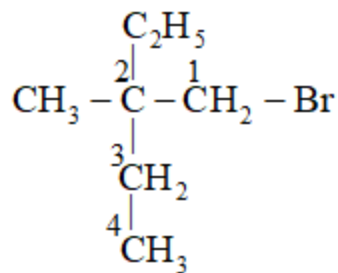
Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

2 – Bromo – 3 – methylbutane

(secondary alkyl halide)

(vi)



Substitute = $-\text{C}_2\text{H}_5$ (ethyl)

Secondary prefix = $-\text{Br}$ (Bromo)

(Word root) Parent Carbon chain = 4 (but)

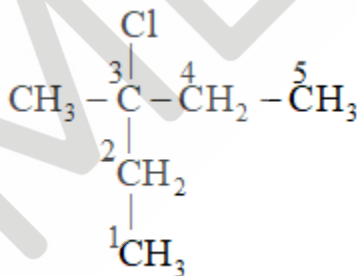
Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

1 – Bromo – 2 – ethyl – 2 – methylbutane

(primary alkyl halide)

(vii)



Substitute $-\text{CH}_3$ (Methyl)

Secondary prefix = $-\text{Cl}$ (Chloro)

(Word root) Parent Carbon chain = 5 (pent)

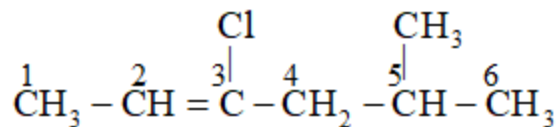
Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

3 – Chloro – 3 – methylpentane

(Tertiary alkyl halide)

(viii)



Substitute = $-\text{CH}_3$ (Methyl)

Secondary prefix = $-\text{Cl}$ (Chloro)

(Word root) Parent Carbon chain = 6 (hex)

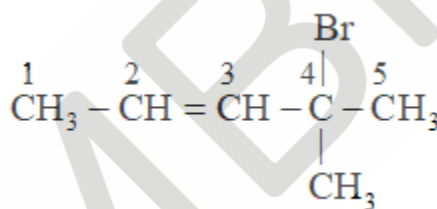
Primary Suffix = ene

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

3 - Chloro - 5 - methylhex - 2 - ene

(Vinyl halide)

(ix)



Substitute $-\text{CH}_3$ (Methyl)

Secondary prefix = $-\text{Br}$ (Bromo)

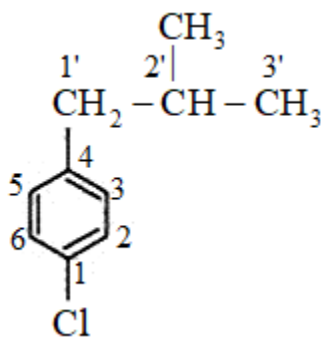
(Word root) Parent Carbon chain = 5 (pent)

Primary Suffix = ene

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

4-Bromo-4-methylpent-2-ene

(x)



Substitute = $(\text{CH}_3)_2\text{CHCH}_2 -$ (Methylpropyl)

Secondary prefix = $-\text{Cl}$ (Chloro)

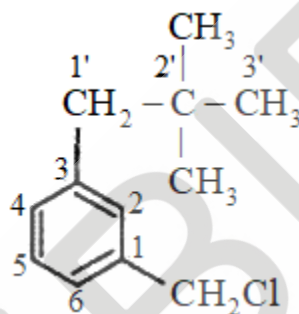
(Word root) Parent Carbon chain = benzene

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

1 – Chloro – 4 – (2 – methylpropyl) benzene

(Aryl halide)

(xi)



Substitute = $(\text{CH}_3)_3\text{CCH}_2 -$ (Dimethylpropyl)

Secondary prefix = $-\text{CH}_2\text{Cl}$ (Chloromethyl)

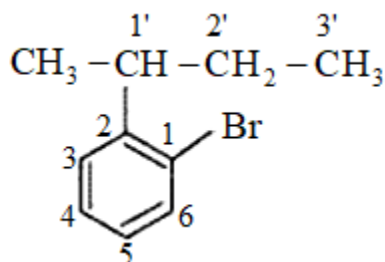
(Word root) Parent Carbon chain = benzene

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

1 – chloromethyl – 3 – (2,2 – dimethylpropyl) benzene

(Primary benzyl halide)

(xii)



Substitute = $\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3$ (methylpropyl)

Secondary prefix = $-\text{Br}$ (Bromo)

(Word root) Parent Carbon chain = benzene

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

1 – Bromo – 2 – (1 – methylpropyl) benzene

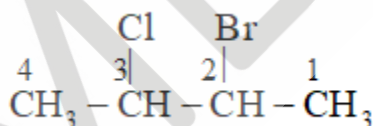
(Aryl halide)

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) $\text{CH}_3\text{C}(\text{p} - \text{ClC}_6\text{H}_4)_2\text{CH}(\text{Br})\text{CH}_3$
- (vi) $(\text{CH}_3)_3\text{CCH} = \text{CClC}_6\text{H}_4\text{I} - \text{p}$

Solution:

(i)



Secondary prefix = –Br(Bromo), –Cl (Chloro)

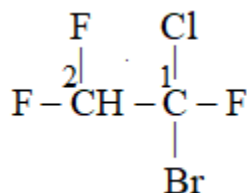
(Word root) Parent Carbon chain = 4 (bute)

Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

2 – Bromo – 3 – chlorobutane

(ii)



Secondary prefix = –Br(Bromo), –Cl (Chloro), –F (Fluoro)

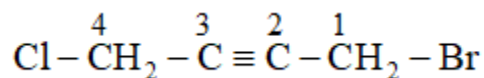
(Word root) Parent Carbon chain = 2 (eth)

Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

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

(iii)



Secondary prefix = -Br(Bromo), -Cl (Chloro)

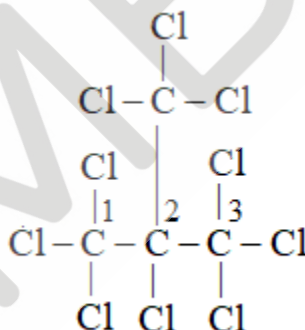
(Word root) Parent Carbon chain = 4 (bute)

Primary Suffix = yne

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

1 - Bromo - 4 - chlorobut - 2 - yne

(iv)



Secondary prefix = -Cl (Chloro)

Substitute = -CCl₃ (trichloromethyl)

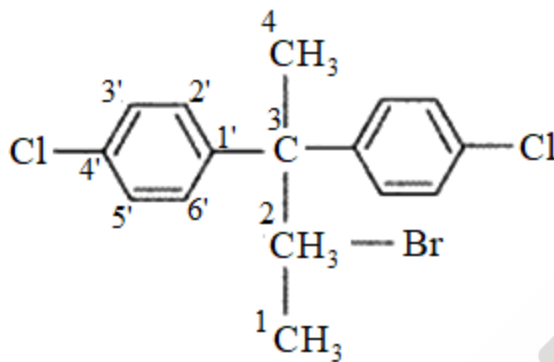
(Word root) Parent Carbon chain = 3 (prop)

Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

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

(v)



Secondary prefix = -Br (Bromo)

Substitute = para - phCl (4-chlorophenyl)

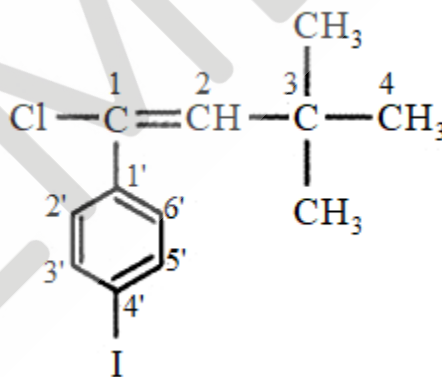
(Word root) Parent Carbon chain = 4 (bute)

Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

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

(vi)



Secondary prefix = -Cl (Chloro)

Substitute = para - pHI (iodophenyl)

(Word root) Parent Carbon chain = 4 (bute)

Primary Suffix = ene

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

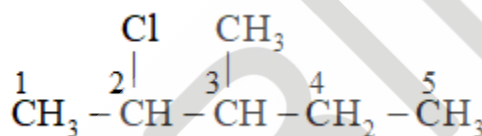
1 - chloro - 1 - (4 - iodophenyl) - 3,3 - dimethylbut - 1 - ene

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) 2-Bromobutane
- (vi) 2-(2-Chlorophenyl)-1-iodooctane
- (vii) 1-Bromo-4-sec-butyl-2-methylbenzene
- (viii) 1,4-Dibromobut-2-ene

Solution:

(i)



Secondary prefix = -Cl (Chloro)

Substitute = -CH₃ (methyl)

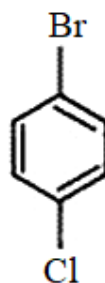
(Word root) Parent Carbon chain = 5 (pent)

Primary Suffix = ane

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

2 - chloro - 3 - methylpentane

(ii)



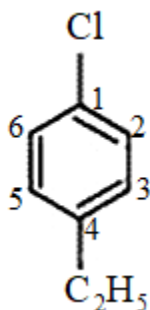
Secondary prefix = -Cl (Chloro), -Br (Bromo)

(Word root) Parent Carbon chain = 6 (benzene)

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

p-Bromochlorobenzene

(iii)

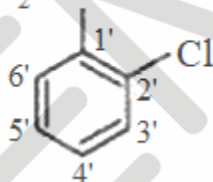
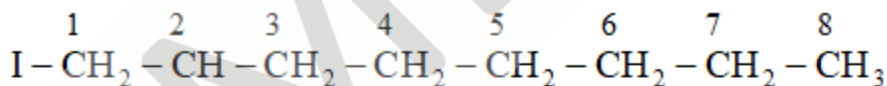
Secondary prefix = $-\text{Cl}$ (Chloro)Substitute = $-\text{C}_2\text{H}_5$ (ethyl)

(Word root) Parent Carbon chain = 6 (benzene)

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

1 - Chloro - 4 - ethylcyclohexane

(iv)

Secondary prefix = $-\text{I}$ (iodo)

Substitute = (Chlorophenyl)

(Word root) Parent Carbon chain = 6 (benzene)

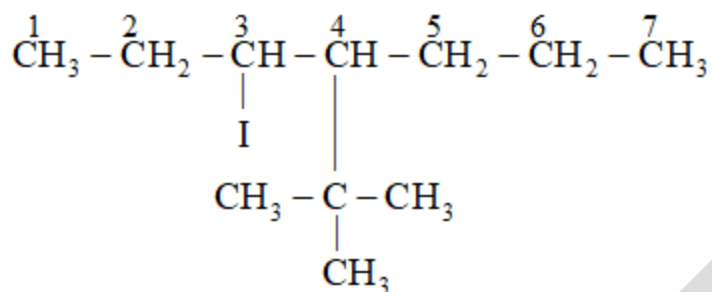
IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

