

## Halogen Derivatives

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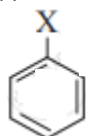
### EXERCISE [PAGES 231 - 233]

#### Exercise | Q 1.01 | Page 231

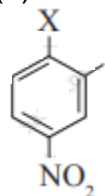
Choose the most correct option.

The correct order of increasing reactivity of C-X bond towards nucleophile in the following compounds is

(I)



(II)



(III)  $(\text{CH}_3)_3\text{C-X}$

(IV)  $(\text{CH}_3)_2\text{CH-X}$

1.  $\text{I} < \text{II} < \text{III} < \text{IV}$
2.  $\text{II} < \text{I} < \text{III} < \text{IV}$
3.  $\text{III} < \text{IV} < \text{II} < \text{I}$
4.  $\text{IV} < \text{III} < \text{I} < \text{II}$

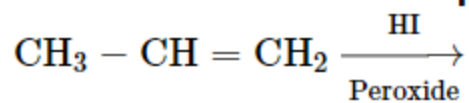
**Solution:**

$\text{I} < \text{II} < \text{III} < \text{IV}$

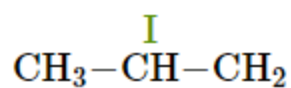
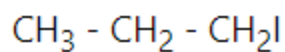
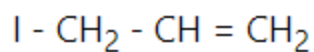
**Explanation:**

Alkyl halides are more reactive than aryl halides. This is because of the partial double bond character between the benzene ring and the halogen. Further, in alkyl halides, the greater the stability of carbocation formed, the more would be the reactivity. Thus, the tertiary halide is more reactive. Nitro group which is electron-withdrawing increases the reactivity of aryl halide.

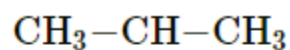
**Choose the most correct option.**



The major product of the above reaction is, \_\_\_\_\_.



**Solution:**

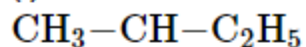


**Exercise | Q 1.03 | Page 231**

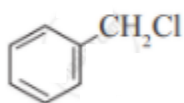
**Choose the most correct option.**

Which of the following is likely to undergo racemization during alkaline hydrolysis?

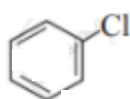
(I)



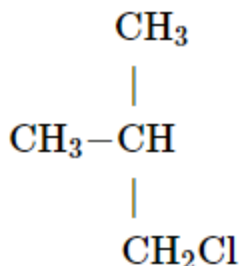
(II)



(III)



(IV)



1. Only I
2. Only II
3. II and IV
4. Only IV

**Solution:** Only I

**Exercise | Q 1.04 | Page 231**

**Choose the most correct option.**

The best method for the preparation of alkyl fluorides is \_\_\_\_\_.

1. Finkelstein reaction
2. Swartz reaction
3. Free radical fluorination
4. Sandmeyer's reaction

**Solution:** The best method for the preparation of alkyl fluorides is **Swartz reaction**.

**Exercise | Q 1.04 | Page 231**

**Choose the most correct option.**

The best method for the preparation of alkyl fluorides is \_\_\_\_\_.

1. Finkelstein reaction
2. Swartz reaction
3. Free radical fluorination
4. Sandmeyer's reaction

**Solution:** The best method for the preparation of alkyl fluorides is **Swartz reaction**.

**Exercise | Q 1.05 | Page 231**

**Choose the most correct option.**

Identify the chiral molecule from the following.

- a. 1 - Bromobutane
- b. 1,1-Dibromobutane
- c. 2,3-Dibromobutane
- d. 2-Bromobutane

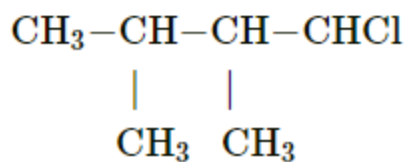
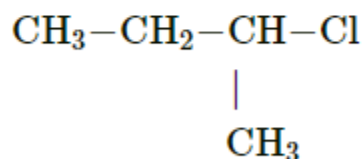
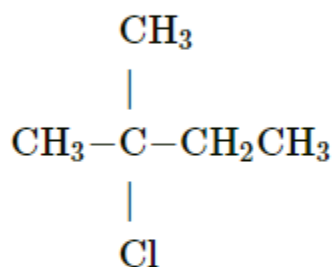
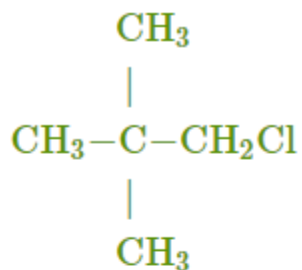
**Solution:** c) 2,3-Dibromobutane and d) 2-Bromobutane

**Exercise | Q 1.06 | Page 231**

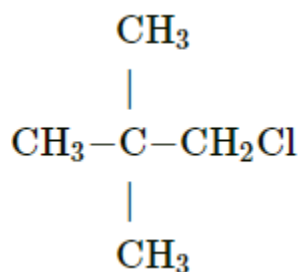
**Choose the most correct option.**

An alkyl chloride on Wurtz reaction gives 2,2,5,5-tetramethylhexane. The same alkyl chloride on reduction with a zinc-copper couple in alcohol gives hydrocarbon with molecular formula  $C_5H_{12}$ . What is the structure of alkyl chloride?

