Class XII : Chemistry Chapter 6 : Haloalkanes And Haloarenes

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Q1 :

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)

$$\dot{c}H_{3}$$
 $-\dot{c}H_{2}$ $-\dot{c}H$ $-\dot{c}H$ $-\dot{c}H_{2}$ $-\dot{c}H_{2}$ $-\dot{c}H_{3}$
 CH_{3} $-\dot{c}H_{3}$ $-\dot{c}H_{3}$
 CH_{3} $-\dot{c}H_{3}$

4- tert-Butyl-3-iodoheptane

(iv)
$$Br - CH_2 - CH = CH_2 - CH_2 - Br$$

1, 4-Dibromobut-2-ene

(v)

$$CH_{3} - CH - CH_{2} - CH_{3}$$

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

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Q2 :

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

Answer:

In the presence of sulphuric acid (H₂SO₄), KI produces HI

$$2 \text{KI} + \text{H}_2 \text{SO}_4 \longrightarrow 2 \text{KHSO}_4 + 2 \text{HI}$$

Since H_2SO_4 is an oxidizing agent, it oxidizes HI (produced in the reaction to I_{2}).

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O_2$$

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 H₃PO₄ is used.

Q3 :

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.

1, 1-Dibromopropane

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2, 2-Dibromopropane

(iii)

1, 2-Dibromopropane

(iv)

1, 3-Dibromopropane

Q4 :

Among the isomeric alkanes of molecular formula C₅H₁₂, 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 $C_{s}H_{12}$. 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 C_5H_{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.

$$C\dot{H}_{3}-C\dot{H}_{2}-C\dot{H}_{2}-C\dot{H}_{2}-C\dot{H}_{3}$$

n-Pentane

(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of Hatoms labelled as *a*, *b*, *c*, and *d* in 2-methylbutane.

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Q5 :

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



(iv) $\begin{array}{c} & & \\ & & \\ & & \\ & & \\ \end{array}^{CH_3} + HI \longrightarrow & \\ & & \\ 1 - Methylcyclohexene & 1 - Iodo - 1 - methylcyclohexane \\ (v) & \\ & \\ & \\ CH_3CH_2Br + NaI \longrightarrow & CH_3CH_2I + NaBr \\ & \\ & Bromoethane & Iodoethane \\ (vi) & \\ & \\ & \\ & \\ & \\ & \\ \end{array}$

Cyclohexene 3 – Bromocyclohexene

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Q6 :

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

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

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

Answer :			Br	Br
(i)	CH ₃ — Cl	CH ₃ — Br	CH ₂ — Br	Br-CH-B
	Chloromethane	Bromomethane	Dibromomethane	Bromoform

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 CI, 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) $\begin{array}{c} CI \\ I \\ CH_3 \longrightarrow CH \longrightarrow CH_3 \\ Isopropyl chloride \\ I - Chloropropane \\ I - Chloroputane \\ I - Chlo$

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

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Q7 :

Which alkyl halide from the following pairs would you expect to react more rapidly by an S_№2 mechanism? Explain your answer.

(i)

CH₃CH₂CH₂CH₂CH₂Br or CH₃CH₂CHCH₃ Br(ii) CH₃CH₂CHCH₃ or H₃C-C-D Br

(iii)

Br

H₃C or CH₃CH₂CHCH₂Br CH3CHCH2CH2Br or CH₃ CH₃

CH₃

Answer :

(i)

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 2bromobutane by an S_N 2 mechanism.

(ii)

$$\begin{array}{c} CH_3 \longrightarrow CH_2 \longrightarrow CH_3 \longrightarrow CH$$

2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3° alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide to hinder the approaching nucleophile. Hence, 2bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S2 mechanism.

