Chapter – 14

Haloalkanes and Haloarenes

Textbook Evaluation:

I. Choose the best Answer:

Question 1.



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Answer:
b) 4 – Bromo pent – 2 – ene
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Question 2.

Of the following compounds, which has the highest boiling point? a) n – Butyl chloride b) Isobutyl chloride c) t – Butyl chloride d) n – Propyl chloride

Answer: a) n – Butyl chloride

Question 3.

Arrange the following compounds in increasing order of their density A) CCl₄ B) CHCl₃ C) CH₂Cl₂ D) CH₃Cl

a) D < C < B < A

 \dot{b} C > B > A > D

c) A < B < C < D d) C > A > B > D

Answer:

a) D < C < B < A

Question 4.

With respect to the position of – Cl in the compound $CH3 - CH = CH - CH_2 - Cl$, it is classified as a) Vinyl

a) viiiyi

- b) Allyl
- c) Secondary
- d) Aralkyl

Answer:

b) Allyl

Question 5.

What should be the correct IUPAC name of diethyl chloromethane?

- a) 3 Chloro pentane
- b) 1 Chloropentane
- c) 1 Chloro 1, 1 diethyl methane
- d) 1- Chloro-1-ethyl propane

Answer:

a) 3 – Chloro pentane

Question 6.

C – X bond is strongest ina) Chloromethaneb) Iodomethanec) Bromomethaned) Fluoromethane

Answer:

d) Fluoromethane





Question 8.

Which of the following compounds will give racemic mixture on nucleophilic substitution by OH- ion?

$$CH_3 - CH - CH_2Br$$

$$CH_3 - CH_2Br$$

$$CH_3 - CH_2Br$$

$$CH_3$$

$$H_{3}C - C - C_{2}H_{5}$$

$$H_{3}C - C - C_{2}H_{5}$$

$$H_{3}C - C_{2}H_{5}$$

H $CH_3 - C - C_2H_5$ iii) Cl a) (i) b) (ii) and (iii) c) (iii) d) (i) and (ii)

Answer:

c) (iii)

Question 9.

The treatment of ethyl format with excess of RMgX gives

 $\begin{array}{c}
\mathbf{R} - \mathbf{C} - \mathbf{R} \\
\mathbf{a} \\
\mathbf{R} - \mathbf{CH} - \mathbf{R} \\
\mathbf{O} \\
\mathbf{R} - \mathbf{CH} - \mathbf{R} \\
\mathbf{O} \\
\mathbf{H} \\
\mathbf{C} \\
\mathbf{R} - \mathbf{CHO} \\
\mathbf{d} \\
\mathbf{R} - \mathbf{O} - \mathbf{R} \\
\end{array}$

Answer:

c) R – CHO

Question 10.

Benzene reacts with \mbox{Cl}_2 in the presence of \mbox{FeCl}_3 and in absence of sunlight to form

- a) Chlorobenzene
- b) Benzyl chloride
- c) Benzal chloride
- d) Benzene hexachloride

Answer:

a) Chlorobenzene

Question 11.

The name of $C_2F_4C_{12}$ is a) Freon – 112 b) Freon – 113 c) Freon – 114 d) Freon – 115

Answer:

c) Freon - 114

Question 12.

Which of the following reagent is helpful to differentiate ethylene dichloride and ehtylidene chloride?
a) Zn / methanol
b) KQH / ethanol
c) aqueous KOH
d) ZnCl₂ / Con HCl

Answer:

c) aqueous KOH

Question 13.