**Options**



**Solution:**



**Exercise | Q 1.07 | Page 231**

**Choose the most correct option.**

Butanenitrile may be prepared by heating \_\_\_\_\_.

1. propanol with KCN
2. butanol with KCN
3. n-butyl chloride with KCN
4. **n-propyl chloride with KCN**

**Solution:** Butanenitrile may be prepared by heating **n-propyl chloride with KCN.**

**Exercise | Q 1.08 | Page 232**

**Choose the most correct option.**

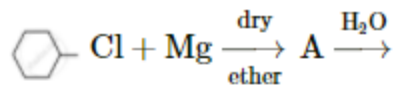
Choose the compound from the following that will react fastest by S<sub>N</sub>1 mechanism

1. 1-Iodobutane
2. 1-Iodopropane
3. **2-Iodo-2 methylbutane**
4. 2-Iodo-3-methylbutane

**Solution:** 2-Iodo-2 methylbutane

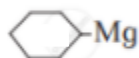
**Exercise | Q 1.09 | Page 232**

**Choose the most correct option.**



The product 'B' in the above reaction sequence is, \_\_\_\_\_.

Options



**Solution:**



**Exercise | Q 1.1 | Page 232**

**Choose the most correct option.**

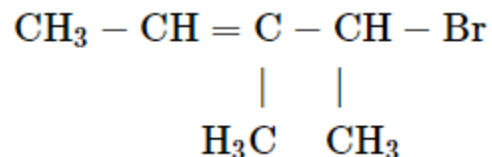
Which of the following is used as a source of dichlorocarbene?

1. tetrachloromethane
2. **chloroform**
3. iodoform
4. DDT

**Solution:** chloroform

**Exercise | Q 2.1 | Page 232**

**Write IUPAC name of the following compound.**

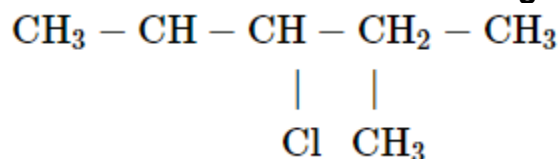


**Solution:**

2-Bromo-3-methylpent-3-ene

**Exercise | Q 2.1 | Page 232**

**Write IUPAC name of the following compound.**

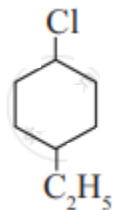


**Solution:**

2-Chloro-3-methylpentane

**Exercise | Q 2.1 | Page 232**

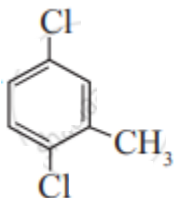
**Write IUPAC name of the following compound.**



**Solution:** 1-Chloro-4-ethylcyclohexane

**Exercise | Q 2.1 | Page 232**

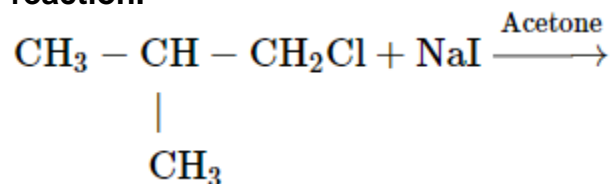
**Write IUPAC name of the following compound.**



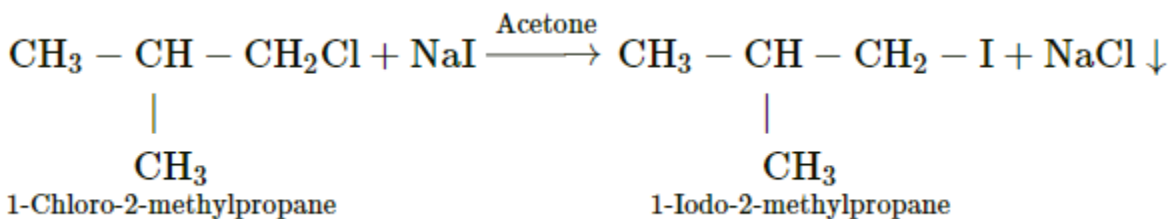
**Solution:** 1,4-Dichloro-2-methylbenzene

**Exercise | Q 2.2 | Page 232**

Write the structure and IUPAC name of the major product in the following reaction.