(iii)

$$\begin{array}{c} CH_3 \longrightarrow CH \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow Br \\ | \\ CH_3 \\ I - Bromo - 3 - methylbutane (1^\circ) \\ \end{array} \qquad \begin{array}{c} CH_3 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow Br \\ | \\ CH_3 \\ I - Bromo - 2 - methylbutane (1^\circ) \\ \end{array}$$

Both the alkyl halides are primary. However, the substituent $-CH_3$ 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 $S_N 2$ mechanism.

Q8 :

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



 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. Since 3° carbocation is more stable than 2° carbocation. (I), i.e. 2-chloro-2-methylpropane, undergoes faster S_N1 reaction than (II) i.e., 3-chloropentane.

(ii)



Cl 1 - chlorohexane (1°) (II)

The alkyl halide (I) is 2° while (II) is 1°. 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2chloroheptane, undergoes faster $S_N 1$ reaction than (II), 1-chlorohexane.

Q9 :

Identify A, B, C, D, E, R and R¹ in the following:

X.



Answer :



Since D of D₂O gets attached to the carbon atom to which MgBr is attached, C is

CH3CHCH3 MgBr IsopropyImagnesium bromide

Therefore, the compound R - Br is

CH3CHCH3 Br 2 - Bromopropane CHCH2 + M2 dry ethe



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, R¹-X, is



Therefore, compound D is



And, compound E is

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Q1:

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

- (i) (CH₃)₂CHCH(CI)CH₃
- (ii) CH₃CH₂CH(CH₃)CH(C₂H₅)CI
- (iii) CH₃CH₂C(CH₃)₂CH₂I
- (iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$
- (v) $CH_3CH(CH_3)CH(Br)CH_3$
- (vi) $CH_3C(C_2H_5)_2CH_2Br$
- (vii) $CH_3C(CI)(C_2H_5)CH_2CH_3$
- (viii) CH₃CH=C(CI)CH₂CH(CH₃)₂
- (ix) CH₃CH=CHC(Br)(CH₃)₂
- (x) p-CIC₆H₄CH₂CH(CH₃)₂
- (xi) m-CICH₂C₆H₄CH₂C(CH₃)₃
- (xii) o-Br-C₆H₄CH(CH₃)CH₂CH₃

Answer :

Å

(i)

2-Chloro-3-methylbutane

(Secondary alkyl halide)

(ii)

$$CH_3 CI$$

 $4 | 3 | 2 I$
 $CH_3 - CH_2 - CH - CH - CH_2 - CH_3$

3-Chloro-4-methyhexane

(Secondary alkyl halide)

(iii)



1-lodo-2, 2 -dimethylbutane (Primary alkyl halide) (iv)

$$\begin{array}{c} CH_3 & Br \\ \downarrow \\ CH_3 & CH_2 & \downarrow \\ CH_3 & CH_2 & CH \end{array}$$

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

(v)

$$\begin{array}{c} CH_3 & Br \\ 4 & 3 & 2 \\ CH_3 & CH & CH \\ \end{array}$$

2-Bromo-3-methylbutane

(Secondary alkyl halide) (vi)

$$\begin{array}{c} C_2H_5\\ CH_3 \longrightarrow C \longrightarrow CH_2\\ 3 \\ CH_2\\ 4 \\ CH_3\\ CH_3\end{array} = Br$$

1-Bromo-2-ethyl-2-methylbutane

(Primary alkyl halide)

(vii)

$$CH_{3} \rightarrow C - CH_{2} \rightarrow CH_{3}$$

$$CH_{3} \rightarrow C - CH_{2} - CH_{3}$$

$$CH_{2} - CH_{2} - CH_{3}$$

$$CH_{3} - CH_{3}$$

3-Chloro-3-methylpentane

(Tertiary alkyl halide)

(viii)

$$ch = ch^{-2} ch^{-2}$$

3-Chloro-5-methylhex-2-ene

(Vinyl halide)

(ix)

$$c_{H_3}^2 - c_H = c_H^3 - c_H^{H_1} - c_H^{H_2} - c_{H_3}^{Br}$$

4-Bromo-4-methylpent-2-ene

(Allyl halide)