2 - (2 - Chlorophenyl) - 1 - iodoctane

(v) $\text{CH}_3 - \text{CH}(\text{Br}) - \text{CH}_2 - \text{CH}_3$

2 - Bromobutane

(vi)



Secondary prefix = -I (iodo)

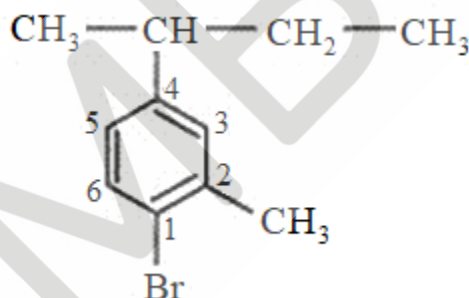
Substitute = -C(CH₃)₃ (tert-Butyl)

(Word root) Parent Carbon chain = 7 (hept)

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

4 - tert - Butyl - 3 - iodoheptane

(vii)



Secondary prefix = -Br (Bromo)

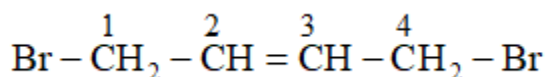
Substitute = (sec-butyl), -CH₃(methyl)

(Word root) Parent Carbon chain = 6 (benzene)

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

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

(viii)



Secondary prefix = -Br (Bromo)

(Word root) Parent Carbon chain = 4 (bute)

primary suffix = ene

IUPAC name = Secondary prefix + Primary prefix + Word root + primary suffix + secondary suffix

1,4 – Dibromobut – 2 – ene

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

- (i) CH_2Cl_2
- (ii) CHCl_3
- (iii) CCl_4

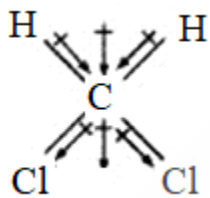
Solution:

Dipole moment = Charge \times Distance

$$\mu = q \times d$$

It is a vector quantity.

(i)

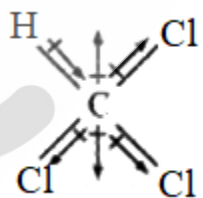


Dichloromethane (CH_2Cl_2)

$$\mu = 1.60 \text{ D}$$

In CH_2Cl_2 , the resultant of the dipole moments of two 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 . CH_2Cl_2 has the highest dipole moment.

(ii)



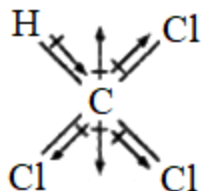
Chloroform (CHCl_3)

$$\mu = 1.08 \text{ D}$$

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.

(iii)

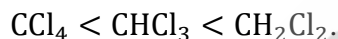


Carbon tetrachloride (CCl_4)

$$\mu = 0 \text{ D}$$

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

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



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.

Solution:

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

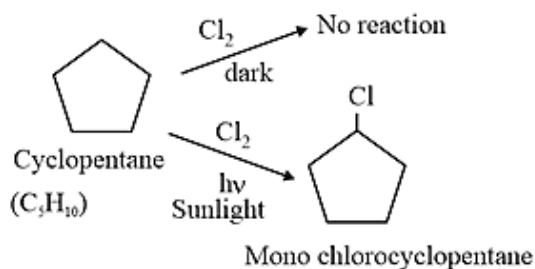
It is a cycloalkane because hydrocarbons do not react with chlorine in the dark; it cannot be an alkene.

Also, the hydrocarbon gives a single monochloro compound, $\text{C}_5\text{H}_9\text{Cl}$ by reacting with chlorine in bright sunlight. A single monochloro compound means that the hydrocarbon must contain hydrogen atoms that are all equivalent. And as all hydrogen atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.



Cyclopentane (C_5H_{10})

The reactions involved are:

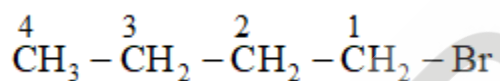


6. Write the isomers of the compound having formula C₄H₉Br.

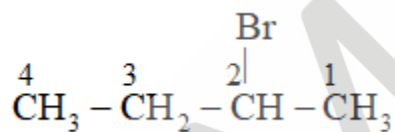
Solution:

There are four isomers of the compound having the formula C₄H₉Br. These isomers are given below.

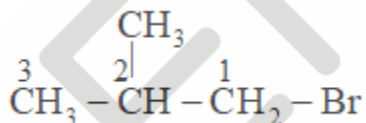
- (a) 1-Bromobutane



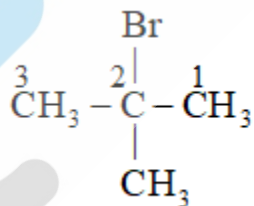
- (b) 2-Bromobutane



- (c) 1-Bromo-2-methylpropane



- (d) 2-Bromo-2-methylpropane

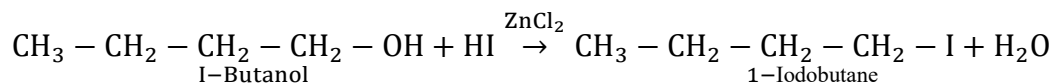


7. Write the equations for the preparation of 1-iodobutane from

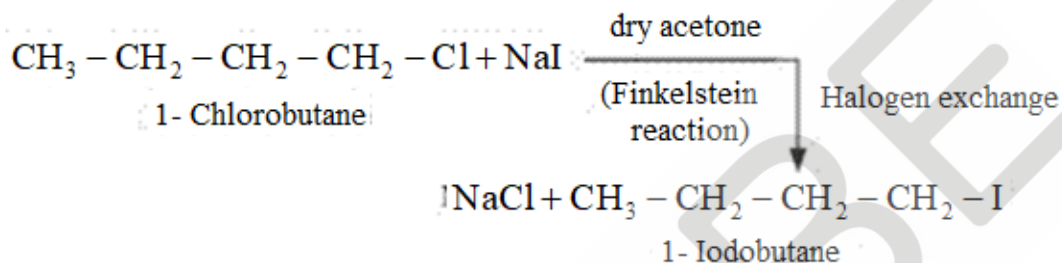
- (i) 1-butanol
- (ii) 1-chlorobutane
- (iii) but-1-ene

Solution:

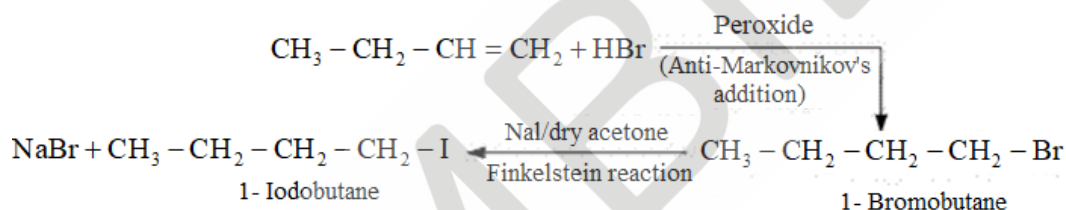
(i)



(ii)



(iii)



In the presence of peroxide, alkene gives antimarkovnikov's product, Electrophilic addition.

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

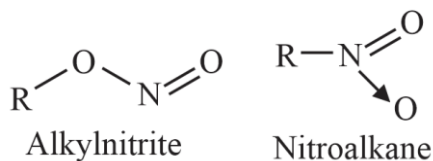
Solution:

Nucleophiles having two nucleophilic sites are ambident nucleophiles. Hence, ambident nucleophiles have two sites through which they can attack.

Nitrite ion is an example of an ambident nucleophile.



Nitrite ion can either attack through oxygen resulting in the formation of alkyl nitrites or 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 OH^- ?

- (i) CH_3Br or CH_3I
 (ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

Solution:

Rate of $\text{S}_\text{N}2$ reaction $\propto [\text{RX}][\text{nu}^-]$

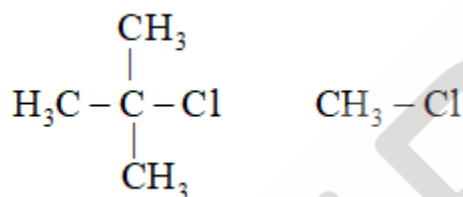
Rate of $\text{S}_\text{N}2$ reaction \propto leaving group ability

- (i) In $\text{S}_\text{N}2$ mechanism, the reactivity of halides for the same alkyl group increases in the order $-\text{F} \ll \text{R}-\text{Cl} < \text{R}-\text{Br} < \text{R}-\text{I}$.

As the size of the ion increases, it becomes a better leaving group.

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

- (ii)



Rate of $\text{S}_\text{N}2$ reaction $\propto [\text{RX}][\text{nu}^-]$

Rate of $\text{S}_\text{N}2$ reaction $\propto \frac{1}{\text{Hindrance}}$

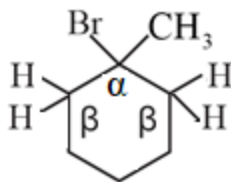
The $\text{S}_\text{N}2$ mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in the case of $(\text{CH}_3)_3\text{CCl}$, the attack of the nucleophile at the carbon atom is hindered because of the presence of bulky substituents on that carbon atom bearing the 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^- .

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

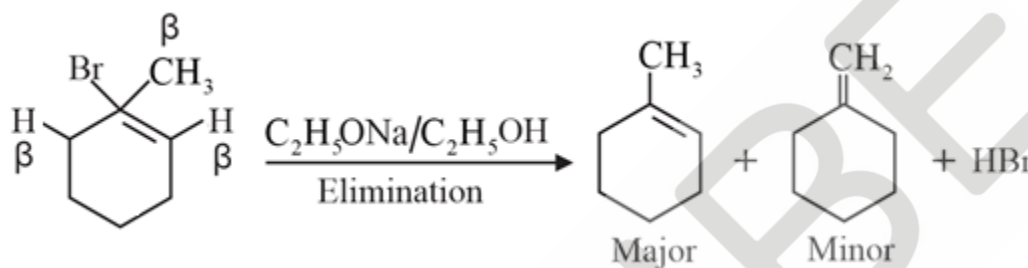
- (i) 1-Bromo-1-methylcyclohexane
 (ii) 2-Chloro-2-methylbutane
 (iii) 2,2,3-Trimethyl-3-bromopentane.

