Haloalkanes and Haloarenes

Chapter at a Glance

1. In aliphatic or aromatic compounds, the replacement of hydrogen atom(s) by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.
2. In case of haloalkanes, halogen atom is attached to the sp^3 hybridised carbon atom of an alkyl group whereas in haloarenes, halogen atom is attached to sp^2 hybridised carbon atom of an aryl group.
3. On the basis of the nature of the carbon to which halogen atom is attached, halogen derivatives are classified as 1°, 2°, 3°, allylic, benzylic, vinylic and aryl derivatives.
4. Due to electronegativity difference between the carbon and halogen, the shared pair of electron lies closer to the halogen atom. As a result, the halogen carries a small negative charge, while the carbon carries a small positive charge. Consequently, C-X bond is a polar covalent bond.
5. **Methods of Preparation of Haloalkanes:** Haloalkanes can be prepared from displacement of alcoholic group in alkyl alcohol by halogen acid, PCl_5 and PCl_3. Haloalkanes can also be prepared by addition of halogen acids or halogens on alkene and alkyne. Alkyl halides can also be prepared by free radical halogenation of alkene.
   (a) From alcohol:
   The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride to give the corresponding alkyl halide.
   $R-OH + HX \xrightarrow{ZnCl_2} R-X + H_2O$
   $R-OH + NaBr + H_2SO_4 \longrightarrow R-Br + NaHSO_4 + H_2O$
   $R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$ (Where, X = Cl, Br)
   $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$
   $R-OH + X_2 \xrightarrow{RedP} R-X$ (Where, $X_2 = Br_2, I_2$)
   $R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$
   (b) By electrophilic addition of HX to alkene:
   An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.
   $RCH = CH_2 + HX \longrightarrow RCH-CH_3$ (Where, X = CI, Br, I)
   (c) By free radical halogenation of alkanes:
   Chlorination or bromination of alkane usually gives a complete mixture of isomeric mono and poly halo alkanes.
   $$CH_4 + Cl_2 \xrightarrow[\text{or Heat}]{\text{uv light}} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$$
6. **Physical Properties of Haloalkanes:**
   (a) Boiling point orders 1. R—I > R—Br > R—CI > R—F
   (b) $CH_3-(CH_2)_2-CH_2Br > (CH_3)_2CHCH_2Br > (CH_3)_3CBr$
   (c) $CH_3CH_2CH_2 > CH_3CH_2X > CH_3X$
   (d) Bond strength of haloalkanes decreases as the size of the halogen atom increases. Thus, the order of bond strength is $CH_3F > CH_3Cl > CH_3Br > CH_3I$.
   (e) Dipole moment decreases as the electronegativity of the halogen decreases.

(f) Haloalkanes though polar but are insoluble in water as they do not form hydrogen bonding with water.

(g) Density order is RI > RBr > RCl > RF

(For the same alkyl group) $CH_3I > C_2H_5I > C_3H_7I$

7. Chemical reactions of haloalkanes:

(a) Nucleophilic substitution reactions:

(i) C-X bond in alkyl halide is more polar due to electron repelling nature of alkyl group (–) and thus readily undergo nucleophilic substitution reaction. These are of two types:

(1) S_N1 (Substitution, nucleophilic, unimolecular): In such type of reactions, rate = k[RX], *i.e.*, rate, is independent of concentration of nucelophilic and occurs in two steps. Such reactions are favoured by polar solvents.

(2) S_N2 (Substitution, nucleophilic, bimolecular): In such type of reactions, rate = k[RX] $[Nu]^-$, *i.e.*, rate of reaction depends on concentration of nucleophile and take place in one step.

(ii) A S_N2 reaction proceeds with complete stereochemical inversion while a S_N1 reaction proceeds with racemisation.

(b) Elimination reaction: when a haloalkane with β-halogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from α-carbon and a halogen atom from the α-carbon atom. An alkene is formed as a product, also called β-elimination.

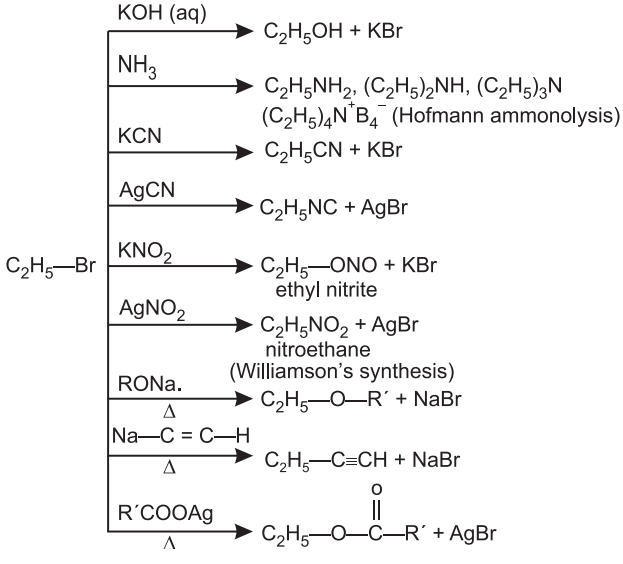
Reaction with metals:

(a) $R-X + Mg \xrightarrow{\text{Dry ether}} R-Mg-X$

Alkyl halides — Grignard reagent

(b) Wurtz reaction: $R-\boxed{X + 2Na + X}-R \xrightarrow{\text{Dry ether}} R-R + 2Na^+X^-$

Alkane



8. Methods of preparation of Haloarenes.

Haloarenes can be prepared by side chain halogenation or nuclear halogenation of aromatic hydrocarbons. From diazonium salts:

(a) By Sandmeyer reaction

(b) By Gattermann reaction.

9. Electrophilic substitution reaction: Haloarenes undergo the usual electrophilic substitution reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom is slightly deactivating and *o*, *p*-directing.

10. Trichloromethane (Chloroform):

The major use of chloroform today is in the production of the freon refrigerant R-22.

Chloroform is stored in closed dark coloured bottles completely filled so that air is kept out because it is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride (Phosgene).

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

11. Freons are the chlorofluorocarbons compounds of methane and ethane. They are extremely stable, unreactive, non-toxic, noncorrosive and easily liquefiable gases. Freon-12 (CCl_2F_2) is most common freons in industrial use.

Multiple choice questions

1. Halogenation of alkane gives:
- (a) Only required alkyl halide
- (b) Alkyl halide and unreacted halogen
- (c) A mixture of mono-, di-, tri- and tetra-halogen derivatives
- (d) Alkyl halide and unreacted alkane

2. Alkyl halides undergo:
- (a) Electrophilic substitution reactions
- (b) Electrophilic addition reactions
- (c) Nucleophilic substitution reactions
- (d) Nucleophilic addition reactions

3. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as:
- (a) A dehydrohalogenation reaction
- (b) A substitution reaction
- (c) An addition reaction
- (d) A dehydration reaction

4. Which alkyl halides react most readily by nucleophilic substitution ?
- (a) CH_3CH_2Cl (b) CH_3CH_2I
- (c) CH_3CH_2Br (d) CH_3CH_2F

5. Ethylene chloride and ethylidene chloride are isomers. Identify the correct statements.
- (a) Both the compounds form same product on treatment with alcoholic KOH.
- (b) Both the compounds form same product on treatment with aq. NaOH.
- (c) Both the compounds form same product on reduction.
- (d) Both the compounds are optically active.

6. What is the IUPAC name of $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2Cl$?
- (a) 2-dimethylchloropropane
- (b) 1-chloro-2-dimethyl-pentane
- (c) 2, 2-dimethyl-chlorobutane
- (d) 1-chloro-2, 2-dimethyl propane

7. Which of the following compound has been suggested as causing depletion of the ozone layer in the upper stratosphere?
- (a) CH_4 (b) CCl_2F_2
- (c) CF_4 (d) CH_2Cl_2

8. Which of the following reagent cannot be used to prepare an alkyl chloride from an alcohol?
- (a) $HCl + ZnCl_2$ (b) $SOCl_2$
- (c) NaCl (d) PCl_5

9. Chloromethane on treatment with excess of ammonia yields mainly:
- (a) N, N-Dimethylmethanamine $\left(CH_3-N\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}\right)$
- (b) N–methylmethanamine ($CH_3-NH-CH_3$)
- (c) Methanamine (CH_3NH_2)
- (d) Mixture containing all these in equal proportion

10. Carbylamine test involves heating a mixture of:
- (a) Alcoholic KOH, methyl iodide, and sodium metal
- (b) Alcoholic KOH, methyl iodide, and primary amine
- (c) Alcoholic KOH, chloroform, and primary amine
- (d) Alcoholic KOH, methyl alcohol, and primary amine

11. When chloroform is heated with aqueous NaOH, it gives:
- (a) Formic acid (b) Sodium formate
- (c) Acetic acid (d) Sodium acetate

12. What should be the correct IUPAC name for diethylbromomethane?

(a) 1-Bromo-1,1-diethylmethane
(b) 3-Bromopentane
(c) 1-Bromo-1-ethylpropane
(d) 1-Bromopentane

13. Conversion of ethyl bromide to ethylene is an example of:
(a) Hydrohalogenation
(b) Intramolecular dehydrohalogenation
(c) Dehydration
(d) Hydration