(X)



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

(xi)

$$\begin{array}{c} \begin{array}{c} CH_{3}\\ CH_{2} \xrightarrow{2^{\prime}} C \xrightarrow{2^{\prime}} CH_{3}\\ \begin{array}{c} 3\\ \end{array} \\ \begin{array}{c} 3\\ \end{array} \\ \begin{array}{c} 3\\ \end{array} \\ \begin{array}{c} 2\\ \end{array} \\ \begin{array}{c} CH_{2}\\ \end{array} \\ \begin{array}{c} CH_{3}\\ \end{array} \\ \begin{array}{c} CH_{2}CI \end{array} \end{array}$$

CH.

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

(Primary benzyl halide)

(xii)

$$CH_{3} \xrightarrow{I'}_{CH} \xrightarrow{2'}_{CH_{2}} \xrightarrow{3'}_{CH_{3}} CH_{3}$$

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

(Aryl halide)

Q2 :

Give the IUPAC names of the following compounds:

(i) CH₃CH(CI)CH(Br)CH₃

(ii) CHF₂CBrCIF

(iii) CICH₂Câ‰Â¡CCH₂Br

(iv) (CCI₃)₃CCI

(v) $CH_3C(p-CIC_6H_4)_2CH(Br)CH_3$

(vi) (CH₃)₃CCH=CCIC₆H₄I-p

Answer :

(i)

$$CI$$
 Br
 $_{4}$ $_{3}$ $_{2}$ $_{1}$ $_{2}$ $_{1}$

2-Bromo-3-chlorobutane

(ii)



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

Å

(iii)

$$CI = {}^{4}CH_{2} = {}^{3}C \equiv {}^{2}C = {}^{1}CH_{2} = Br$$

1-Bromo-4-chlorobut-2-yne

(iv)



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

(v)



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

(vi)



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

Q3 :

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

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- (v) Perfluorobenzene
- (vi) 4-tert-Butyl-3-iodoheptane
- (vii) 1-Bromo-4-sec-butyl-2-methylbenzene
- (viii) 1,4-Dibromobut-2-ene

Answer :

(i)

$$\begin{array}{ccc} CI & CH_3 \\ 1 & 2 \\ CH_3 & CH & CH \\ \hline \end{array} \begin{array}{c} CH & CH_3 \\ -CH & CH \\ \hline \end{array} \begin{array}{c} CH_3 \\ -CH \\ -CH \\ \hline \end{array} \begin{array}{c} CH_3 \\ -CH_3 \\ \hline \end{array} \begin{array}{c} SH_3 \\ -CH_3 \\ -CH_3 \\ \hline \end{array} \begin{array}{c} SH_3 \\ -CH_3 \\ -CH_3 \\ \hline \end{array} \begin{array}{c} SH_3 \\ -CH_3 \\ -CH_3 \\ -CH_3 \\ \hline \end{array} \begin{array}{c} SH_3 \\ -CH_3 \\ -CH_$$



(ii)



p-Bromochlorobenzene

(iii)



1-Chloro-4-ethylcyclohexane

(iv)



2-(2-Chlorophenyl)-1-iodooctane

(v)





Å





4-Tert-Butyl-3-iodoheptane

(vii)

$$CH_3 \longrightarrow CH \longrightarrow CH_2 \longrightarrow CH_3$$

 $5 \longrightarrow 4$
 $6 \longrightarrow 1$
 CH_3
 CH_3

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

(viii)

$$Br - CH_2 - CH = CH_2 - H_2 - BH_2 - BH_2$$

1,4-Dibromobut-2-ene

Q4 :

Which one of the following has the highest dipole moment?