Match the compounds given in Column I with suitable items given in Column II:

Column I (Compound)	Column II (Uses)
A. Iodoform	1. Fire extinguisher
B. Carbon tetra chloride	2. Insecticide
C. CFC	3. Antiseptic
D. DDT	4. Refrigerants

Code

a) $A \rightarrow 2 B \rightarrow 4 C \rightarrow 1 D \rightarrow 3$ b) $A \rightarrow 3 B \rightarrow 2 C \rightarrow 4 D \rightarrow 1$ c) $A \rightarrow 1 B \rightarrow 2 C \rightarrow 3 D \rightarrow 4$ d) $A \rightarrow 3 B \rightarrow 1 C \rightarrow 4 D \rightarrow 2$

Answer:

d) A \rightarrow 3 B \rightarrow 1 C \rightarrow 4 D \rightarrow 2

Question 14.

Assertion:

Inmonohaloarenes, electrophilic substitution occurs at ortho and para positions.

Reason:

Halogen atom is a ring deactivator.

Assertion and Reason type questions.

Directions:

In the following questions, a statement of assertion (A) is followed by a statement of reason (R) mark the correct choice as

(i) If both assertion and reason are true and reason is the correct explanation of assertion.

(ii) If both assertion and reason are true but reason is not the correct explanation of assertion.

(iii) If assertion is true but reason is false.

(iv) If both assertion and reason are false.

- a) (i)
- b) (ii)
- c) (iii)
- d) (iv)

Answer:

b) (ii)

Question 15.

Consider the reaction, $CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$ This reaction will be the fastest in a) ethanol b) methanol c) DMF (N, N' – dimethyl formamide) d) water

Answer:

c) DMF (N, N' – dimethyl formamide)

Question 16.

Freon – 12 manufactured from tetrachloro methane by a) Wurtz reaction

b) Swarts reaction

- c) Haloform reaction
- d) Gattermann reaction

Answer:

b) Swarts reaction

Question 17.

The most easily hydrolysed molecules under S_N^1 condition is a) allyl chloride b) ethyl chloride c) isopropyl chloride d) benzyl chloride

Answer:

a) allyl chloride

Question 18.

The carbon cation formed in S_N^1 reaction of alkyl halide in the slow step is a) sp³ hybridized b) sp² hybridized c) sp hybridized d) none of these

Answer:

b) sp² hybridized

Question 19.

The major products obtained when chlorobenzene is nitrated with HNO_3 and con H_2SO_4

- a) 1 chloro 4 nitrobenzene
- b) 1 chloro 2 nitrobenzene
- c) 1 chloro 3 nitrobenzene
- d) 1 chloro 1 nitrobenzene

Answer:

a) 1 - chloro - 4 - nitrobenzene

Question 20.

Which one of the following is most reactive towards nucleophilic substitution reaction?



Cl d)

Question 21. Ethylidene chloride on treatment with aqueous KOH gives a) acetaldehyde b) ethylene glycol c) formaldehyde d) glycoxal

Answer:

a) acetaldehyde

Question 22.

The raw material for Raschig process a) chloro benzene b) phenol c) benzene d) anisole

Answer:

c) benzene

Question 23.

Chloroform reacts with nitric acid to produce a) nitro toluene b) nitro glycerine c) chloropicrin d) chloropicric acid

Answer:

c) chloropicrin

Question 24.

i) $CH_{3}MgI$ Acetone ii) $H_{2}O / H^{-1}$ X, X is a) 2 – propanol b) 2 – methyl – 2 – propanol c) 1 – propanol d) acetonol

Answer: b) 2 – methyl – 2 – propanol

Question 25.

Silver propionate when refluxed with Bromine in carbon tetrachloride gives a) propionic acid b) chloroethane c) Bromo ethane d) chloro propane

Answer: c) bromo ethane

Question 26.

Classify the following compounds in the form of alkyl, allylic, vinyl, benzylic halides. i) $CH_3 - CH = CH - Cl$ ii) $C_6H_5CH_2I$

iv) $CH_2 = CH - Cl$

Answer:

i) $CH_3 - CH = CH - Cl = Allylic halide$

ii) $C_6H_5CH_2I =$ Benzylic halide

 $\begin{array}{c} \mathbf{CH}_{3} - - \mathbf{CH} - - \mathbf{CH}_{3} \\ | \\ \mathbf{Br} \\ \end{array} = \text{Alkyl halide}$

iv) $CH_2 = CH - Cl = Vinyl halide$

II. Write brief answer to the following questions:

Question 27.

