

# CHAPTER - 10

## HALOALKANES & HALO ARENES INTEXT SOLUTIONS

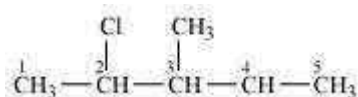
### Question 10.1:

Write structures 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

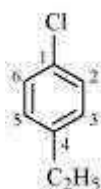
Answer

(i)



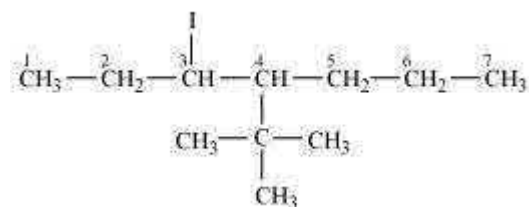
2-Chloro-3-methyl pentane

(ii)



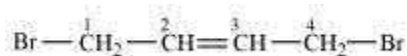
1-Chloro-4-ethylcyclohexane

(iii)



4- tert-Butyl-3-iodoheptane

(iv)



1, 4-Dibromobut-2-ene

(v)



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

**Question 10.2:**

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

Answer

In the presence of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), KI produces HI



Since  $\text{H}_2\text{SO}_4$  is an oxidizing agent, it oxidizes HI (produced in the reaction) to I<sub>2</sub>.



As a result, the reaction between alcohol and HI to produce alkyl iodide cannot occur. Therefore, sulphuric acid is not used during the reaction of alcohols with KI. Instead, a non-oxidizing acid such as H<sub>3</sub>PO<sub>4</sub> is used.

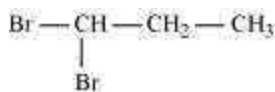
**Question 10.3:**

Write structures of different dihalogen derivatives of propane.

Answer

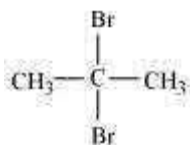
There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

(i)



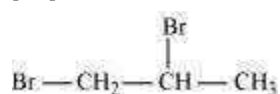
1, 1-Dibromopropane

(ii)



2, 2-Dibromopropane

(iii)



1, 2-Dibromopropane

(iv)



1, 3-Dibromopropane

#### Question 10.4:

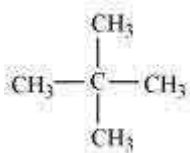
Among the isomeric alkanes of molecular formula  $\text{C}_5\text{H}_{12}$ , identify the one that on photochemical chlorination yields (i) A single monochloride.

(ii) Three isomeric monochlorides.

(iii) Four isomeric monochlorides.

Answer

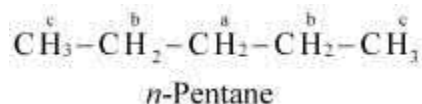
(i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula  $\text{C}_5\text{H}_{12}$ . This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.



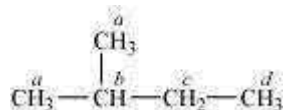
Neopentane

(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula  $\text{C}_5\text{H}_{12}$  should contain three different types of H-atoms.

Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H atoms labelled as *a*, *b* and *c* in *n*-pentane.



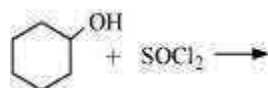
(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C<sub>5</sub>H<sub>12</sub> should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c*, and *d* in 2-methylbutane.



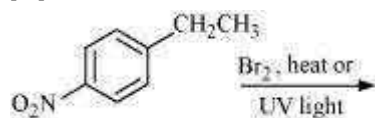
#### Question 10.5:

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

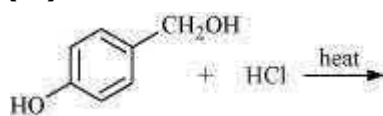
(i)



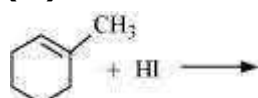
(ii)



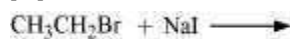
(iii)



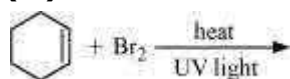
(iv)



(v)

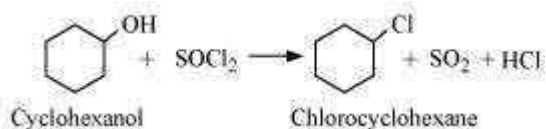


(vi)

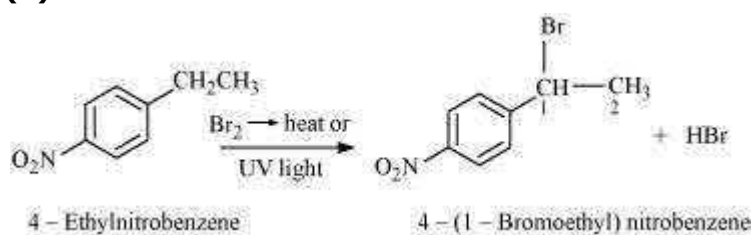


Answer

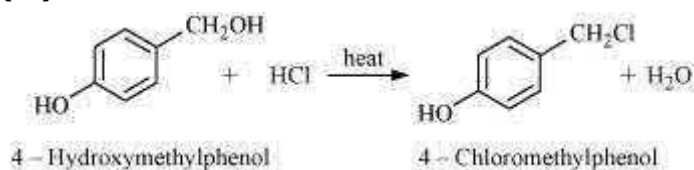
(i)