(i) CH₂Cl₂

(ii) CHCl₃

(iii) CCI₄

Answer :

(i)

Dichlormethane (CH₂Cl₂)

μ = 1.60D

(ii)

Chloroform (CHCl₃)

μ = 1.08D

(iii)



Carbon tetrachloride (CCl₄)

 $\tilde{A}\check{Z}\hat{A}^{1}_{4} = 0D$

CCl₄ is a symmetrical molecule. Therefore, the dipole moments of all four C-Cl bonds cancel each other. Hence, its resultant dipole moment is zero.

As shown in the above figure, in CHCI₃, the resultant of dipole moments of two C-CI bonds is opposed by the resultant of dipole moments of one C-H bond and one C-CI bond. Since the resultant of one C-H bond and one C-CI bond dipole moments is smaller than two C-CI bonds, the opposition is to a small extent. As a result, CHCI₃ has a small dipole moment of 1.08 D.

On the other hand, in case of CH_2CI_2 , the resultant of the dipole moments of two C-CI bonds is strengthened by the resultant of the dipole moments of two C-H bonds. As a result, CH_2CI_2 has a higher dipole moment of 1.60 D than $CHCI_3$ i.e., CH_2CI_2 has the highest dipole moment.

Hence, the given compounds can be arranged in the increasing order of their dipole moments as: CCl_4 < $CHCl_3 < CH_2Cl_2$

Q5 :

A hydrocarbon C₅H₁₀ does not react with chlorine in dark but gives a single monochloro compound C₅H₅CI in bright sunlight. Identify the hydrocarbon.

Answer :

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

Since hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane.

Further, the hydrocarbon gives a single monochloro compound, C_5H_3CI by reacting with chlorine in bright sunlight. Since a single monochloro compound is formed, the hydrocarbon must contain H-atoms that are all equivalent. Also, as all H-atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.

Cyclopentane (C₅H₁₀)

The reactions involved in the question are:

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Q6 :

Write the isomers of the compound having formula C_4H_9Br .

Answer :

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

$$\overset{4}{C}H_{3}\overset{}{\longrightarrow}\overset{3}{C}H_{2}\overset{}{\longrightarrow}\overset{2}{C}H_{2}\overset{}{\longrightarrow}\overset{1}{C}H_{2}\overset{}{\longrightarrow}Br$$

1-Bromobutane

(b)

(c)

$$2 H_3$$

CH₃-CH-CH₂-B

1-Bromo-2-methylpropane

(d)



2-Bromo-2-methylpropane

Q7 :

Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol

(ii)1-chlorobutane (iii) but-1-ene.

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Answer: (i) $CH_3 - CH_2 - CH_2 - CH_2 - OH + HI \xrightarrow{ZnCl_2} CH_3 - CH_2 - CH_2 - CH_2 - 1 + H_2O$ 1 - Iodobutane 1 - Butanol (ii) dry acetone $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CI + NaI$ (Finkelstein 1 - Chlorobutane reaction) NaCl + CH₃-CH₂-CH₂-CH₂-CH₂-T 1 - Iodobutane (iii) Peroxide $CH_3 - CH_2 - CH = CH_2 + HBr \frac{Peroxide}{(Anti - Markovnikov's)}$ addition) NaBr + CH₃-CH₂-CH₂-CH₂-I Nal/dry acetone CH₃-CH₂ 1 - Iodobutane I - Bromobutane

Q8 :

What are ambident nucleophiles? Explain with an example.

Answer :

Ambident nucleophiles are nucleophiles having two nucleophilic sites. Thus, ambident nucleophiles have two sites through which they can attack.

For example, nitrite ion is an ambident nucleophile.

$$[0 - N = 0]$$

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

$$R^{0}$$

R - N

Alkylnitrite

Nitroalkane

Q9:

Which compound in each of the following pairs will react faster in S_N2 reaction with OH?

(i) CH₃Br or CH₃I

(ii) (CH₃)₃CCI or CH₃CI

Answer :

(i) In the $S_N 2$ mechanism, the reactivity of halides for the same alkyl group increases in the order. This happens because as the size increases, the halide ion becomes a better leaving group.