Why chlorination of methane is not possible in dark?

Answer:

The reaction of chlorine and methane is a free radical reaction under the influence of light energy. Chlorine molecule first split into two Cl atoms or radicals. These are both very reactive species in contact with methane they form methyl radical and HCl.

Methyl radical further reacts with Cl to give CH_3Cl and another Cl atom thus of a chain reaction. So this reaction takes place only under the influence of light. Hence the reaction does not take place in dark condition.

Question 28.

How will you prepare n propyl iodide from n – propyl bromide?

Answer:

Finkelstein reaction,



Question 29.

Which alkyl halide from the following pair is i) chiral ii) undergoes faster S_N^2 reaction? Br



It contains one chiral carbon atom. 2 – bromo butane undergoes $S_{N^{2}}$ mechanism faster than 1- Chloro butane.

Question 30.

How does chlorobenzene react with sodium in the presence of ether? What is the name of the reaction?

Answer:

Haloarenes react with sodium metal in dry ether, two aryl groups combine to give biaryl products.

This reaction is called fittig reaction.

 $\begin{array}{c} \xrightarrow{\text{Ether}} \\ C_6H_5Cl + 2Na + Cl - C_6H_5 & \Delta & C_6H_5 - C_6H_5 + 2NaCl \\ Chlorobenzene & Biphenyl \end{array}$

Question 31.

Give reasons for polarity of C – X bond in halo alkane.

Answer:

Carbon halogen bond is a polar bond as halogens are more electro negative than carbon. The carbon atom exhibits a partial positive charge (δ^+) and halogen atom a partial negative charge (δ^-)



The C -X bond is formed by overlap of sp³ orbital of carbon atom with halffilled p- orbital of the halogen atom. The atomic size of halogen increases from fluorine to iodine, which increases the C – X bond length. Larger the size, greater is the bond length, and weaker is the bond formed. The bond strength of C – X decreases from C – F to C – I in CH_3X .

Question 32.

Why is it necessary to avoid even traces of moisture during the use of Grignard reagent?

Answer:

Grignard reagents are mostly reactive and react with the source of product to give hydrocarbons. Even alcohols, amines, H₂O are sufficiently acidic to convert them to corresponding hydrocarbons.

$$R Mg X + H_2O \rightarrow RH + \overset{Mg}{\smile} OH$$

Due to its high reactivity, it is necessary to avoid even traces of moisture from Grignard reagent.

Question 33.

What happens when acetyl chloride is treated with an excess of CH_3MgI ?



Question 34.

Arrange the following alkyl halide in increasing order of bond enthalpy of RX. CH₃Br, CH₃F, CH₃Cl, CH₃I

Answer:

The order is: $CH_3I < CH_3Br < CH_3Cl < CH_3F$.

Question 35.

What happens when chloroform reacts with oxygen in the presence of sunlight?

Answer:

 $2 \text{ CHCl}_3 + O_2 \rightarrow 2 \text{ COCl}_2 + 2 \text{ HCl}$

Question 36.

Write down the possible isomers of $C_5H_{11}Br$ and give their IUPAC and common names.