Solution:

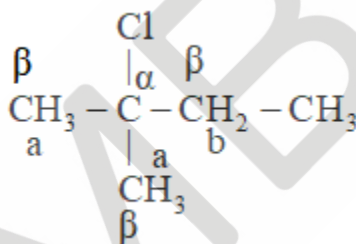
- (i) 1-bromo-1-methylcyclohexane



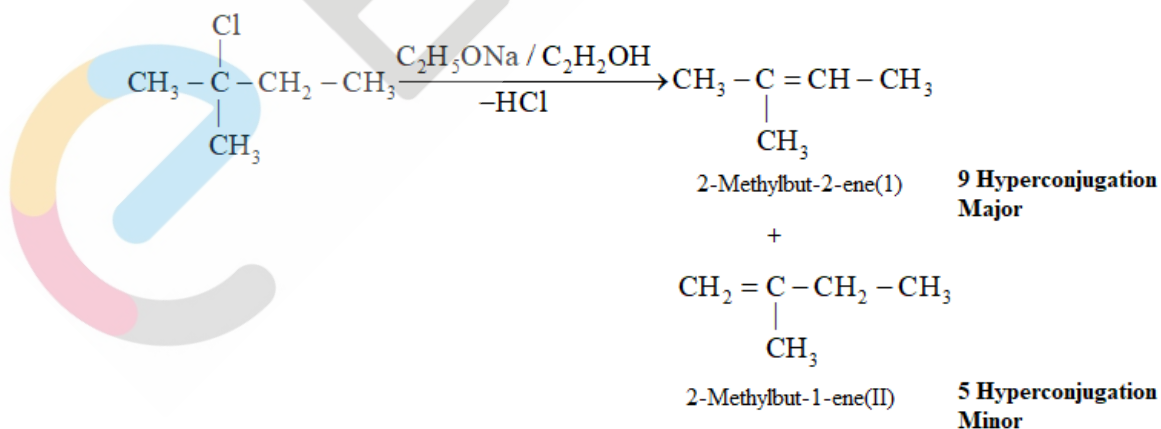
In the given compound, all β -hydrogen atoms are equivalent. Thus, the dehydrohalogenation of this compound gives only one alkene.



(ii)

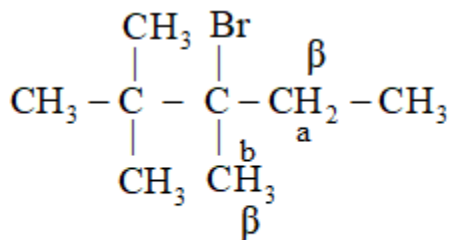


In the given compound there are two different sets of equivalent β -hydrogen atoms labelled as a and b. Thus, dehydrohalogenation of the compound yields two alkenes.



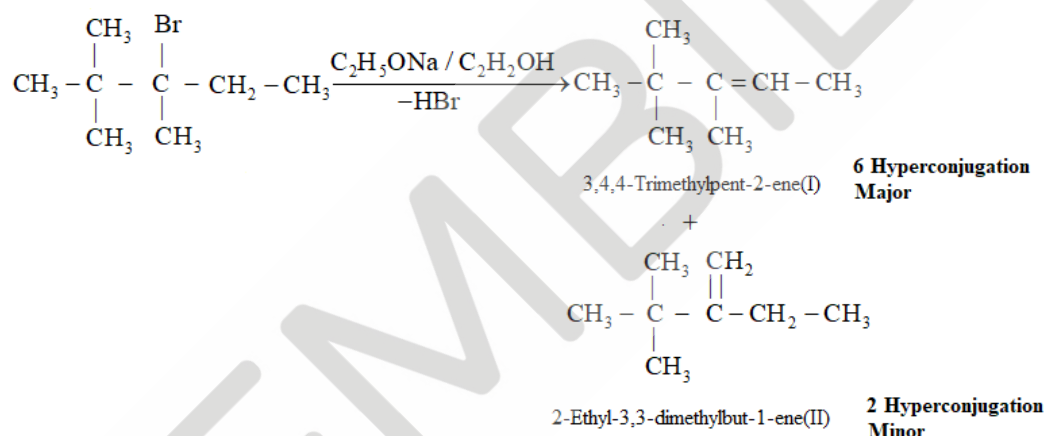
Saytzeff's rule implies that in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced i.e. more stable alkane formed major product

Therefore, alkene (i) i.e., 2-methylbut-2-ene is the major product in this reaction,
(iii)



2,2,3-Trimethyl-3-bromopentane

2,2,3-Trimethyl-3-bromopentane there are two different sets of equivalent (β - hydrogen atoms labelled as a and b. Thus, dehydrohalogenation of the compound yields two alkenes,



According to Saytzeff's rule, in dehydrohalogenation reactions, the alkenes 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.

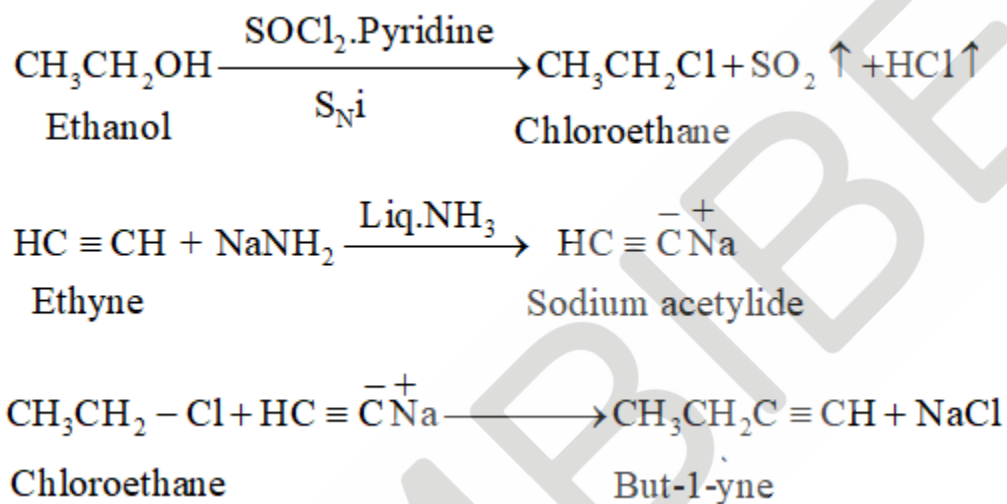
11. How will you bring about the following conversions?

- (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) Bromoethane to propanone

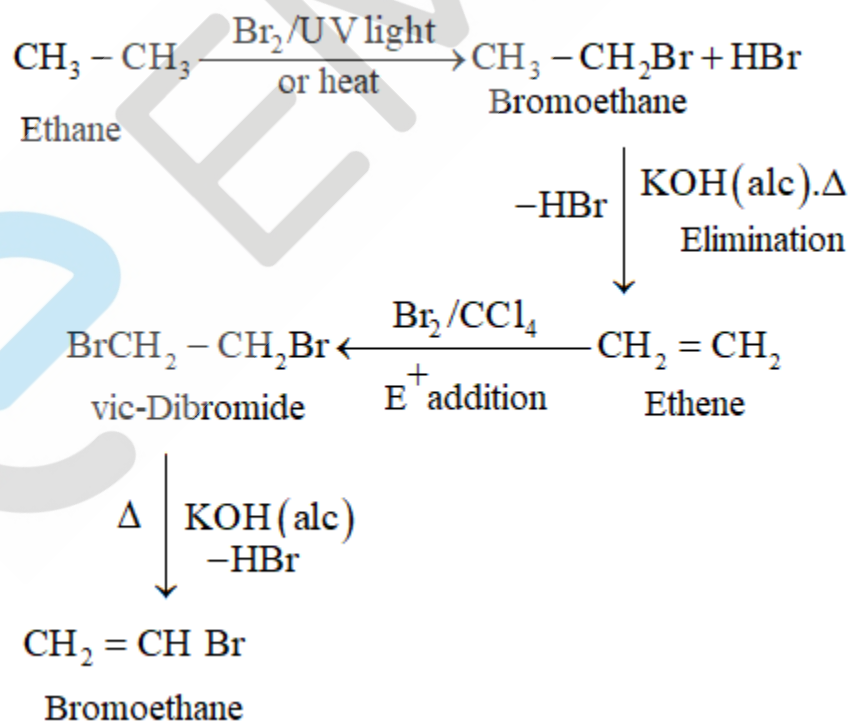
- (viii) But-1-ene to but-2-ene
 (ix) 1-Chlorobutane to n-octane
 (x) Benzene to biphenyl.

Solution:

(i)

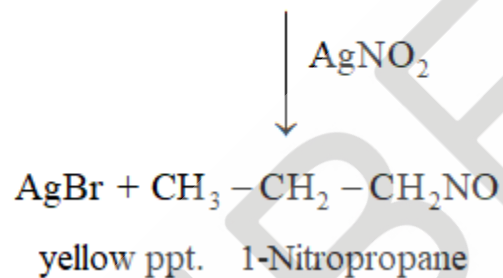
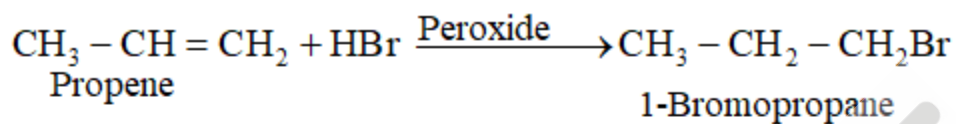


(ii)

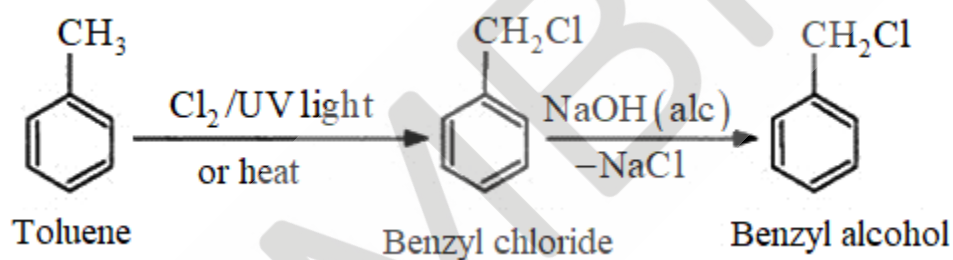


Ethyne has acidic hydrogen (hydrogen attached with carbon S_p) NH_2^- is a base so there acidic-base reaction taking place.