R-F << R-Cl < R-Br < R-I

Therefore, CH_3I will react faster than CH_3Br in S_N2 reactions with OH.

(ii)

$$H_{3}C \xrightarrow{CH_{3}}{l}C H_{3} \xrightarrow{CH_{3}}{CH_{3}} CH_{3} \xrightarrow{CH_{3}}{CH_{3}} CH_{3}$$

The $S_N 2$ mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in case of $(CH_3)_3CCI$, 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_3CI . Hence, CH_3CI reacts faster than $(CH_3)_3CCI$ in $S_N 2$ reaction with OH.

Q10:

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

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

Answer:

(i)

(i)

In the given compound, there are two types of ÃŽÂ²-hydrogen atoms are present. Thus, dehydrohalogenation of this compound gives two alkenes.

(ii)

In the given compound, there are two different sets of equivalent $\tilde{A}\check{Z}\hat{A}^2$ -hydrogen atoms labelled as *a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.

Saytzeff's rule implies that in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced.

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

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

In the given compound, there are two different sets of equivalent $\tilde{A}\check{Z}\hat{A}^2$ -hydrogen atoms labelled as *a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.

According to Saytzeff's rule, in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to the doubly bonded carbon atom is preferably formed.

Hence, alkene (I) i.e., 3,4,4-trimethylpent-2-ene is the major product in this reaction.

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Q11 :

How will you bring about the following conversions?

(i) Ethanol to but-1-yne

(ii) Ethane to bromoethene

(iii) Propene to 1-nitropropane

(iv) Toluene to benzyl alcohol

(v) Propene to propyne

(vi) Ethanol to ethyl fluoride

(vii) Bromomethane to propanone

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

Answer :

(i)

 $\begin{array}{c} CH_{3}CH_{2}OH \xrightarrow{SOCl_{2}. Pyridine} CH_{3}CH_{2}Cl + SO_{2} + HCl \\ Ethanol Chloroethane \\ HC \equiv CH + NaNH_{2} \xrightarrow{Liq.NH_{3}} HC \equiv C \overset{+}{N} a \\ Ethyne Sodium acetylide \\ CH_{3}CH_{2} - Cl + HC \equiv C \overset{+}{N} a \longrightarrow CH_{3}CH_{2}C \equiv CH + NaCl \\ Chloroethane But - 1 - yne \\ (ii) \\ CH_{3} - CH_{3} \xrightarrow{Br_{2}/UV \ light} CH_{3} - CH_{2}Br + HBr \\ Ethane & -HBr KOH(ale), \Delta \end{array}$

Br
$$CH_2 - CH_2$$
 Br 4 Br_2/CCl_4 $CH_2 = CH_2$
vic-Dibromide Ethene
 $\Delta \downarrow$ KOH(alc)
 $CH_2 = CH$ Br
Bromoethane

Å

(iii) $CH_3 - CH = CH_2 + HBr$ Peroxide \sim $CH_3 - CH_2 - CH_2Br$ 1-Bromopropane Propene Ag NO₂ Ag Br + CH3 - CH2 - CH2 NO2 1-Nitropropane CH₃ CH₂Cl CH₂OH Cl₂/UV light NaOH (alc) (iv) or heat NaCl Toluene Benzyl chloride Benzyl alcohol NaNH: Br₂/CCl₄ (v) $CH_3 - CH = CH_2$ $H_3 - C \equiv CH$ CH3 CH LiqNH₃ Propene Propyne Br Br 1, 2-Dibromopropane PC15 (vi) CH3 - CH2 - OH -CH₃ - CH₂ - Cl -POCl₃, -HCl Ethanol Chloroethane AgF CH3-CH2-F Ethyl fluoride KCN (alc) \leftarrow CH₃ - CN $\xrightarrow{CH_3 - MgBr}$ CH₃ - C = NMgBr (vii) CH₂ - Br Bromethane Acetonitrile CH₃ Hydrolysis H₃O⁺ $CH_3 - C = O$ CH₃ Propanone

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Q12 :

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?