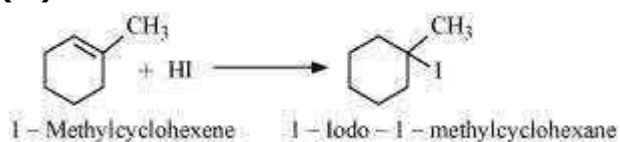
(ii)



(iii)



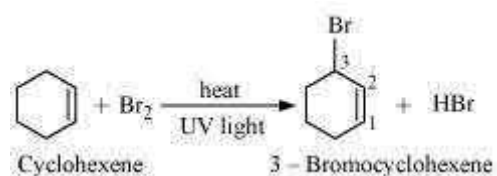
(iv)



(v)



(vi)



### Question 10.6:

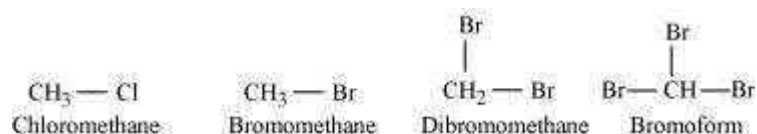
Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

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

Answer

**(i)**



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

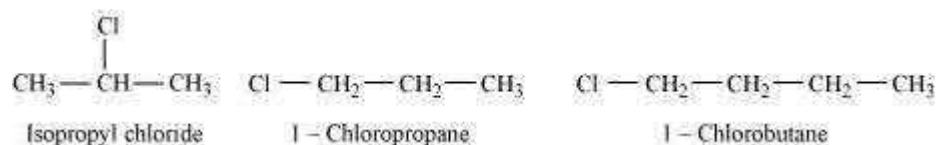
Since the atomic mass of Br is greater than that of Cl, the boiling point of bromomethane is higher than that of chloromethane.

Further, for alkyl halides containing the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of Dibromomethane is higher than that of chloromethane and bromomethane, but lower than that of bromoform.

Hence, the given set of compounds can be arranged in the order of their increasing boiling points as:

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

**(ii)**



For alkyl halides containing the same halide, the boiling point increases with an increase in the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than that of isopropyl chloride and 1-chloropropane.

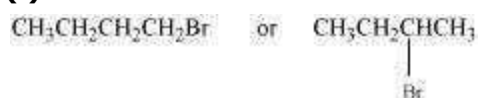
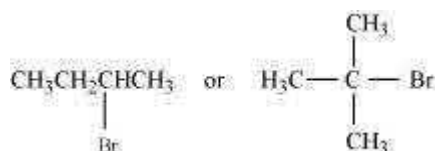
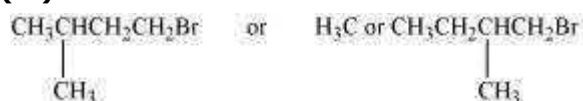
Further, the boiling point decreases with an increase in branching in the chain. Thus, the boiling point of isopropyl alcohol is lower than that of 1-chloropropane.

Hence, the given set of compounds can be arranged in the increasing order of their boiling points as:

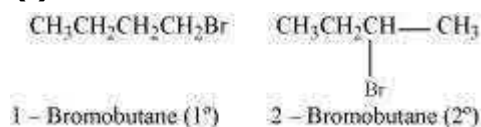
Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

**Question 10.7:**

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

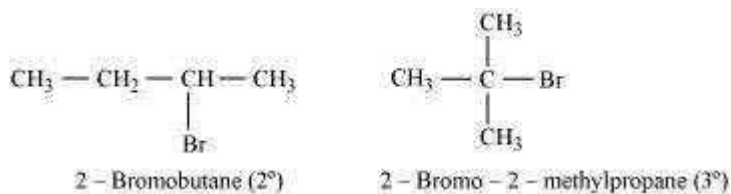
**(i)****(ii)****(iii)**

Answer

**(i)**

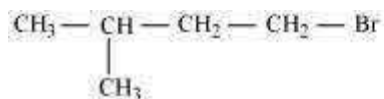
1 - Bromobutane ( $1^\circ$ )      2 - Bromobutane ( $2^\circ$ )

2-bromobutane is a  $2^\circ$  alkylhalide whereas 1-bromobutane is a  $1^\circ$  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.

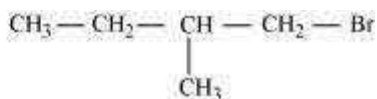
**(ii)**

2-Bromobutane is  $2^\circ$  alkylhalide whereas 2-bromo-2-methylpropane is  $3^\circ$  alkyl halide. Therefore, greater numbers of substituents are present in  $3^\circ$  alkyl halide than in  $2^\circ$  alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an  $S_N2$  mechanism.