Solution:

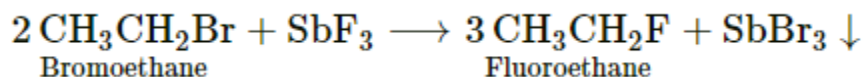


**Exercise | Q 2.2 | Page 232**

Write the structure and IUPAC name of the major product in the following reaction.

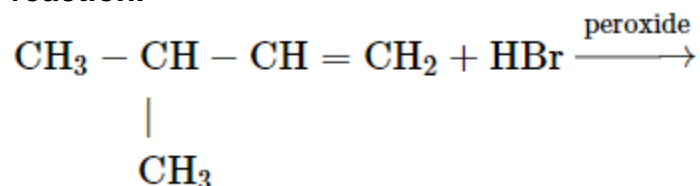


Solution:

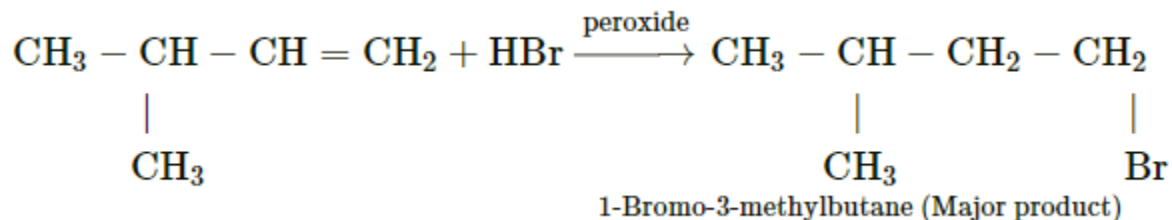


**Exercise | Q 2.2 | Page 232**

Write the structure and IUPAC name of the major product in the following reaction.



Solution:

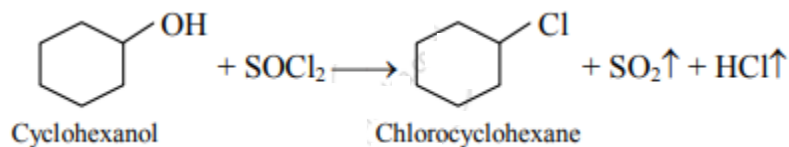


**Exercise | Q 2.2 | Page 232**

Write the structure and IUPAC name of the major product in the following reaction.

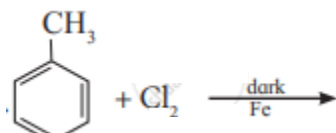


**Solution:**

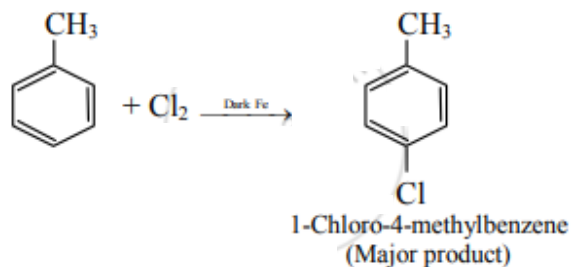


**Exercise | Q 2.2 | Page 232**

Write the structure and IUPAC name of the major product in the following reaction.



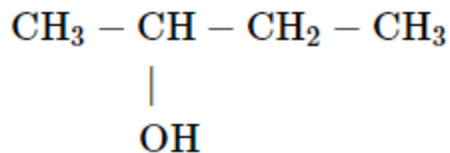
**Solution:**



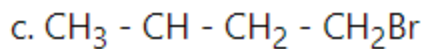
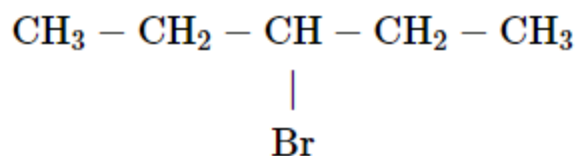
**Exercise | Q 2.3 | Page 232**

Identify chiral molecule/s from the following.

a.

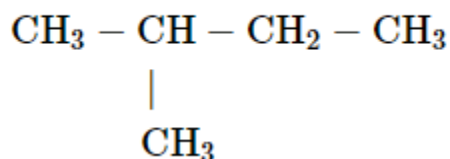


b.

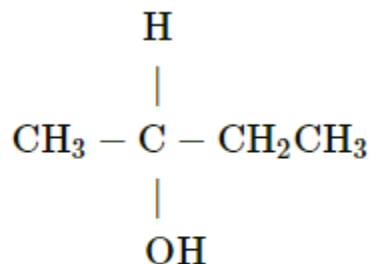




d.