Answer :





Chlorobenzene

Cyclohexyl chloride

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In chlorobenzene, the CI-atom is linked to a sp^2 hybridized carbon atom. In cyclohexyl chloride, the CI-atom is linked to asp^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 CI-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 waterwater forces of attraction. Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the alkyl halide-alkyl halide and water-water forces of attraction. Hence, alkyl halides (though polar) are immiscible with water.

(iii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes.

$$\begin{array}{ll} \overset{\delta-}{R}\overset{\delta+}{M}g\overset{\delta-}{X} &+ H_2O \longrightarrow R-H + Mg(OH)X \\ Grigrand & Alkane \end{array}$$

reagent

Therefore, Grignard reagents should be prepared under anhydrous conditions.

Q13 :

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

Answer :

Uses of Freon - 12

Freon-12 (dichlorodifluoromethane, CF_2CI_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 (CCI₄)

(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.

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

Uses of iodoform (CHI₃)

lodoform 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.

Q14 :

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

(i)
$$CH_3CH_2CH_2Cl + Nal \xrightarrow{acetone}{beat}$$

- (ii) $(CH_3)_3 CBr + KOH \xrightarrow{\text{ethanol}} heat$
- (iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{water} \rightarrow$

(iv)
$$CH_3CH_3Br + KCN \xrightarrow{aq.ethanol}$$

(v)
$$C_6H_5ONa + C_2H_5Cl \longrightarrow$$

(vi)
$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$$

(vii)
$$CH_3CH_3CH = CH_3 + HBr \xrightarrow{Peroxide}$$

(viii)
$$CH_3CH = C(CH_3)_2 + HBr \longrightarrow$$

Answer :

(i)
$$CH_3CH_2CH_2CI + NaI \xrightarrow{acetone} CH_3CH_2CH_2I + NaCl1-Chloropropane
$$\begin{pmatrix} Finkelstein \\ reaction \end{pmatrix} 1-Iodopropane$$$$

(ii)

$$(CH_3)_3 CBr + KOH \xrightarrow{\text{ethanol}} CH_3 - C = CH_2 + KBr + H_2O$$
2-Bromo-2-methylpropane (Dehydrohalogenation)
$$CH_3$$

2-Methylpropene

(iii)
$$CH_3CH(Br)CH_2CH_3 + NaOH \longrightarrow CH_3CH(OH)CH_2CH_3 + NaBr$$

2-Bromobutane Butan - 2 - ol

<mark>∛</mark>Saral

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Q15 :

Write the mechanism of the following reaction:

 $nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$

Answer :

The given reaction is:

 $nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$

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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. CN ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



Q16 :

Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

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

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

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

Answer :

(i)

Br Br CH3CH2CH2CHCH3 CH3CH5CCH3 CH3CH5CH5CH5CH5-Bt CH3 2-Bromo-2-methylbutane (3°) 1-Bromopentane (1°) 2-Bromopentane (2°)

An $S_N 2$ reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards $S_N 2$ displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases in the following order.

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

Hence, the increasing order of reactivity towards S_{N^2} displacement is:

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

(ii)



Since steric hindrance in alkyl halides increases in the order of $1^{\circ} < 2^{\circ} < 3^{\circ}$, the increasing order of reactivity towards S_N2 displacement is $3^{\circ} < 2^{\circ} < 1^{\circ}$.

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

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

is incorrectly given in NCERT]

(iii)

CH₃ | CH₃ - CH₂ - CH - CH₂ - Br $CH_3 = CH_3 - C - CH_2 - Br$

1-Bromo-2-methylbutane

1-Bromo-2, 2-dimethylpropane

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: 1-Bromobutane < 1-Bromo-2-methylbutane

< 1-Bromo-2, 2-dimethylpropane

Hence, the increasing order of reactivity of the given compounds towards S_N2 displacement is: 1-Bromo-2, 2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3- methylbutane < 1-Bromobutane

Q17 :

Out of C6H5CH2CI and C6H5CHCIC6H5, which is more easily hydrolysed by aqueous KOH?