Answer: C₅H₁₁Br – Possible isomers 1. $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - Br \rightarrow 1$ – bromo pentane $CH_3 - CH_2 - CH_2 - CH - CH_3$ Br $\rightarrow 2$ - bromo pentane 2. $\begin{array}{c} \mathbf{CH}_3 - \mathbf{CH}_2 - \mathbf{CH} - \mathbf{CH}_2 - \mathbf{CH}_3 \\ \mathbf{Br} \\ \mathbf{Br} \\ \mathbf{Br} \end{array} \rightarrow 3 - \text{bromo pentane} \end{array}$ 3. $CH_3 \longrightarrow CH_2 \longrightarrow Br$ $CH_3 \longrightarrow CH_2 \longrightarrow Br$ $CH_3 \longrightarrow 1 - bromo 2, 2 - dimethyl propane$ 4. $\begin{array}{c} \operatorname{CH}_3 & \longrightarrow \operatorname{CH}_2 & \longrightarrow \operatorname{CH}_2 & \longrightarrow \operatorname{CH}_2 & \longrightarrow \operatorname{Br} \\ & & & & \\ & & & \\ & & & \\ & & & &$ 5. $\begin{array}{cccc} CH_3 & \longrightarrow & CH & \longrightarrow & CH & \longrightarrow & CH_3 \\ & & & & & | & & \\ & & & & | & & \\ & & & CH_3 & & Br & & \rightarrow 2 - bromo \ 3 - methyl \ butane \end{array}$ 6. $CH_{3} \xrightarrow{CH_{3}} CH_{2} \xrightarrow{CH_{2}} CH_{3}$ $H_{3} \xrightarrow{H_{2}} CH_{2} \xrightarrow{H_{3}} CH_{3} \xrightarrow{H_{2}} CH_{3}$ $H_{3} \xrightarrow{H_{3}} DR_{2} \xrightarrow{H_{3}} DR_{2} \xrightarrow{H_{3}} DR_{2} \xrightarrow{H_{3}} DR_{3}$ 7. $CH_3 \longrightarrow CH_2 \longrightarrow CH \longrightarrow CH_2 \longrightarrow Br$ | $CH_3 \longrightarrow 1 - bromo 2- methyl butane$ 8.



Question 37.

Mention any three methods of preparation of haloalkanes from alcohols.

Answer:

Haloalkanes are prepared by the following methods.

1) From alcohols:

Alcohols can be converted into halo alkenes by reacting it with any one of the following reagent.

- 1. Hydrogen halide
- 2. Phosphorous halides
- 3. Thionyl chloride.

a) Reaction with hydrogen halide:

Mixture of con. HCl and anhydrous ZnCl₂ is called Lucas Reagent.



The order of reactivity of halo acids with alcohol is in the order HI > HBr > HCl.

The order of reactivity of alcohols with halo acid is tertiary > secondary > primary.

b) Reaction with phosphorous halides:

Alcohols react with PX₅ or PX₃ to form haloalkanes.

Example:

 $CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$ Ethane Chloro ethane

 $\begin{array}{ll} 3CH_{3}CH_{2}OH + PCl_{3} \rightarrow 3 \ CH_{3}CH_{2}Cl + H_{3}PO_{3} \\ Ethanol & Chloro \ ethane \end{array}$

c) Reaction with Thionyl chloride(Sulphonyl Chloride)

 $\begin{array}{c} \text{CH}_3\text{CH}_3\text{OH} + \text{SOCl}_2 \xrightarrow{\text{Pyridine}} \text{CH}_3\text{CH}_2\text{Cl} + \text{SO}_2\uparrow + \text{HCl}\uparrow\\ \text{Ethanol} & \text{Chloro ethane} \end{array}$

Question 38.

Compare $S_{N}{}^{1}$ and $S_{N}{}^{2}$ reaction mechanisms.

	S _N 1	S _N ²
Rate law	Unimolecular (Substrate	Biomolecular (substrate and
	only)	nucleophile)
"Big Barrier"	Carbocation stability	Steric hindrance
Alkyl halide	$3^{\circ} > 2^{\circ} > 1^{\circ}$	$1^{\circ} > 2^{\circ} > 3^{\circ}$
(electrophile)		
Nucleophile	Weak (generally neutral)	Strong (generally bearing a
		negative charge)
Solvent	Polar protic (e.g.,	Polar aprotic (e.g., DMSO,
	alcohols)	acetone)
Stereo Chemistry	Mix of retention and	inversion
	inversion	

Question 39.