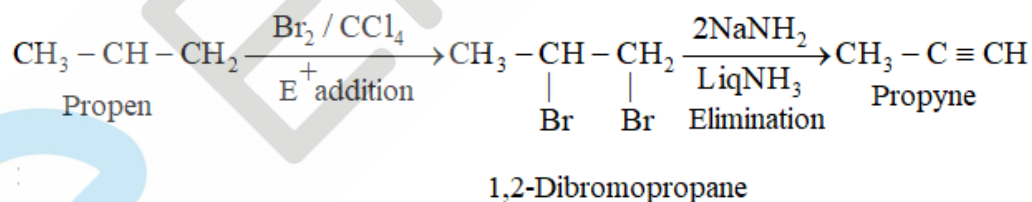
(iii)



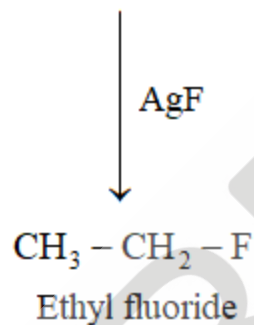
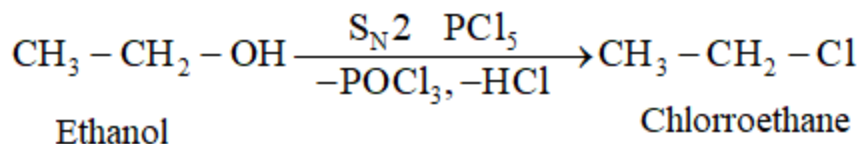
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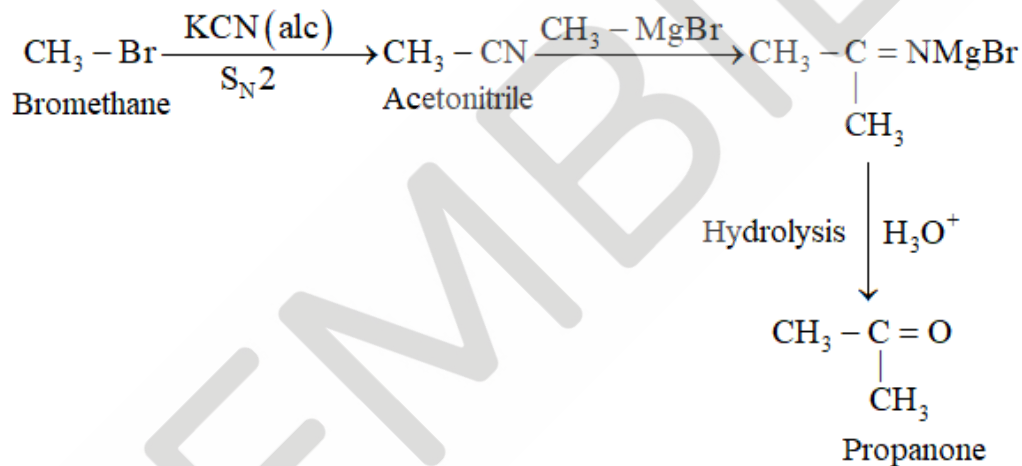
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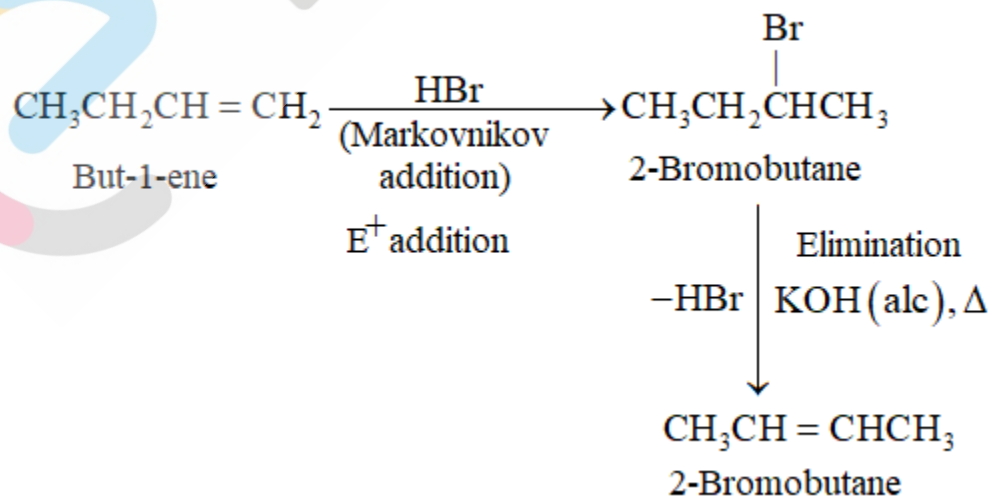
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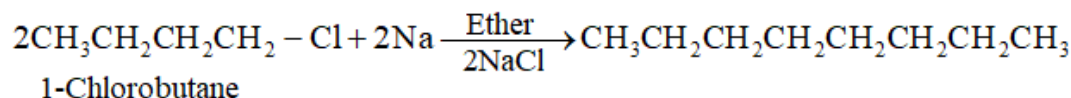
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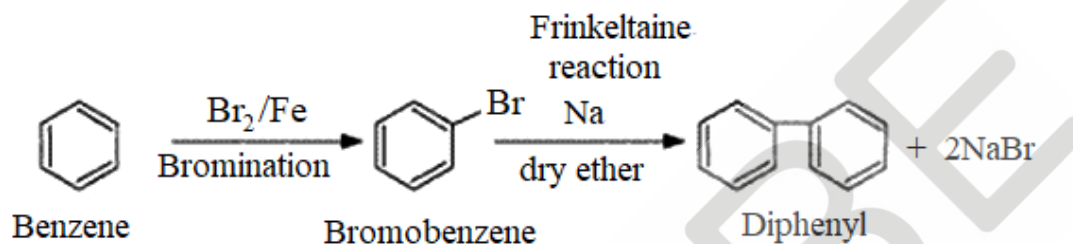
(viii)



(ix) Wurtz reaction



(x)

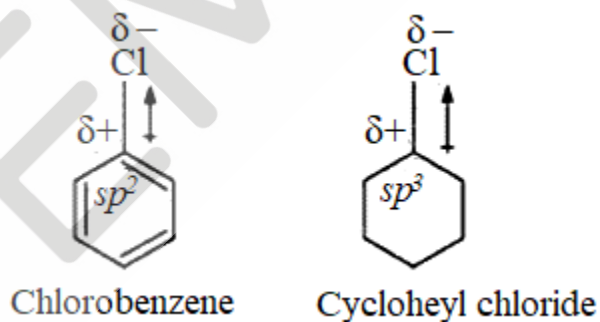


12. Explain why

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

Solution:

(i)



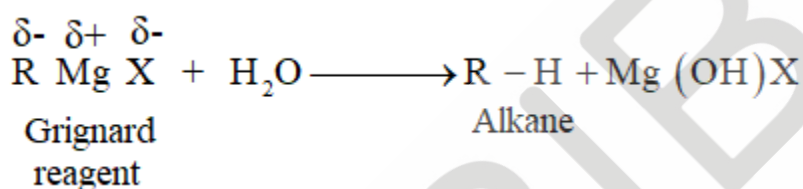
Dipole moment is vector Quantity

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 water, they react and gives alkanes because R^- is act as a base and water has acidic hydrogen



Therefore, Grignard reagents should be prepared under anhydrous conditions,

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

Solution:

Uses of Freon -12

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

Uses of DDT

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

Uses of carbontetrachloride (CCl_4)

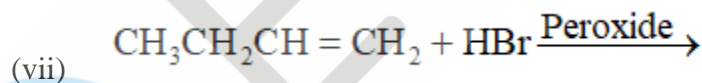
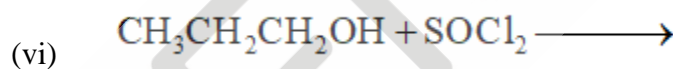
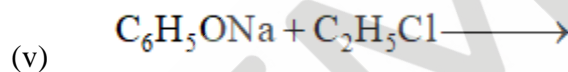
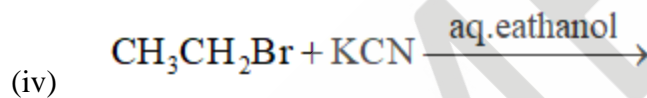
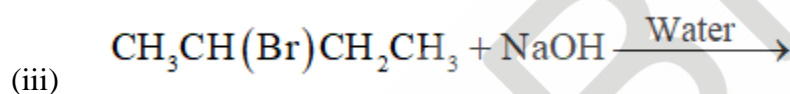
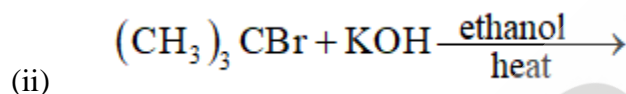
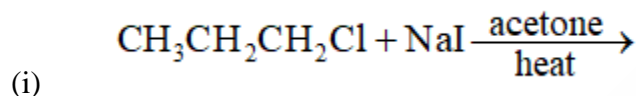
- (i) It is used for manufacturing refrigerants and propellants for aerosol cans.
- (ii) It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.
- (iii) It is used as a solvent in the manufacture of pharmaceutical products.

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

Uses of iodoform (CHI_3)

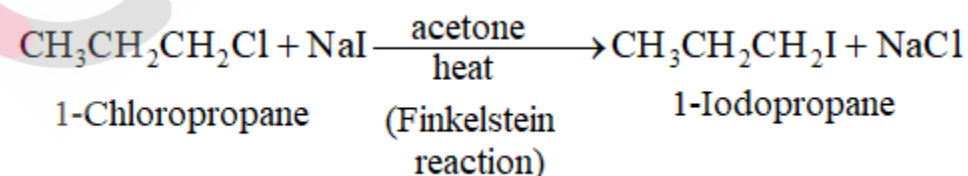
Iodoform was used earlier as an antiseptic, but now it has been replaced by other formulations-containing iodine-due to its objectionable smell. The antiseptic property of iodoform is only due to the liberation of free iodine when it comes in contact with the skin.

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

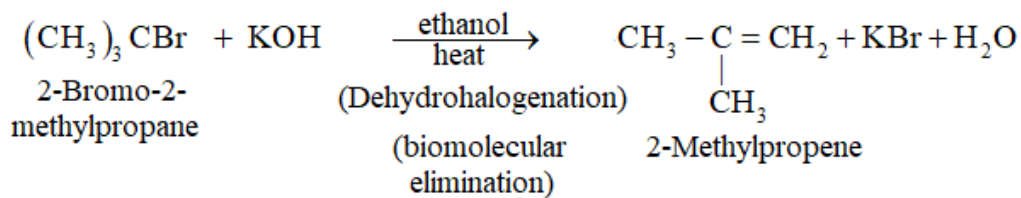


Solution:

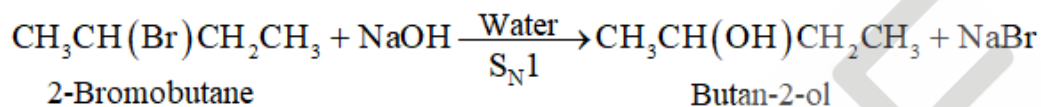
(i)