Answer :

Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. Now, forms 1°-carbocation, while forms 2°-carbocation, which is more stable than 1°-carbocation. Hence, is hydrolyzed more easily than by aqueous KOH.

Q18 :

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

Discuss.

Answer :

<mark>∛</mark>Saral



p-Dichlorobenzene o-Dichlorobenzene m-Dichlorobenzene

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.

Q19:

How the following conversions can be carried out?

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

Answer :

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(i) HBr / Peroxide CH1-CH=CH2 CH₃-CH₂-CH₂-Br 1 - Bromopropane Propene (Ani - Markovnikov addition (Nucleophilic Aq KOH / A substitution) $CH_3 - CH_2 - CH_2 - OH$ Propan - 1 - ol (ii) red P / Br₂ ► CH₃CH₂Br -Mg / ether CH₃CH₂MgBr CH3CH2OH Ethanol Ethyl bromide Ethyl magnesium bromide (Grignard reaction) ether H/H2O [CH₃CH₂CH₂CH₂OMgBr] CH3CH2CH2CH2OH 1 - Butanol Addition product red P/I2 KOH (alc) $/\Delta$ CH3CH2CH2CH2-I CH3CH2CH=CH2 (Dehydrohalogenation) But - 1 - ene Iodobutane (Electrophilic Br₄/CCl₄ addition) CH₃CH₂CH - CH₂ NaNH2, liq NH3 CH₃CH₂CH = CH 196 K Br Br But - 1 - yne (Dehydrohalogenation) 1, 2 - Dibromobutane (iii) CH3-CH2-CH2-Br KOH (alc) / Δ $CH_3 - CH = CH_2$ 1 - Bromopropane (Dehydrohalogenation) Markovnikov Propene HBr addition Br CH₃-CH-CH₃ 2 - bromopropane (iv) CH₂Cl CH₂OH CH3 Cl2 / UV light Aq. KOH / A or heat (nucleophilic substitution) Benzyl Benzyl Toluene alcohol chloride

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X.

(xi) KCN, aq. ethanol CH₃-CH₂-CI CH₃ - CH₂ - CN + KCl (nucleophilic Ethylchloride Propanenitrile substitution) (Hydrolysis) H^+/H_2O CH3 - CH2 - COOH Propanoic acid (xii) CH₃-CH₂-CH=CH₂ HBr / Peroxide CH₃ - CH₂ - CH₂ - CH₂ - Br (Anti - Markovnikov But-1-ene 1 - Bromobutane addition) Finkelstein NaI, dry acetone reaction $CH_3 - CH_2 - CH_2 - CH_2 - I$ n - Butyliodide (xiii) Cl KOH (alc) / Δ CH₃ - CH - CH₃ $CH_3 - CH = CH_2$ HCI 2 - Chloropropane (Dehydrohalogenation) Propene (Anti - Markovnikov HBr / Peroxide addition) Aq. KOH / A CH₃ - CH₂ - CH₂ - Br CH3-CH2-CH2-OH · (Nucleophilic 1 - Bromopropane 1 - Propanol substitution) (xiv) OH CrO₃ CH₃ – CH – CH₃ CH3 (Oxidation) Propanone Isopropyl alcohol (Iodoform reaction) NaOI CH3 + CHI₂ ONa