Reagents and the conditions used in the reactions are given below. Complete the table by writing down the product and the name of the reaction.

Reaction	Product	Name of the reac- tion
$CH_3CH_2OH + pyridine SOCl_2 \xrightarrow{pyridine} ?$		
$CH_{3}CH_{2}Br + AgF \longrightarrow ?$		
$C_{6}H_{5}Cl + Na$ ether ?		

Reaction	Product	Name of the reaction
$\frac{CH_3CH_2OH + SOCI_2}{\xrightarrow{Pyridine}}?$	$\begin{array}{c} \mathrm{CH_3CH_2Cl} + \\ \mathrm{SO_2\uparrow + HCl\uparrow} \end{array}$	Darzen's reaction
CH ₃ CH ₂ Br + AgF → ?	CH ₃ CH ₂ F + AgBr	Swartz reaction
$C_6H_5CI + Na \xrightarrow{\text{ether}} ?$	$C_6H_5 - C_6H_5 + 2NaCl$	Fittig reaction

Question 40.

Discuss the aromatic nucleophilic substitutions reaction of chlorobenzene.

Answer:

The halogen of haloarenes can be substituted by OH^- , NH_2^- or CN^- with appropriate nucleophilic reagents at high temperature and pressure.

Example:

(i) Chlorobenzene reacts with ammonium at 250 and at 50 atm to give aniline.

 $\begin{array}{c} 250^{\circ}\text{C} \\ \hline 50 \text{ atm} \end{array}$ C₆H₅Cl + 2NH₃
C₆H₅NH₂ + NH₄Cl
Chlorobenzene
Aniline

(ii) Chlorobenzcne reacts with CuCN in presence of pyridine at 250 to give phenyl cyanide.

	250°C
$C_6H_5Cl + CuCN$	Pyridine C ₆ H ₅ CN + CuCl
Chlorobenzene	Phenyl cyanide

(iii) Dows process: $C_6H_5Cl + NaOH$ C₆H₅OH + NaCl Chlorobenzene This reaction is known as Dow's process.

Question 41. Account for the following:

(i) t – butyl chloride reacts with aqueous KOH by $S_{N}{}^{1}$ mechanism while n – butyl chloride reacts with $S_{N}{}^{2}$ mechanism.

(ii) p – dichloro benzene has higher melting point than those of o – and m – dichloro benzene.

Answer:

(i) t – butyl chloride reacts with aqueous KOH by S_N^1 mechanism while n – butyl chloride reacts with S_N^2 mechanism.

It general, S_N^1 reaction proceeds through the formation, of carbocation, The tert- butyl chloride readily loses Cl ion to form stable 3° carbocation. Therefore, it reacts with aqueous KOH by S_N^1 mechanism as:

tert-butyl carbocation (stable)



On the other hand n-Butyl chloride does not undergo ionization to form n-Butyl carbocation (1°) because it is not stable. Therefore, it prefers to undergo reaction by S_N^2 mechanism, which occurs is one step through a transition state involving nucleophilic attack of OH⁻ ion from the backside with simultaneous expulsion of Cl⁻ ion from the front side.



 S_N^1 mechanism follows the reactivity order as $3^\circ > 2^\circ > 1^\circ$ while S_N^2 mechanism follows the reactivity order as $1^\circ > 2^\circ > 3^\circ$. Therefore, tertbutyl chloride (3°) reacts by S_N^1 mechanism while n-butyl chloride (1°) reacts by S_N^2 mechanism. (ii) p – dichloro benzene has higher melting point than those of o – and m – dicholoro benzene. The higher melting point of p – isomer is due to its symmetry which leads to more close packing of its molecules in the crystal lattice and consequently strong intermolecular attractive force which requires more energy for melting. p – Dihalo benzene > o – Dichloro benzene Melting point: 323 K 256 K 249 K

Question 42.