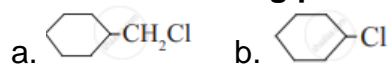
**Solution:**



2-Hydroxybutane is a chiral molecule amongst the given.

**Exercise | Q 2.4 | Page 232**

from the following pair would undergo  $\text{S}_{\text{N}}2$  faster from the other?



**Solution:** Compound (a) will undergo  $\text{S}_{\text{N}}2$  mechanism faster than (b).

**Exercise | Q 2.4 | Page 232**

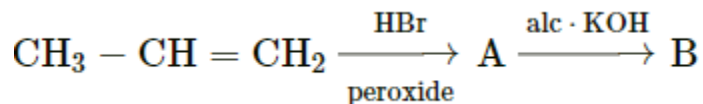
from the following pair would undergo  $\text{S}_{\text{N}}2$  faster from the other?



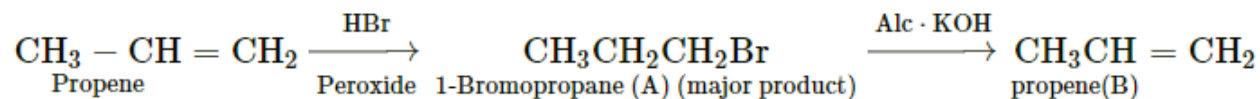
**Solution:** Compound (a) will undergo  $\text{S}_{\text{N}}2$  mechanism faster than (b).

**Exercise | Q 2.5 | Page 232**

Complete the following reaction giving major products.

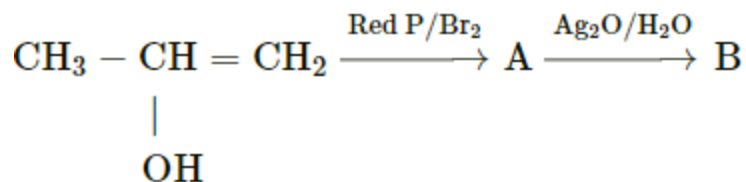


**Solution:**

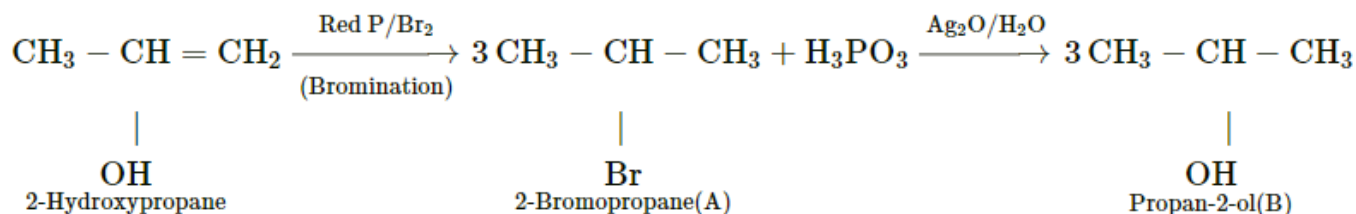


**Exercise | Q 2.5 | Page 232**

Complete the following reaction giving major products.

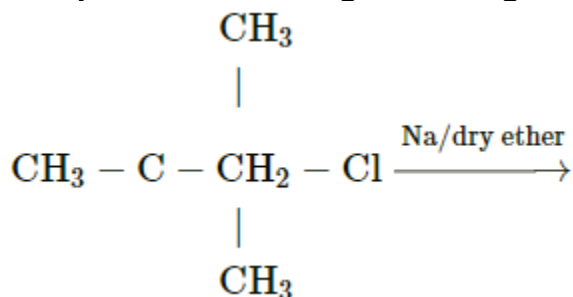


**Solution:**

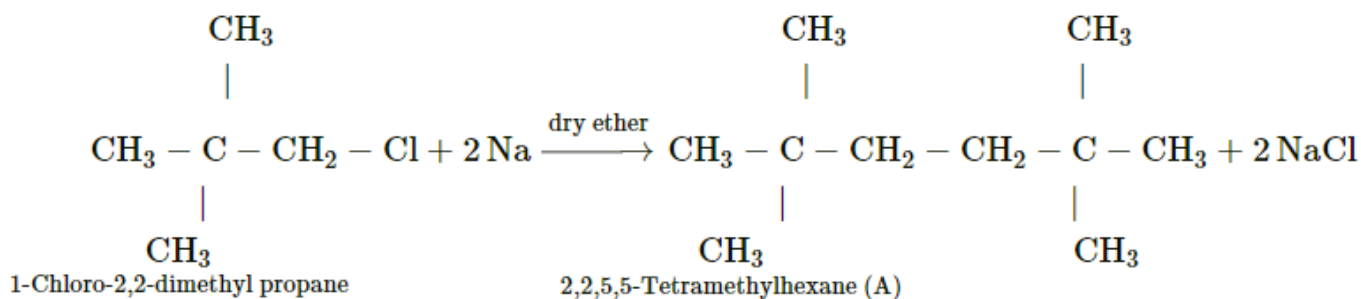


**Exercise | Q 2.5 | Page 232**

Complete the following reaction giving major products.