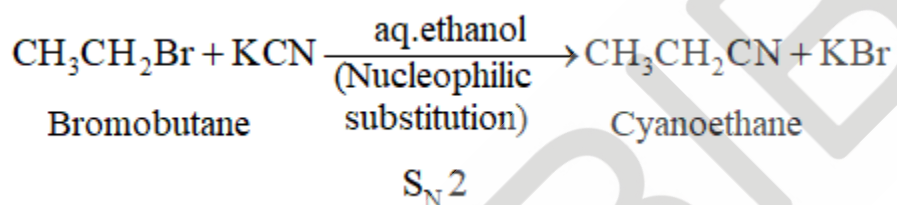
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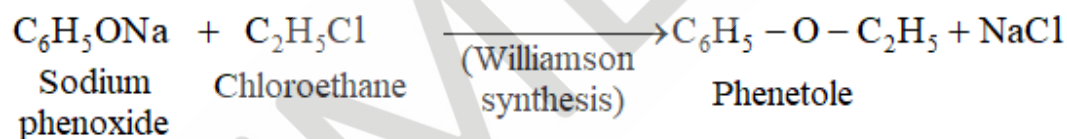
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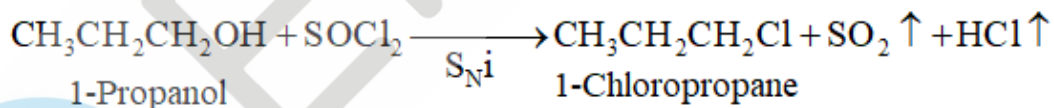
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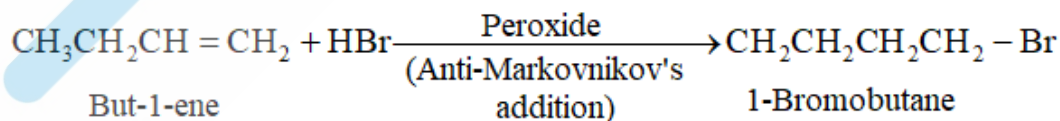
(v)



(vi)

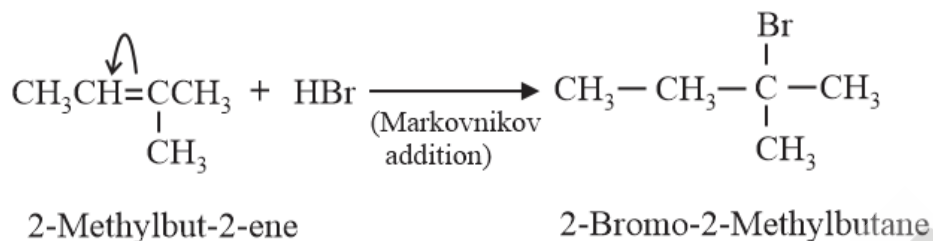


(vii)



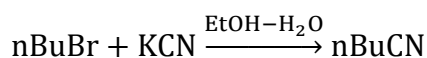
According to Anti-Markovnikov's rule H add at which carbon where H atoms are less and Br⁻ (nu⁻) attached

(viii)



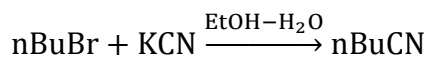
According to markovnikov rule H attached at which carbon where H atoms are more and Br^- (nu^-) attack where H are less.

15. Write the mechanism of the following reaction:

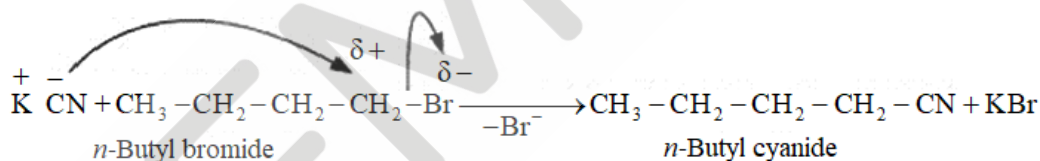


Solution:

The given reaction is:



The given reaction is an S_N^2 reaction. In this reaction CN^- acts as the nucleophile and attacks the carbon atom to which Br is attached and less hindered CN^- ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.

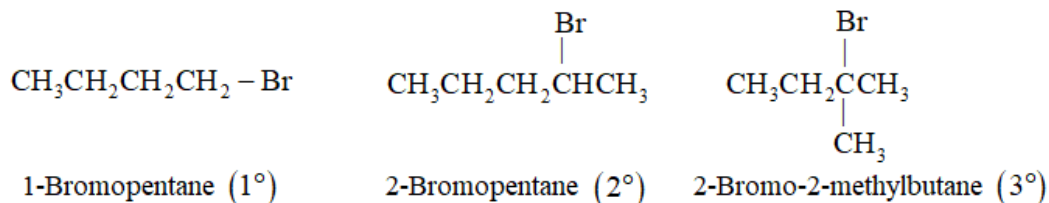


16. Arrange the compounds of each set-in order of reactivity towards S_N^2 displacement:

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

Solution:

-



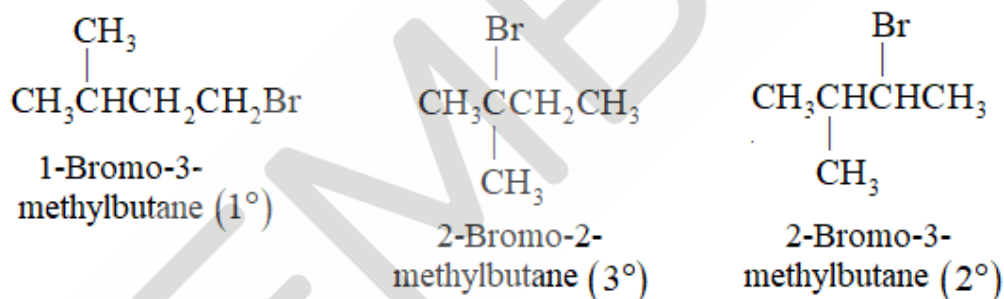
An SN^2 reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group ($-\text{Br}$) is attached. When the nucleophile is sterically hindered; then the reactivity towards SN^2 displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile decreases SN^2 order $1^\circ > 2^\circ > 3^\circ$ (alkyl halide).

1-Bromopentane > 2-bromopentane > 2-Bromo-2-methylbutane (nu^- approach tendency)

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

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

(ii)



$$\text{Rate of } \text{SN}^2 \text{ reaction} \propto \frac{1}{\text{hindrence}}$$

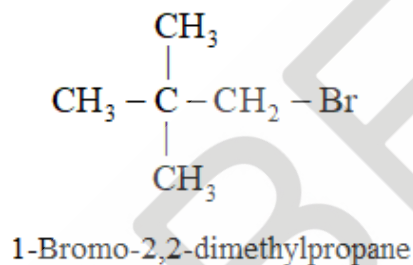
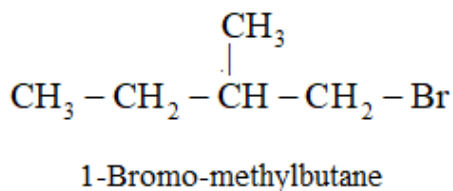
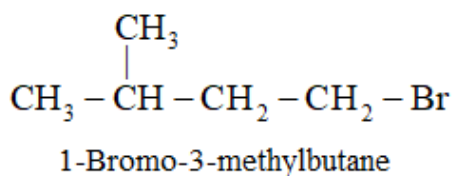
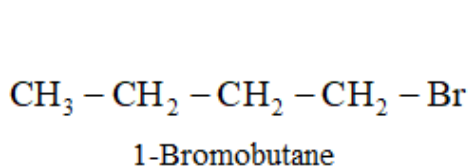
Since steric hindrance in alkyl halides increases in the order of $1^\circ < 2^\circ < 3^\circ$, the increasing order of reactivity towards SN^2 displacement is

$3^\circ < 2^\circ < 1^\circ$,

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

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

(iii)



The steric hindrance to the nucleophile in the S_N^2 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 β alkyl group substituted compound show less S_N^2 reaction.

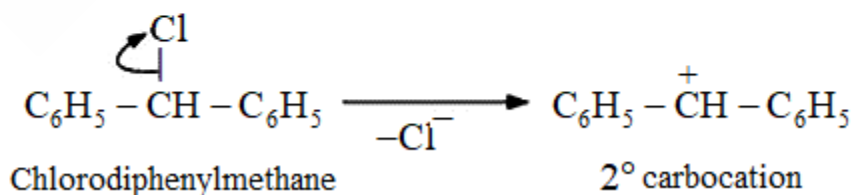
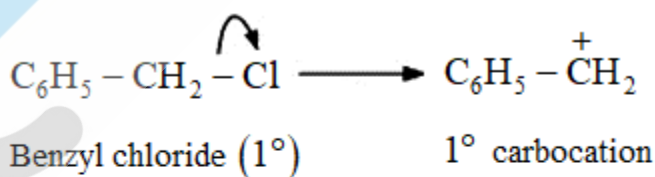
1-Bromobutane < 1-Bromo-3-methylbutane < 1-Bromo-2-methylbutane < 1-Bromo-2,2-dimethylpropane

Hence, the increasing order of reactivity of the given compounds towards $\text{S}_\text{N}2$ displacement is:

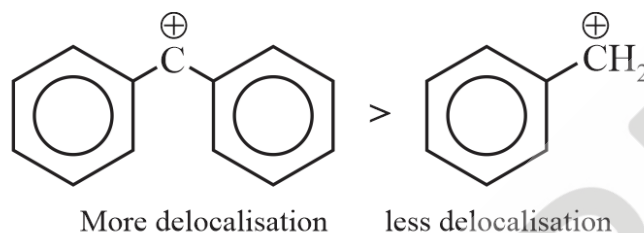
1-Bromo-2,2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3-methylbutane < 1-Bromobutane

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?

Solution:



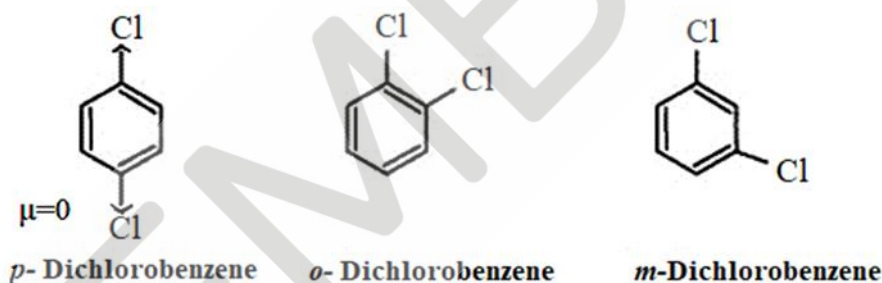
Hydrolysis by aqueous KOH proceeds through SN^1 and by the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. (polar protic solvent) Now, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ forms 1° -carbocation, while $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ forms 2° -carbocation is more stable than 1° -carbocation due to +ve charge is more delocalized.



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 melting point and lower solubility than those of o- and m-isomers, Discuss.

Solution:



Melting point \propto Packing efficiency

Solubility $\propto \mu$ (Dipole moment)

Force of attraction $\& \mu \propto \frac{1}{\theta}$; $\theta \downarrow \mu \uparrow$

Hence solubility decrease.