In an experiment methyl iodide in ether is allowed to stand over magnesium pieces. Magnesium dissolves and product is formed.

a) Name of the product and write the equation for the reaction.

b) Why all the reagents used in the reaction should be dry? Explain.

c) How is acetone prepared from the product obtained in the experiment?

Answer:

a) Name of the product and write the equation for the reaction.

 $CH_3I + Mg \longrightarrow CH_3MgI$

b) Why all the reagents used in the reaction should be dry? Explain. All the reagents used in the reaction should be dry because reagent reacts with H20 to produce alkane. This is the reason that everything has to be very dry during the preparation of Grignard reagents. $CH_3 - MgI + H_2O \rightarrow CH_4 +$ Methane

c) How is acetone prepared from the product obtained in the experiment?

$$\begin{array}{c} 0\\ \parallel\\ CH_3-C-Cl \end{array}$$
 + $CH_3MgI \rightarrow$

Acetyl chloride

$$CH_{3} \xrightarrow[]{O-MgI} \xrightarrow[H_{2}O]{H^{+}} \xrightarrow{H_{2}O} \xrightarrow{H_{2}O} \xrightarrow{H_{2}O}$$

$$CH_3 - C - CH_3 + Mg < I_{C1}$$

Acetone

0

Question 43.

Write a chemical reaction useful to prepare the following.

i) Freon – 12 from Carbon tetrachloride

ii) Carbon tetrachloride from carbon disulphide.

Answer:

i) Freon – 12 from Carbon tetrachloride:

Freon – 12 is prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of catalytic amount of antimony pentachloride.

 $\begin{array}{c} \text{SbCl} \\ \text{CCl}_4 + 2\text{HF} \xrightarrow{\text{SbCl}_5} 2\text{HCl} + \text{CCl}_2\text{F}_2 \\ \text{Carbon tetrachloride} & \text{Freon} - 12 \end{array}$

ii) Carbon tetrachloride from carbon disulphide.

Carbon disulphide reacts with chlorine gas in the presence of anhydrous AlCl3

as catalyst giving carbon tetra chloride.

 $\begin{array}{c} \xrightarrow{\text{Anhydrous}} \\ \text{CS}_2 + 3 \text{ Cl}_2 \\ \text{Carbon disulfide} \\ \end{array} \xrightarrow{\text{AlCl}_3} \\ \text{CCl}_4 + \text{S}_2\text{Cl}_2 \\ \text{Carbon tetrachloride} \\ \end{array}$

Question 44.

What are Freons? Discuss their uses and environmental effects.

Answer:

The chloro fluoro derivatives of methane and ethane are called freons.

Nomenclature:

Freon is represented as Freon – cba Where a = number of carbon atoms – 1; b = number of hydrogen atoms + 1 a = total number of fluorine atoms

Formula	C-1	H+1	F	Name
CFCl ₃	1-1=0	0+1=1	1	Freon-11
CF ₂ Cl ₂	1-1=0	0+1=1	2	Freon-12
$C_2F_2Cl_4$	2-1=1	0+1=1	2	Freon- 112
C ₂ F ₃ Cl ₃	2–1=1	0+1=1	3	Freon- 113

Uses:

i) Freons are used as a refrigerants in refrigerators and air conditioners.

ii) It is used as a propellant for aerosols and foams

iii) It is used as propellant for foams to spray out deodorants, shaving creams, and insecticides.

Question 45.

Predict the products when bromo ethane is treated with the following. i) KNO_2 ii) $AgNO_2$

i) KNO2:

Bromo ethane reacts with alcoholic solution of NaNO2 or KNO2 to form ethyl nitrite. $CH_3CH_2Br + KNO_2 \rightarrow CH_3CH_2 - O - N = O + KBr$ Bromoethane Ethyl nitrite

ii)AgNO₂:

Bromo ethane reacts with alcoholic solution of AgNO2 to form nitro ethane. $CH_3CH_2Br + AgNO_2 \rightarrow CH_3CH_2 NO_2 + AgBr$ Bromoethane Nitro ethane

Question 46.