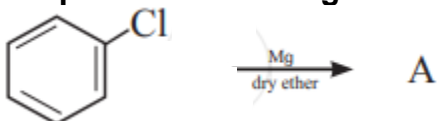


**Solution:**

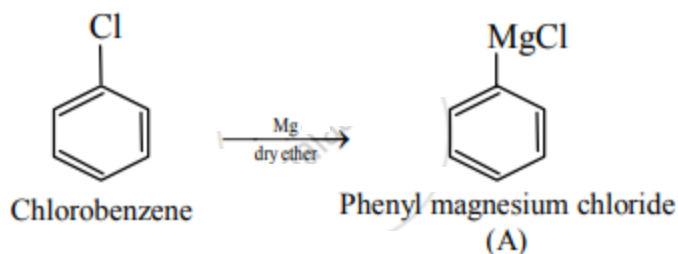


**Exercise | Q 2.5 | Page 232**

Complete the following reaction giving major products.



**Solution:**



**Exercise | Q 2.6 | Page 233**

**Name the reagent used to bring about the following conversion.**

Bromoethane to ethoxyethane

**Solution:** Sodium ethoxide ( $\text{NaOC}_2\text{H}_5$ )

**Exercise | Q 2.6 | Page 233**

**Name the reagent used to bring about the following conversion.**

1-Chloropropane to 1-nitropropane

**Solution:** Silver nitrite ( $\text{AgNO}_2$ )

**Exercise | Q 2.6 | Page 233**

**Name the reagent used to bring about the following conversion.**

Ethyl bromide to ethyl isocyanide

**Solution:** Alcoholic silver cyanide ( $\text{AgCN}$ )

**Exercise | Q 2.6 | Page 233**

**Name the reagent used to bring about the following conversion.**

Chlorobenzene to biphenyl

**Solution:** Na metal in dry ether

**Exercise | Q 2.7 | Page 233**

**Arrange the following in the increasing order of boiling points.**

- 1-Bromopropane
- 2- Bromopropane
- 1- Bromobutane
- 1-Bromo-2-methylpropane

**Solution:** 2-Bromopropane < 1-bromopropane < 1-bromo-2-methylpropane < 1-bromobutane.

**Exercise | Q 2.8 | Page 233**

**Match the pairs.**

Column I	Column II
$\begin{array}{c} \text{CH}_3\text{CH} - \text{CH}_3 \\   \\ \text{X} \end{array}$	vinyl halide
$\text{CH}_2 = \text{CH} - \text{CH}_2\text{X}$	alkyl halide
$\text{CH}_2 = \text{CH} - \text{X}$	allyl halide
	benzyl halide
	aryl halide

**Solution:**

Column I	Column II
$\begin{array}{c} \text{CH}_3\text{CH} - \text{CH}_3 \\   \\ \text{X} \end{array}$	alkyl halide
$\text{CH}_2 = \text{CH} - \text{CH}_2\text{X}$	allyl halide
$\text{CH}_2 = \text{CH} - \text{X}$	Vinyl halide

### Exercise | Q 3.1 | Page 233

**Give reasons:**

Haloarenes are less reactive than haloalkanes.

**Solution:**

- The low reactivity of aryl halides is due to resonance effect and  $sp^2$  hybrid state of carbon to which halogen atom is attached.
- In aryl halides, one of the lone pairs of electrons on halogen atom is in conjugation with  $\pi$ -electrons of the ring. Due to resonance, the C–X bond acquires partial double bond character. Thus, the C–X bond in haloarenes is stronger and shorter than haloalkanes. Hence, it is difficult to break C–X bond in haloarenes. (e.g. C–Cl bond length in chlorobenzene is 169 pm as compared to C–Cl bond length in alkyl chloride which is 178 pm).

Therefore, haloarenes are less reactive than haloalkanes.

### Exercise | Q 3.2 | Page 233

**Give reason:**

Alkyl halides though polar are immiscible with water.

**Solution:**

1. Alkyl halides cannot form hydrogen bonds with water.
2. In addition to this, the attraction between alkyl halide molecules is stronger than the attraction between alkyl halide and water.

Hence, alkyl halides though moderately polar are immiscible with water.

**Exercise | Q 3.3 | Page 233****Give reason:**

Reactions involving Grignard reagent must be carried out under anhydrous condition.