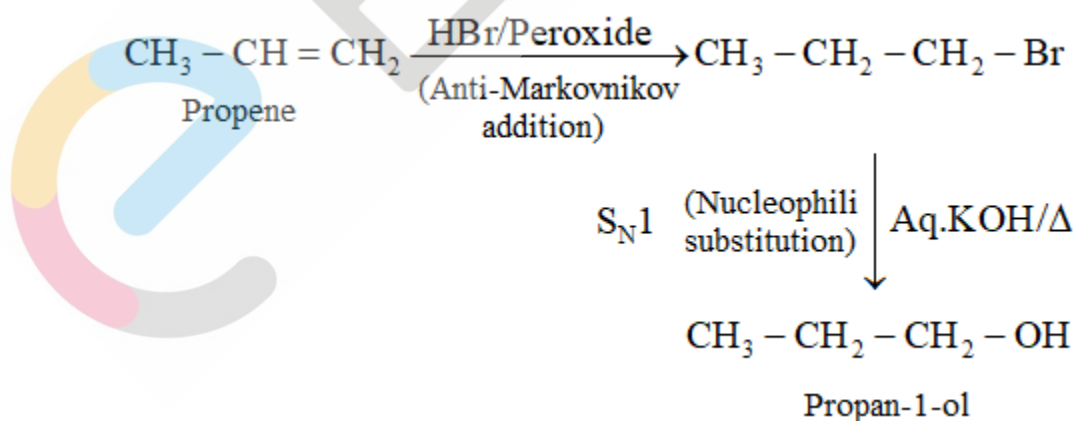
p-Dichlorobenzene is more symmetrical than o- and m-isomers. For this reason, it fits more closely than o- and m-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of p-dichlorobenzene. As a result, p-dichlorobenzene has a higher melting point and lower solubility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

19. (i) Propene to propan-1-ol
(ii) Ethanol to but-1-yne
(iii) 1-Bromopropane to 2-bromopropane

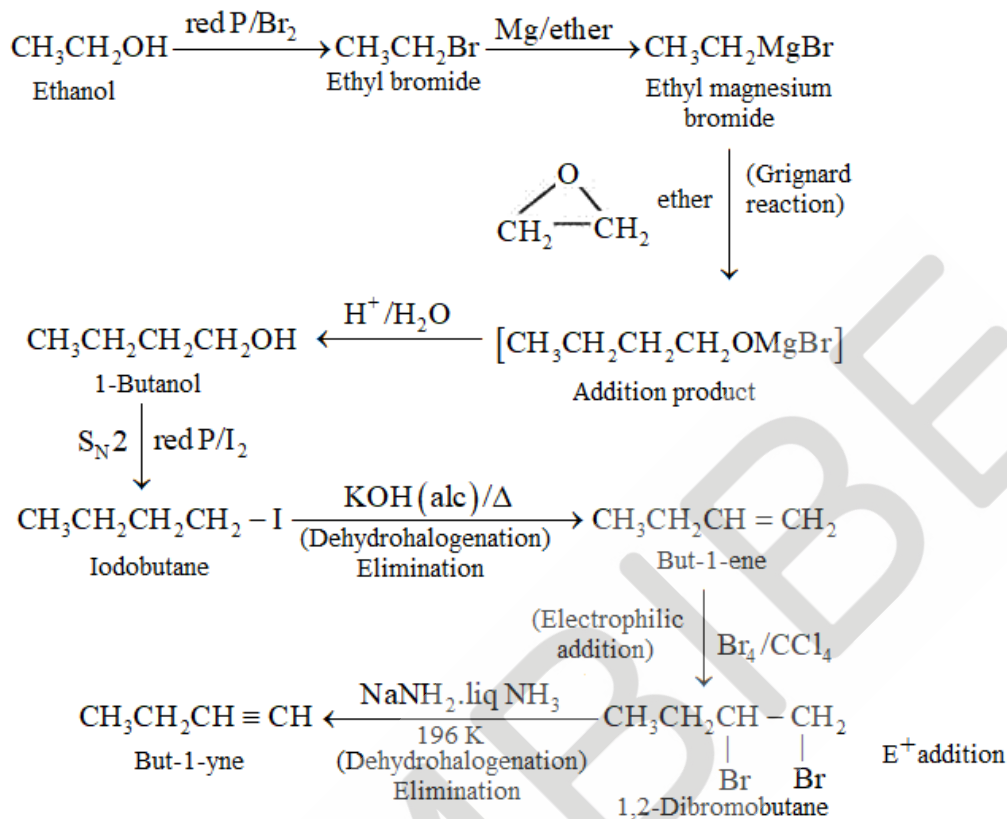
- (iv) Toluene to benzyl alcohol
- (v) Benzene to 4-bromonitrobenzene
- (vi) Benzyl alcohol to 2-phenylethanoic acid
- (vii) Ethanol to propanenitrile
- (viii) Aniline to chlorobenzene
- (ix) 2-Chlorobutane to 3,4-dimethylhexane
- (x) 2-Methyl-1-propene to 2-chloro-2-methylpropane
- (xi) Ethyl chloride 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

Solution:

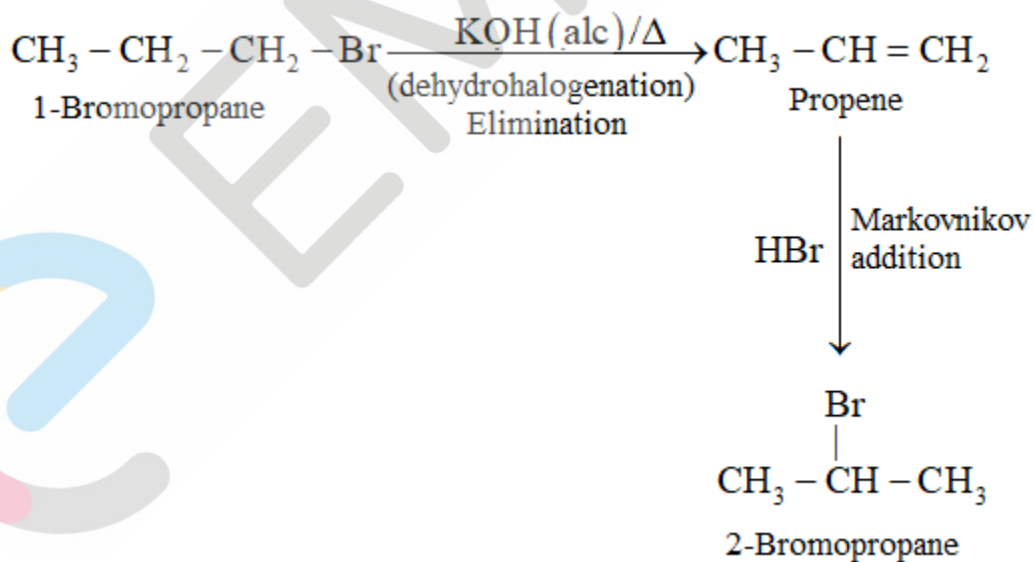
(i)