(iii)



1-Bromo-3-methylbutane ( $1^\circ$ )



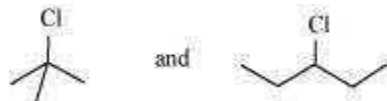
1-Bromo-2-methylbutane ( $1^\circ$ )

Both the alkyl halides are primary. However, the substituent  $-\text{CH}_3$  is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by  $\text{S}_{\text{N}}2$  mechanism.

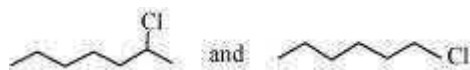
#### Question 10.8:

In the following pairs of halogen compounds, which compound undergoes faster  $\text{S}_{\text{N}}1$  reaction?

(i)



(ii)

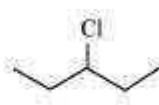


Answer

(i)



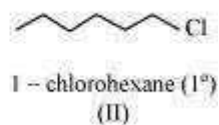
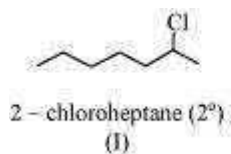
2-Chloro-2-methylpropane ( $3^\circ$ )  
(I)



3-chloropentane ( $2^\circ$ )  
(II)

$\text{S}_{\text{N}}1$  reaction proceeds via the formation of carbocation. The alkyl halide (I) is  $3^\circ$  while (II) is  $2^\circ$ . Therefore, (I) forms  $3^\circ$  carbocation while (II) forms  $2^\circ$  carbocation. Greater the stability of the carbocation, faster is the rate of  $\text{S}_{\text{N}}1$  reaction. Since  $3^\circ$  carbocation is more stable than  $2^\circ$  carbocation. (I), i.e. 2-chloro-2-methylpropane, undergoes faster  $\text{S}_{\text{N}}1$  reaction than (II) i.e., 3-chloropentane. **(ii)**

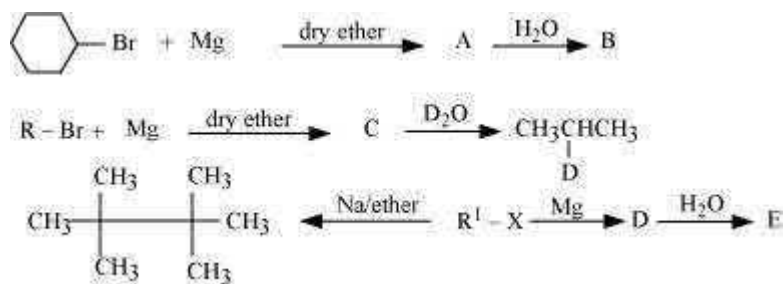




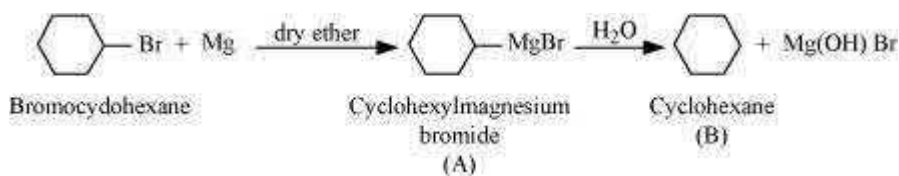
The alkyl halide (I) is 2° while (II) is 1°. 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2-chloroheptane, undergoes faster S<sub>N</sub>1 reaction than (II), 1-chlorohexane.

### Question 10.9:

Identify A, B, C, D, E, R and R<sup>1</sup> in the following:



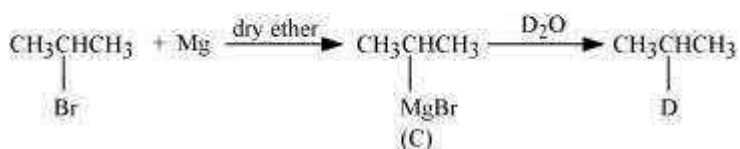
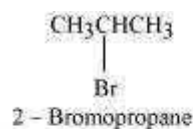
Answer



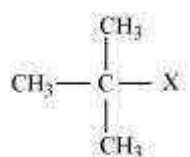
Since D of D<sub>2</sub>O gets attached to the carbon atom to which MgBr is attached, C is



Therefore, the compound R - Br is

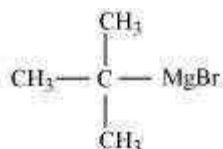


When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product. This is known as Wurtz reaction. Therefore, the halide,  $R^1-X$ , is



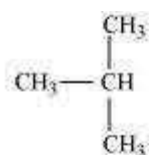
*tert*-Butylhalide

Therefore, compound D is



*tert*-Butylmagnesiumbromide

And, compound E is



2-Methylpropane