**Solution:**

1. Grignard reagents are highly reactive compounds.
2. They react with water or compounds containing hydrogen attached to the electronegative element.

Hence, reactions involving the Grignard reagent must be carried out under anhydrous condition.

**Exercise | Q 3.4 | Page 233****Give reason:**

Alkyl halides are generally not prepared by free radical halogenation of alkanes.

**Solution:**

Free radical halogenation of alkanes leads to the formation of a mixture of mono and poly halogen compounds. Hence, free radical halogenation of alkanes is not suitable for the preparation of alkyl halides.

**Exercise | Q 4 | Page 233**

Distinguish between  $S_N1$  and  $S_N2$  mechanism of substitution reaction.

**Solution:**

Factor	$S_N1$	$S_N2$
Kinetics	2 <sup>nd</sup> order	1 <sup>st</sup> order
Molecularity	Bimolecular	Unimolecular
Number of steps	One step	Two steps

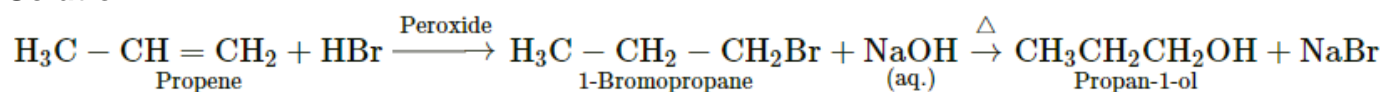
Bond making and bond breaking	Simultaneous	First the bond in the reactant breaks and then a new bond in the product is formed
Transition state	One step, one transition state	Two steps, two transition states
Direction of attack of nucleophile	Only back side attack	Back side attack and front side attack
Stereochemistry	Inversion of configuration (If the substrate is optically active)	Racemisation (If the substrate is optically active)
Type of substrate	Mainly 1° substrate	Mainly 3° substrates
Polarity of solvent	Aprotic (non-polar) or solvent with low polarity favourable	Polar protic solvent favorable
Intermediate	No intermediate	Intermediate involved

### Exercise | Q 6.1 | Page 233

**Convert the following:**

Propene to propan-1-ol

**Solution:**

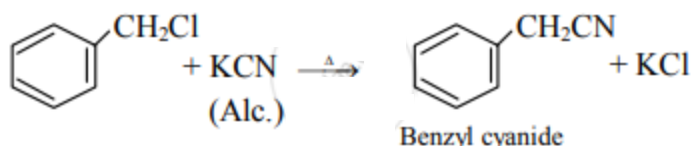
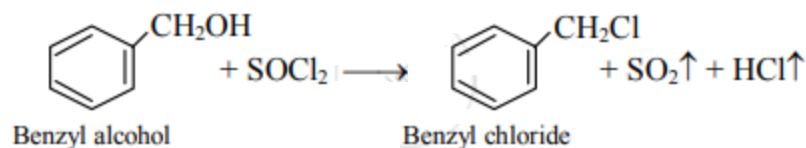


### Exercise | Q 6.2 | Page 233

**Convert the following:**

Benzyl alcohol to benzyl cyanide

**Solution:**

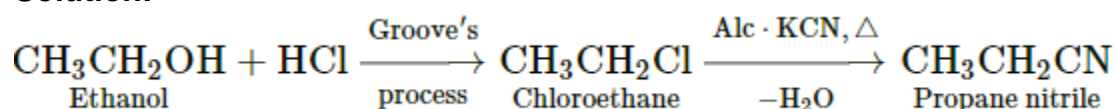


### Exercise | Q 6.3 | Page 233

Convert the following:

Ethanol to propane nitrile

**Solution:**

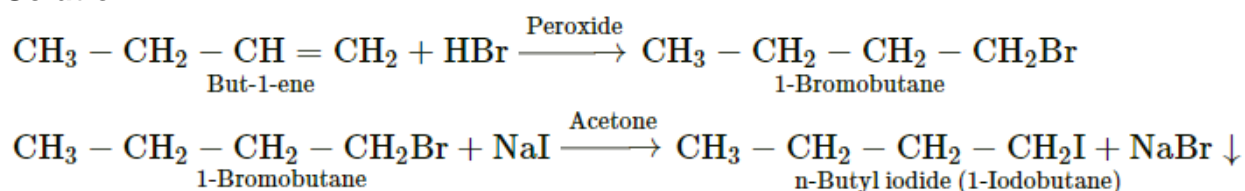


### Exercise | Q 6.4 | Page 233

Convert the following:

But-1-ene to n-butyl iodide

**Solution:**

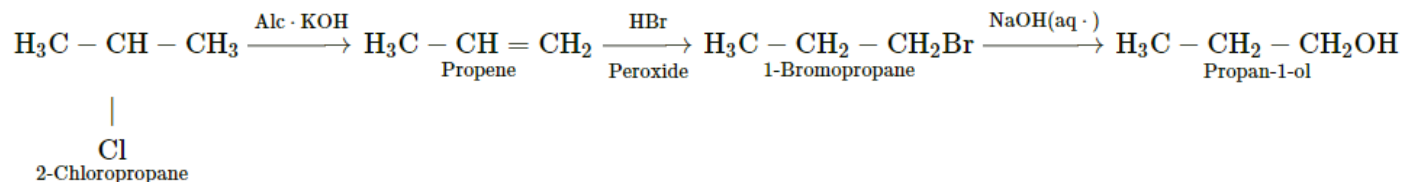


### Exercise | Q 6.5 | Page 233

Convert the following:

2-Chloropropane to propan-1-ol

**Solution:**

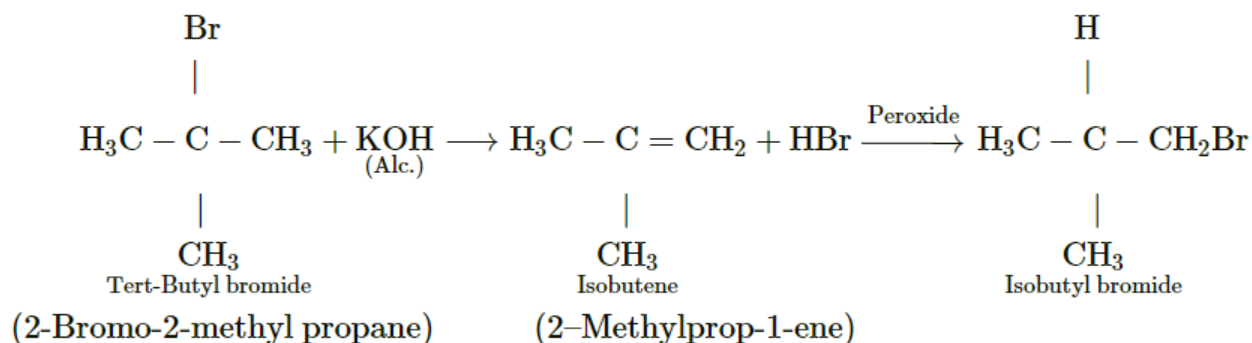


### Exercise | Q 6.6 | Page 233

Convert the following:

tert-Butyl bromide to isobutyl bromide

**Solution:**



**Exercise | Q 6.7 | Page 233**

How the following conversions can be carried out?

Aniline to chlorobenzene

**Solution:**

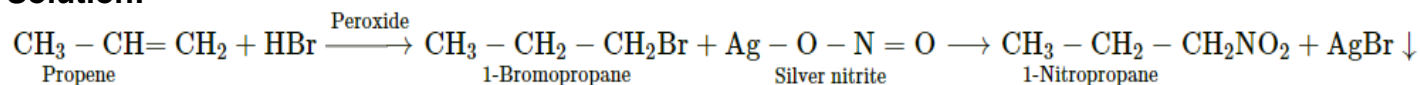


**Exercise | Q 6.8 | Page 233**

How will you bring about the following conversions?

Propene to 1-nitropropane

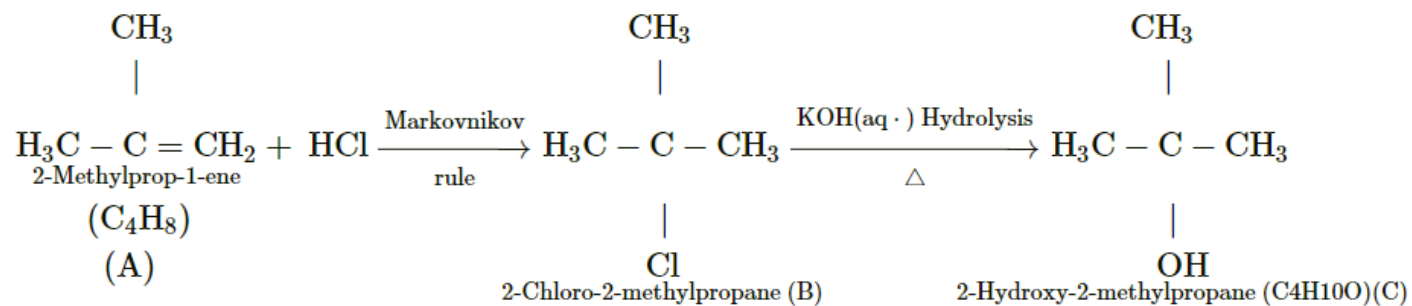
**Solution:**



**Exercise | Q 7.1 | Page 233**

HCl is added to a hydrocarbon 'A' (C<sub>4</sub>H<sub>8</sub>) to give a compound 'B' which on hydrolysis with aqueous alkali forms tertiary alcohol 'C' (C<sub>4</sub>H<sub>10</sub>O). Identify 'A', 'B' and 'C'.