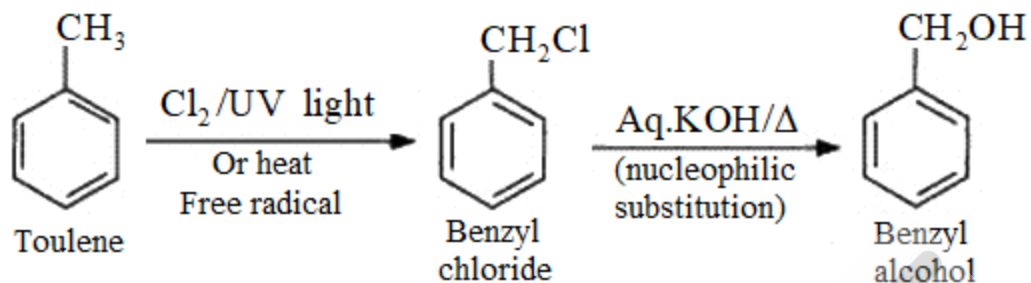
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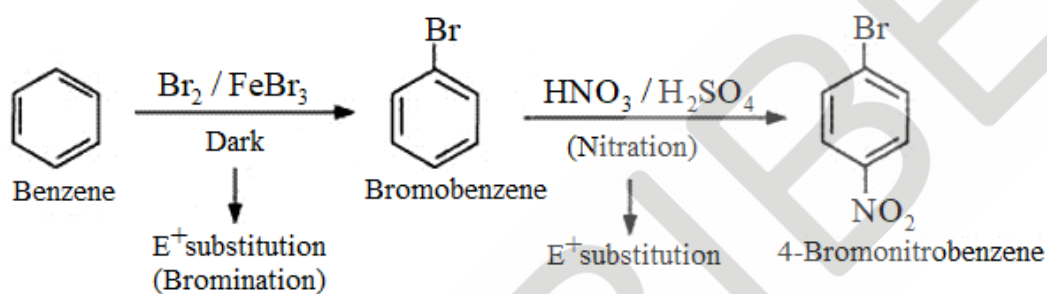
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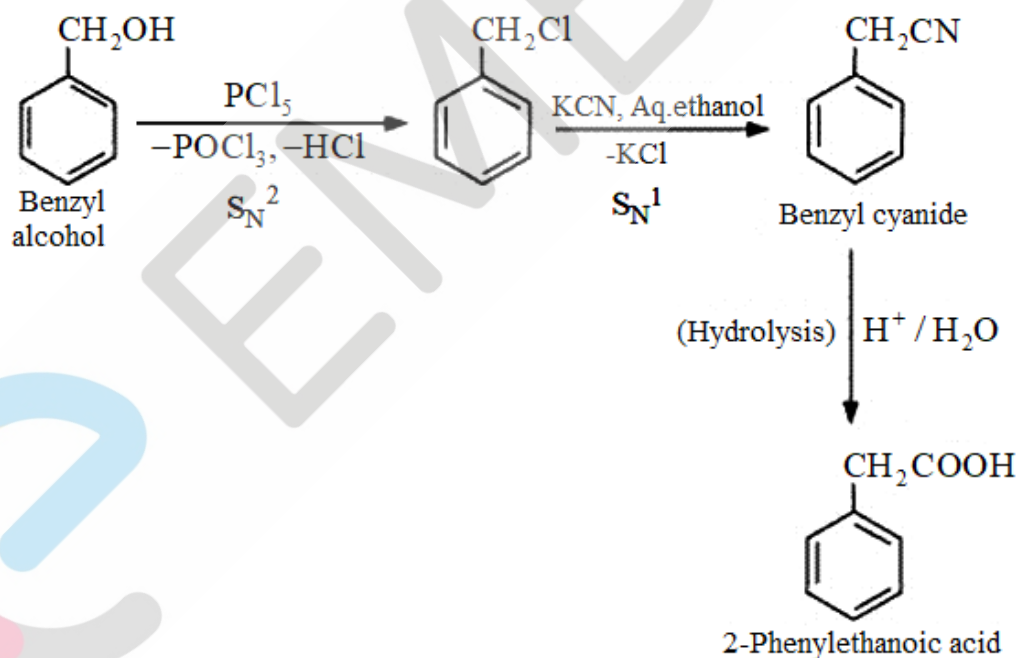
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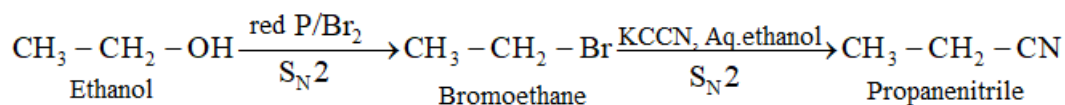
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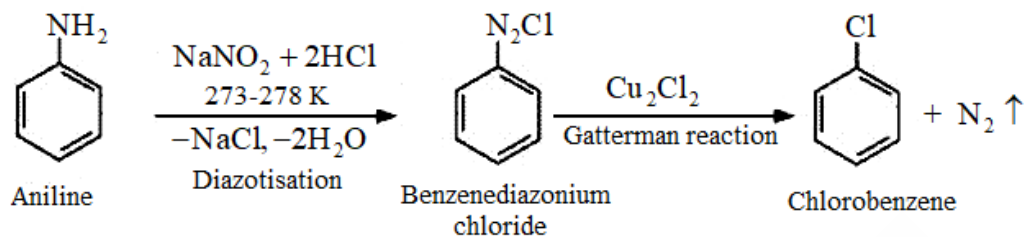
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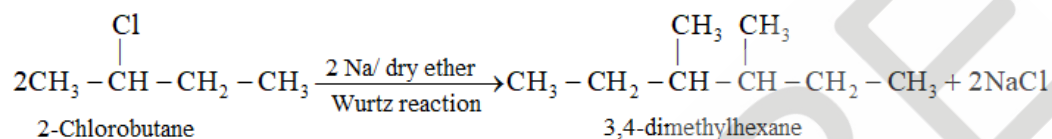
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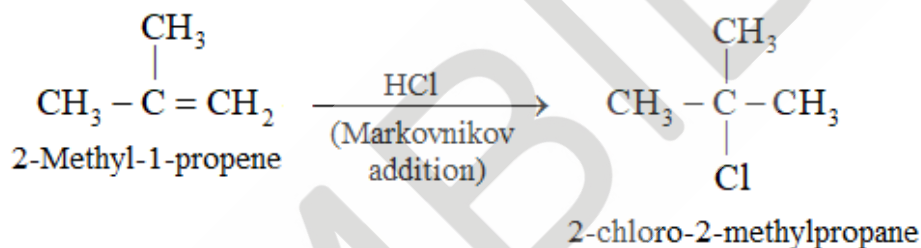
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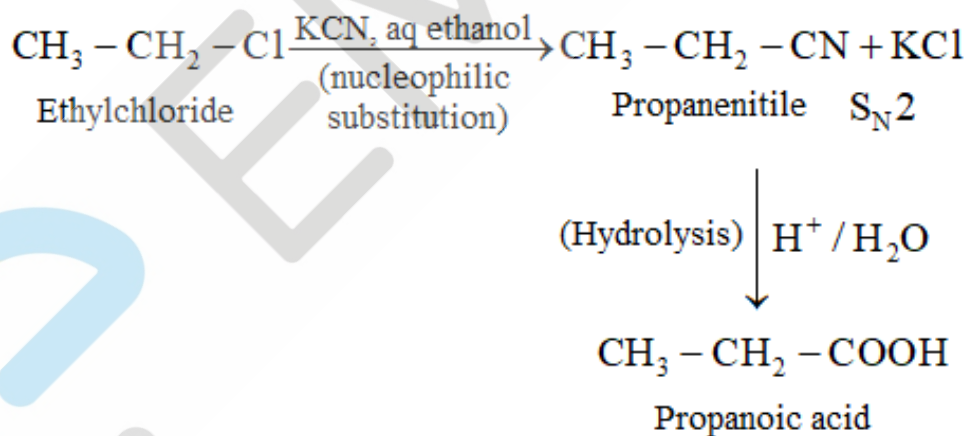
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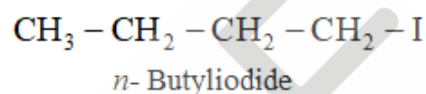
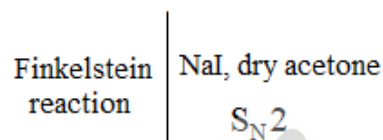
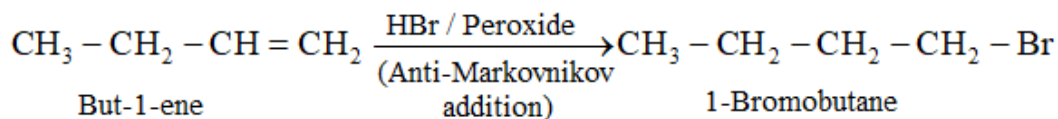
(x) Markovnikov's rule: -



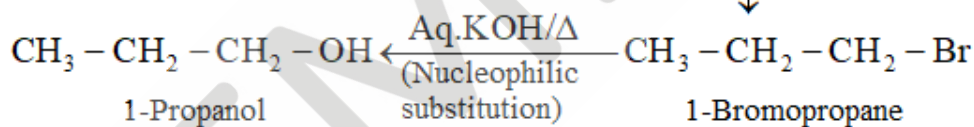
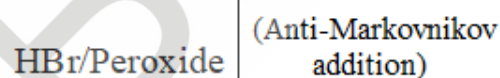
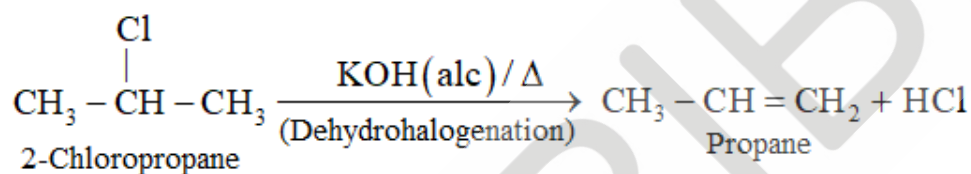
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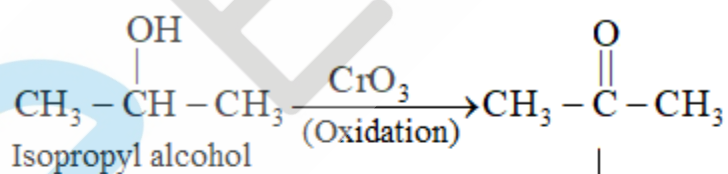
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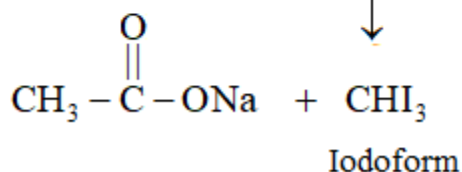
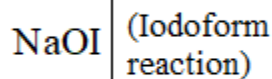
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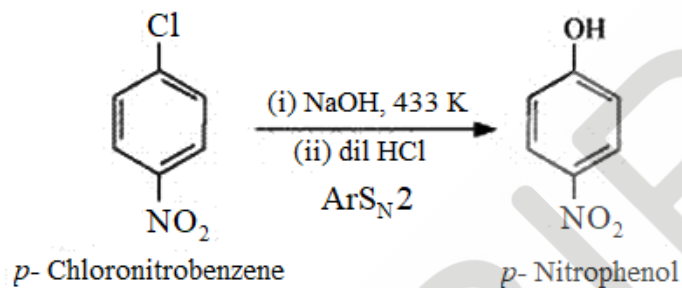
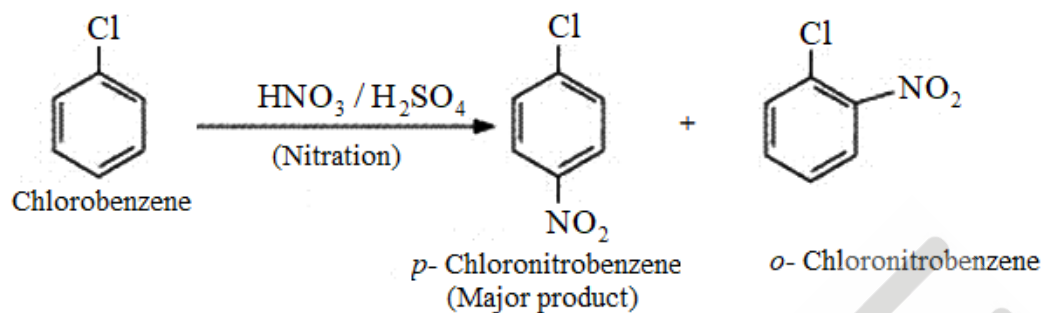
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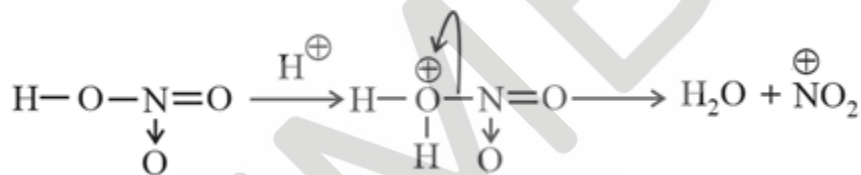
2° Alcohol



(xv)

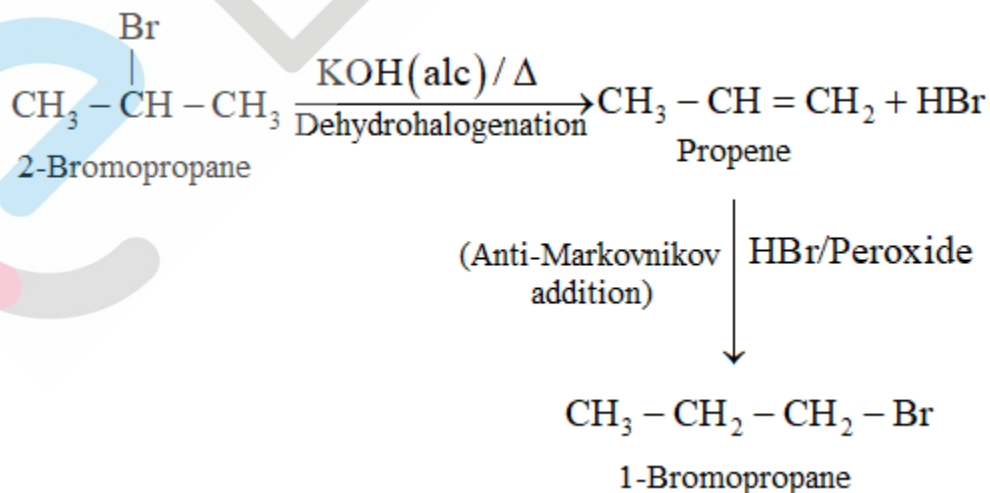


Electrophile generation:

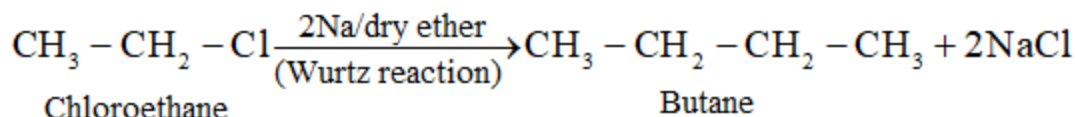


(xvi) Antimarkovnikov's rule: -

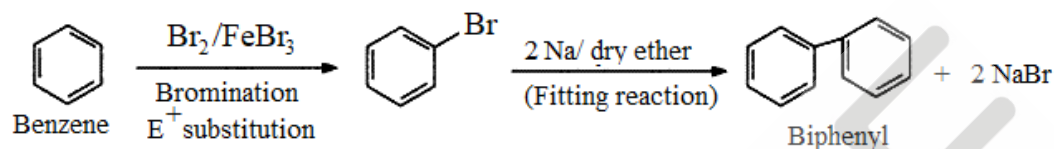
H attached at which carbon where present less are present and Br^- (nu^-) attack where number of H are more



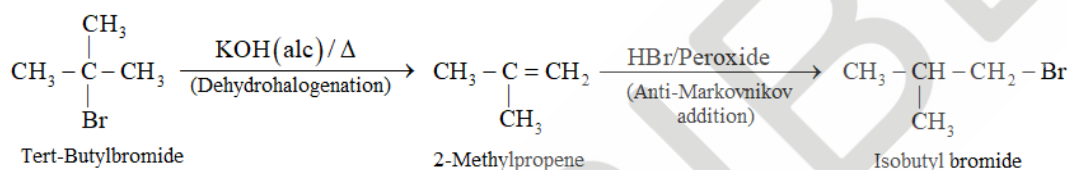
(xvii)



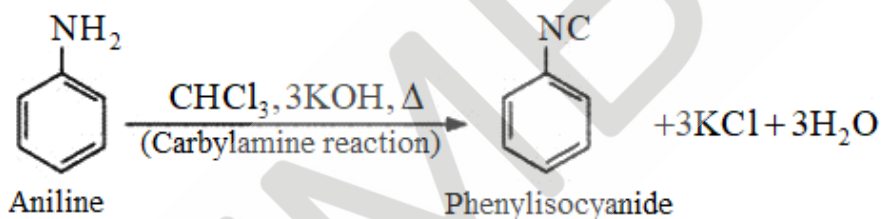
(xviii)



(xix)



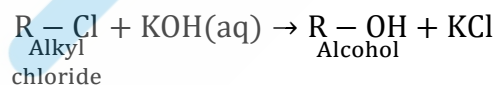
(xx)



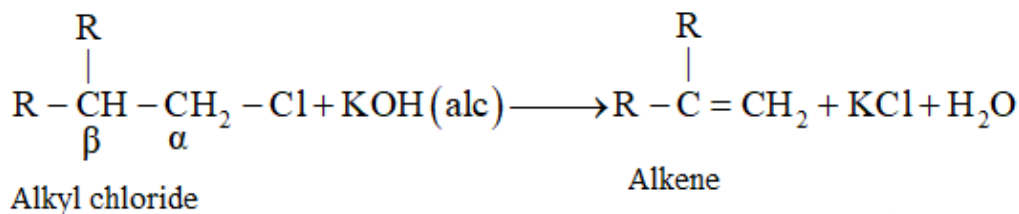
20. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Solution:

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.



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

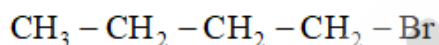


OH^- ion is a much weaker base than RO^- ion. Also, OH^- ion is highly solvated in an aqueous solution and as a result, the basic character of OH^- ion decreases. Therefore, it cannot abstract a hydrogen from the (3-carbon).

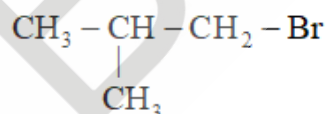
21. Primary alkyl halide $\text{C}_4\text{H}_9\text{Br}$ (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions,

Solution:

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.



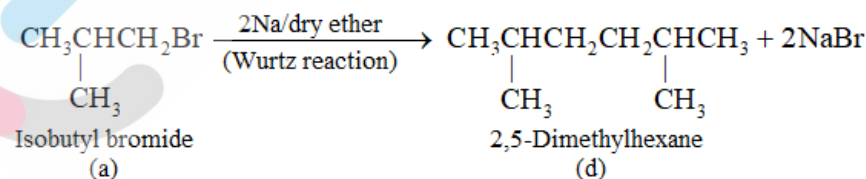
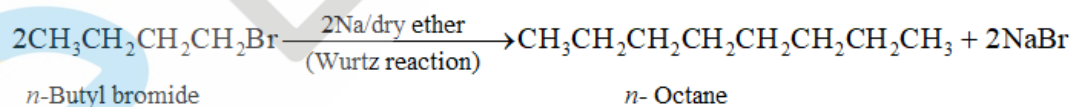
n- Butyl bromide



Isobutyl bromide

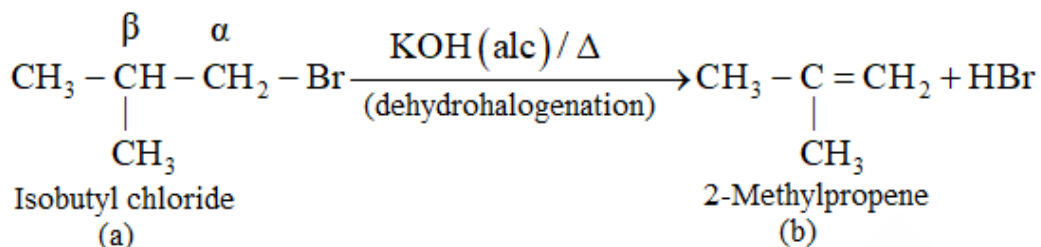
Therefore, compound (a) is either n-butyl bromide or isobutyl bromide,

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.

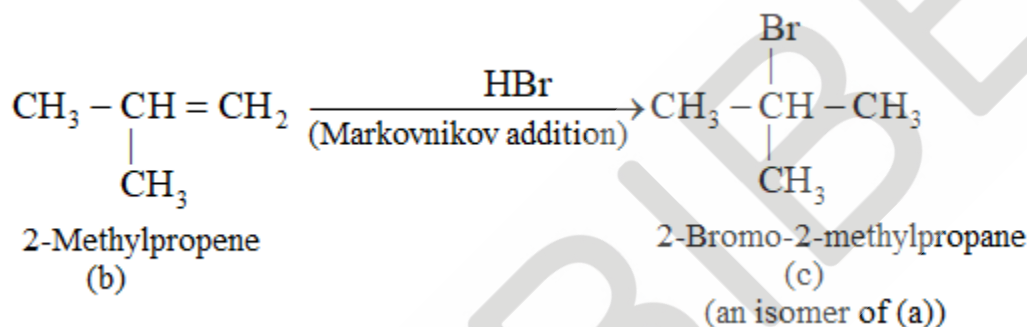


Thus, compound (d) is 2, 5 – dimethylhexane.

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,

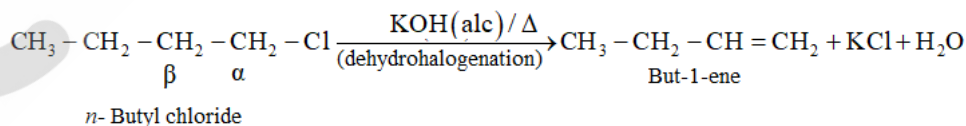


22. What happens when

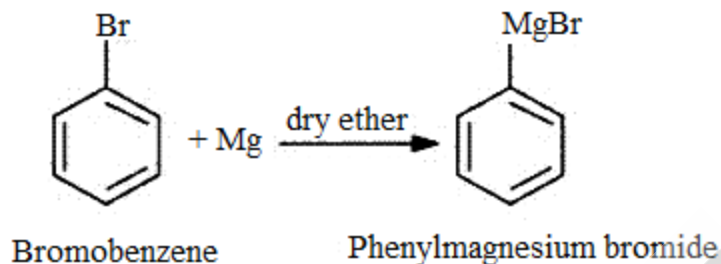
- n-butyl chloride is treated with alcoholic KOH,
- bromobenzene is treated with Mg in the presence of dry ether,
- chlorobenzene is subjected to hydrolysis,
- ethyl chloride is treated with aqueous KOH,
- methyl bromide is treated with sodium in the presence of dry ether,
- methyl chloride is treated with KCN.

Solution:

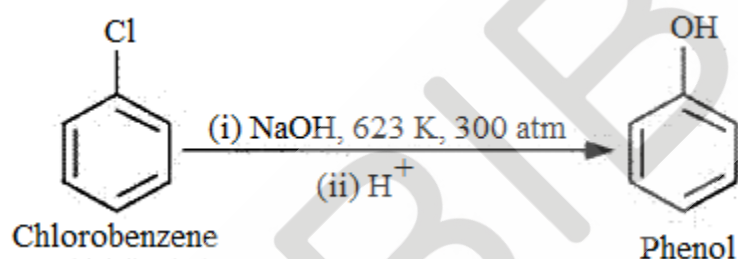
- When n-butyl chloride is treated with alcoholic KOH, the formation of but-1-ene takes place (Hoffman producer). This reaction is a dehydrohalogenation reaction.



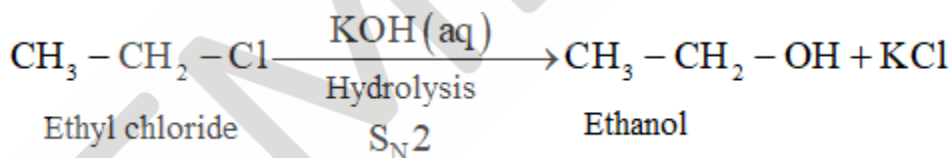
- When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide (Grignard reagent) is formed.



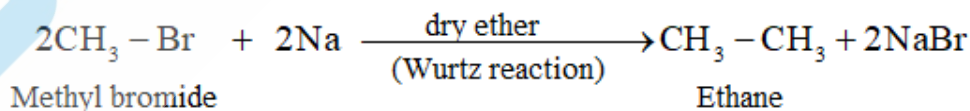
- (iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.



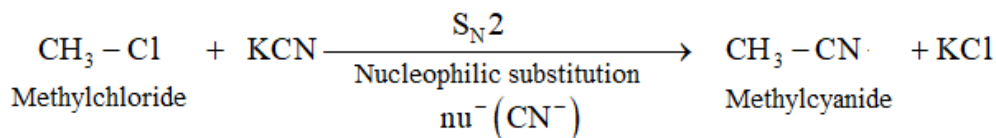
- (iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.



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



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



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