Iodoform

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(xv) HNO3/H2SO4 (Nitration) NO₂ Chlorobenzene p - Chloronitrobenzene m - Chloronitrobenzene o - Chloronitrobenzene (Major product) OH (i) NaOH, 433 K (ii) dil HCl NO₂ NO2 p-Nitrophenol p - Chloronitrobenzene (xvi) Br CH₃-CH-CH₃ KOH (alc) / A $CH_3 - CH = CH_2 + HBr$ 2 - Bromopropane Dehydrohalogenation Propene HBr / Peroxide (Anti-Markovnikov addition) CH₁ - CH₂ - CH₂ - Br 1-Bromopropane (xvii) 2 Na / dry ether (Wurtz reaction) CH₃ - CH₂ - CH₂ - CH₃ CH3-CH2-Cl 2NaCl Butane Chloroethane (xviii) Br₂ / FeBr₃ 2Na / dry ether 2NaBr (Fittig reaction) Benzene Biphenyl (xix) Br KOH (alc) / Δ HBr / Peroxide CH3 CH₃ CH3 CH₃-CH-CH₂-Br (Dehydrohalogenation) (Anti-Markovnikov Br CH₁ addition) ĊH₃ Tert-Butylbromide 2-Methylpropene Isobutyl bromide

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(xx)



Q20 :

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.

Answer :

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.

$$R - Cl + KOH_{(aq)} \longrightarrow R - OH + KCl$$

Alcohol

Alkyl

chloride

On the other hand, an alcoholic solution of KOH contains alkoxide (RO·) ion, which is a strong base. Thus, it can abstract a hydrogen from the ÃŽÂ²-carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCI.

$$R - \underset{\beta}{C}H_{2} - \underset{\alpha}{C}H_{2} - CI + KOH(alc) \longrightarrow R - CH = CH_{2} + KCI + H_{2}O$$

Alkyl chloride Alkene

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 β-carbon.

Q21 :

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

Answer :

There are two primary alkyl halides having the formula, C_4H_9Br . They are *n* - bulyl bromide and isobutyl bromide.

$$CH_3 - CH_2 - CH_2 - CH_2 - Br$$
 $CH_3 - CH - CH_2 - Br$

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, $C_{\$}H_{18}$, which is different from the compound formed when *n*-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

Isobutyl bromide (a)

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 2methylpropene.

2, 5 - Dimethylhexane

(d)

$$\begin{array}{c} CH_{3} - CH - CH_{2} - Br & \hline{KOH(alc)/\Delta} \\ & & & \\ & & \\ & & \\ CH_{3} & & \\ Isobutyl chloride & & \\ & & & \\ & & & \\ &$$

Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2bromo2-methylpropane.

Br

$$CH_{3} - CH = CH_{2} \xrightarrow{HBr} CH_{3} - CH_{3} - CH_{3} - CH_{3}$$

$$\downarrow CH_{3} - CH_{3}$$

Q22 :

What happens when

- (i) n-butyl chloride is treated with alcoholic KOH,
- (ii) bromobenzene is treated with Mg in the presence of dry ether,
- (iii) chlorobenzene is subjected to hydrolysis,
- (iv) ethyl chloride is treated with aqueous KOH,
- (v) methyl bromide is treated with sodium in the presence of dry ether, (vi) methyl chloride is treated with KCN.

Answer :

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

$$CH_3 - CH_2 - CH_2 - CH_2 - Cl \xrightarrow{KOH(alc)/\Delta}$$

n – Butyl chloride

 $CH_3 - CH_2 - CH = CH_2 + KCl + H_2O$ But-l-ene

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



Bromobenzene

Phenylmagensium bromide

(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.

$$CH_3 - CH_2 - CI \xrightarrow[(Hydrolysis)]{KOH_{(aq)}} CH_3 - CH_2 - OH + KCI$$

Ethyl chloride

Ethanol

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

$$2 \text{ CH}_3 - \text{Br} + 2 \text{ Na} \xrightarrow{\text{Dry ether}} \text{CH}_3 - \text{CH}_3 + 2 \text{NaBr}$$

Methyl bromide

N

Ethane

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

$$CH_3 - CI + KCN \xrightarrow{\text{Nucleophilic substitution}} CH_3 - CN + KCl$$

Iethylchloride Methylcyanide