Explain the mechanism of $S_{\ensuremath{\mathbb{N}}\xspace}^1$ reaction by highlighting the stereochemistry behind it.

Answer:



In S_{N^1} reactions, if the alkyl halide is optically active, the product obtained in a racemic mixture. The intermolecular carbocation formed in slowest step being sp2 hybridised is planar species. Therefore the attack of the nucleophile OH on it, can occur from both the faces with equal case forming a mixture of two enantiomers. Thus S_{N^1} reaction of optically active alkyl halides are accompained by racemisation.

Question 47.

Write short notes on the following. i) Raschig process ii) Dows processiii) Darzen's process

Answer:

i) Raschig process:

Chloro benzene is commercially prepared by passing a mixture of benzene vapour, air and HCl overheated cupric chloride, this reaction is called the Raschig process,



ii) Dows Process:

 $C_6H_5Cl + NaOH$ $350^{\circ}C$ $C_6H_5OH + NaCl$ This reaction is known as Dows process.

iii) Darzen's process:

 $\begin{array}{c} 350^{\circ}\text{C} \\ \text{CH}_{3}\text{CH}_{2}\text{OH} + \text{SOCI} \end{array} \xrightarrow{350^{\circ}\text{C}} \text{CH}_{3}\text{CH}_{2}\text{Cl} + \text{SO}_{2}\uparrow + \text{HCl}\uparrow \\ \text{Ethanol Chloro ethane} \end{array}$

This reaction is known as Darzen's process.

Question 48. Starting from CH₃MgI, How will you prepare the following? i) Acetic acid ii) Acetone iii) Ethyl acetate iv) Iso propyl alcohol v) Methyl cyanide

i) Acetic acid:

Solid carbon dioxide reacts with methyl magnesium iodide to form addition product which on hydrolysis yields aceti acid.



ii) Acetone:

Acetyl chloride reacts with methyl magnesium iodide and followed by acid hydrolysis to give acetone.



iii) Ethyl Acetate:

Ethyl chloroformate reacts with methyl magnesium iodide to form ethyl acetate.

 $\begin{array}{c} O \\ H \\ C_{2}H_{5}O-C-CI+CH_{3}MgI \longrightarrow C_{2}H_{5}O & -C-CI \\ I \\ Ethylchloroformate & CH_{3} \\ \hline \\ CH_{3}-C-OC_{2}H_{\sharp} Mg \\ I \\ O \\ Ethylacet \\ ate \end{array}$

iv) Isopropyl alcohol:

Aldehydes (Acetaldehyde) other than formaldehyde, react with methyl magnesium iodide to give addition product which on hydrolysis yields isopropyl alcohol.



v) Methyl cyanide:

Methyl magnesium iodide reacts with cyanogen chloride to give methyl cyanide.

 $\begin{array}{c} CH_3 Mg I + CNCl \longrightarrow CH_3 CN + Mg \\ Cyanogen chloride & Methyl cyanide I \end{array}$

Question 49.

Complete the following reactions.



Peroxide i) $CH_3 - CH = CH_2 + HBr$ $CH_3 - CH_2 - CH_2 - Br$ Propene n – propyl bromide alcohol H₂O ii) $CH_3 - CH_2 - Br + NaSH$ $CH_3 - CH_2 - SH + NaBr$ Propyl bromide Ethanethiol THF C₆H₅MgCl (Phenyl magnesium iii) C₆H₅Cl (Chloro benzene) + Mg chloride) Δ iv) $CHCl_3 + HNO_3$ $CCl_3NO_2 + H$ Chloroform Chloropicrin v) CCl_4 (Carbon tetrachloride) + H_2O COCl₂ (Carbonyl chloride) + 2HClQuestion 50. Explain the preparation of the following compounds. i) DDT ii) Chloroform iii) Biphrnyl iv) Chloropicrin

v) Freon – 12

Answer:

i) DDT:

DDT can be prepared by heating a mixture of chlorobenzene with chloral (Trichloro acetaldehyde) in the presence of $con.H_2SO_4$.



ii) Chloroform:

Preparation: Chloroform is prepared in the laboratory by the reaction between ethyl alcohol with bleaching powder followed by the distillation of the product chloroform. Bleaching powder act as a source of chlorine and calcium hydroxide. This reaction is called haloform reaction. The reaction proceeds in three steps as shown below.