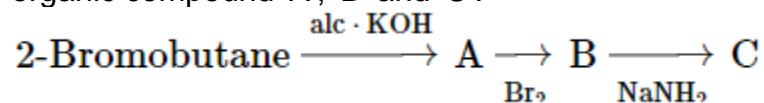
**Solution:**



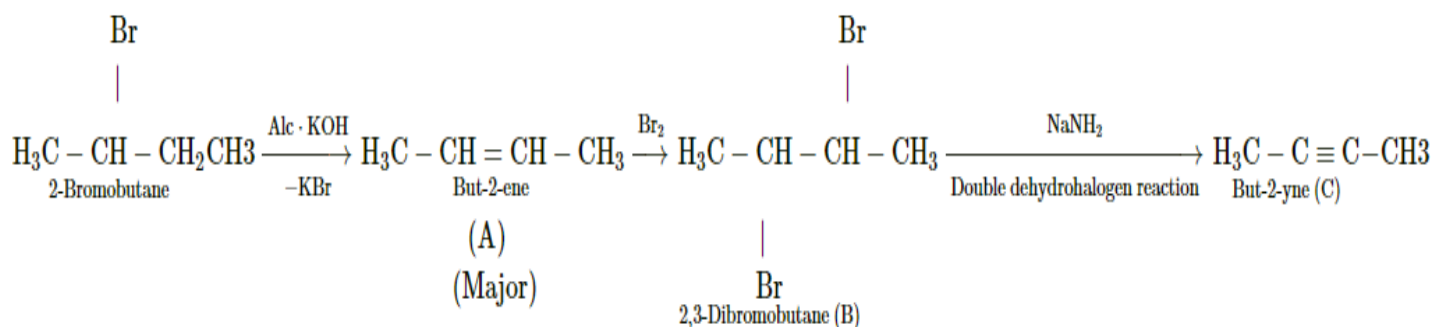


**Exercise | Q 7.2 | Page 233**

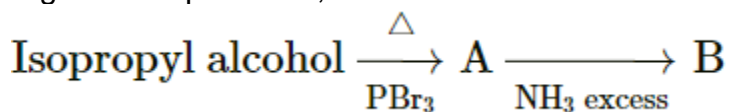
Complete the following reaction sequence by writing the structural formulae of the organic compound 'A', 'B' and 'C'.



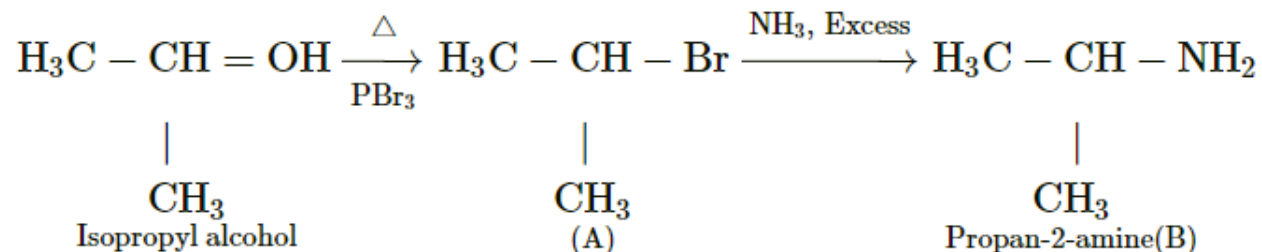
**Solution:**

**Exercise | Q 7.2 | Page 233**

Complete the following reaction sequence by writing the structural formulae of the organic compound 'A', 'B' and 'C'.



**Solution:**

**Exercise | Q 7.3 | Page 233**

Observe the following and answer the question given below.



Name the type of halogen derivative.

**Solution:** Vinylic halide

**Exercise | Q 7.3 | Page 233**

Observe the following and answer the question given below.



Comment on the bond length of C–X bond in it.

**Solution:** The bond length of C – X bond is expected to be shorter than C – X bond in haloalkanes.

**Exercise | Q 7.3 | Page 233**

Observe the following and answer the question given below.



Can it react by S<sub>N</sub>1 mechanism? Justify your answer.

**Solution:**

It will not react by S<sub>N</sub>1 mechanism. The bond between sp<sup>2</sup> hybridized carbon atom and halogen is a strong bond. Also, the electrons of the –X atom are in conjugation with the π bond. Thus, C – X bond acquires a double bond character. Thus, when nucleophile approaches the sp<sup>2</sup> carbon, it gets repelled by the π-electrons of the double bond.