Step – 2: Chlorination $CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl$ Acetaldehyde Trichloro acetaldehyde

Step – 3: Hydrolysis $2CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2 Ca$ Chloral chloroform

iii) Biphenyl:

Chloro benzene react with sodium metal in dry ether, to give biphenyl. This reaction is called fitting reaction.

Ether

Δ

C₆H₅Cl + 2 Na + Cl – C₆H₅ Chloro benzene

 $C_6H_5 - C_6H_5 + 2NaCl$ Biphenyl

iv) Chloropicrin:

Chloroform reacts with nitric acid to form chloropicrin. (Trichloro nitro methane)

 $\begin{array}{c} & & \underline{\Delta} \\ CHCl_3 + HNO_3 & & CCl_3NO_2 + H_2O \\ Chloroform & & Chloropicrin \end{array}$

v) Freon – 12

Freon – 12 is prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of catalytic amount of antimony pentachloride

SbCl ₅	
$CCl_4 + 2 HF$	$2 \text{ HCl} + \text{CCl}_2\text{F}_2$
Carbon tetrachloride	Freon – 12

Question 51.

An organic compound (A) with molecular formula C_2H_5Cl reacts with KOH gives compounds (B) and with alcoholic KOH gives compound (C). Identify (A), (B), (C).

Answer:

 $\begin{array}{ccc} C_{2}H_{5}Cl \xrightarrow{KOH} & C_{2}H_{5}OH \\ \textbf{(A)} & \textbf{(B) Ethyl alcohol} \\ & & \\$

(C) Ethylene

Question 52.

Simplest alkene (A) reacts with HCl to form compound (B). Compound (B) reacts with ammonia to form compound (C) of molecular formula C_2H_7N . Compound (C) undergoes carbylamine test. Identify (A), (B) and (C).

 $CH_2 = CH_2 + HCl \rightarrow C_2H_5Cl$ (A) Ethylene (B) Ethyl chloride

 $C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl$ (C) Ethyl chloride (B) Ethyl amine

Question 53.

A hydrocarbon $C_3H_6(A)$ reacts with HBr to form compound (B). Compound (B) reacts with aqueous potassium hydroxide to give (C) of molecular formula $C_{3}H_{6}O$. What are the (A), (B) and (C). Explain the reactions.

Answer:



Question 54.

Two isomers (A) and (B) have the same molecular formula $C_2H_4Cl_2$. Compound (A) reacts with aqueous KOH gives compound (C) of molecular formula C₂H₄O. Compound (B) reacts with aqueous KOH gives compound (D) of molecular formula $C_2H_6O_2$. Identify (A), (B), (C) and (D).

$$CH_{3} - CH \xrightarrow{CI} \xrightarrow{2 \text{ KOH}} CH_{3} - CH \xrightarrow{OH} OH$$

(A) Ethylidene chloride

$$\xrightarrow{-H_2O}$$
 CH₃ – CHO

(C) Acetaldehyde

$$\begin{array}{c} CH_2 - Cl \\ | \\ CH_2 - Cl \end{array} + 2 \text{ KOH } \xrightarrow{-H_2O} \begin{array}{c} CH_2 - OH \\ | \\ CH_2 - OH \end{array} + 2 \text{ KCl } + 2 \text{ KCl } \end{array}$$

(C) Ethylene dichloride (D) Ethylene glycol