14. The reaction,

$2C_2H_5Br + 2Na \xrightarrow{\text{dry ether}} C_2H_5-C_2H_5 + 2NaBr$

is an example of:
(a) The Wurtz reaction
(b) Sandmeyer's reaction
(c) Aldol condensation
(d) Williamson's reaction

15. Grignard's reagent is prepared by the action of magnesium metal on:
(a) Alcohol (b) Phenol
(c) Alkyl halide (d) Benzene

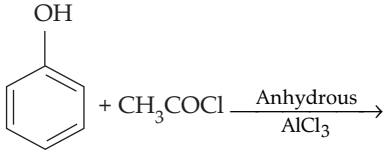
16. A primary alkyl halide would prefer to undergo:
(a) S_N1 reaction (b) S_N2 reaction
(c) a-Elimination (d) Racemisation

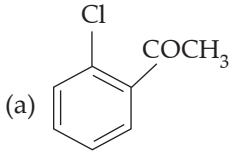
17. The action of sodium on alkyl halide to form an alkane is called:
(a) Grignard reaction
(b) Wurtz coupling reaction
(c) Isocyanide reaction
(d) Halogenation reaction

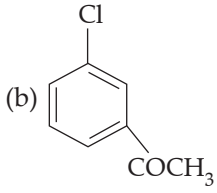
18. Identify the true statement for chloroform:
(a) Its exposure causes cardiac damage
(b) If immersed in chloroform, the skin gets sored.
(c) Central nervous system remains unaffected of chloroform.
(d) 700 ppm of chloroform causes dizziness

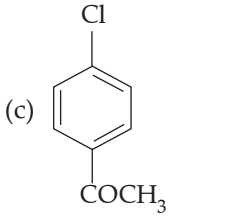
19. Halogenation of alkanes is:
(a) A reductive process
(b) An oxidative process
(c) An isothermal process
(d) An endothermal process

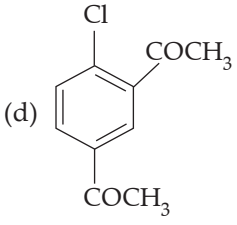
20. The major product of the following reaction is:

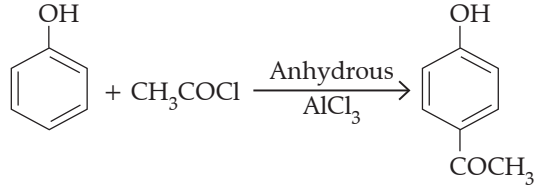


(a) 

(b) 

(c) 

(d) 

A. (c) 

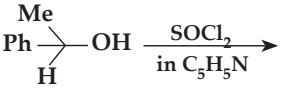
21. Chlorobenzene is:
(a) Less reactive than benzyl chloride
(b) More reactive than ethyl bromide
(c) Nearly as reactive as methyl chloride
(d) More reactive than isopropyl chloride

22. Chlorobenzene on treatment with sodium in dry ether gives diphenyl. The name of the reaction is:
(a) Fittig reaction
(b) Wurtz-Fittig reaction
(c) Sandmeyer reaction
(d) Gattermann reaction

23. Identify A, B and C in the given sequence of reactions,

$$H_2C=CH_2 + \underset{B}{Br_2} \xrightarrow{A} \underset{C}{BrCH_2CH_2Br}$$

	A	B	C
(a)	CCl_4	Colourless	Reddish brown
(b)	CCl_4	Reddish brown	Colourless
(c)	CBr_4	Colourless	Reddish brown
(d)	CBr_4	Reddish brown	Colourless

24. 

Which statement is true for the above reaction?
(a) Retention of configuration
(b) Inversion of configuration
(c) Inversion and retention both
(d) None of the above

25. The action of sodium on alkyl halide to form an alkane is called:

(a) Grignard reaction
(b) Wurtz coupling reaction
(c) Isocyanide reaction
(d) Halogenation reaction

26. The gas obtained on heating iodoform with silver powder is:
(a) Propane (b) Ethane
(c) Ethyne (d) Ethene

27. During the course of S_N1 reaction, the intermediate species formed is:
(a) A free radical
(b) A carbanion
(c) A carbocation
(d) An intermediate complex

28. The reaction : $CH_3Br + OH^- \rightarrow CH_3OH + Br^+$
(i) The expected mechanism of the above reaction is :
(a) S_N1 mechanism (b) S_N2 mechanism
(c) S_E1 mechanism (d) S_E3 mechanism
(ii) The above reaction is :
(a) Elimination reaction
(b) Nucleophilic addition reaction
(c) Nucleophilic substitution reaction
(d) Electrophilic substitution reaction

Fill in the blanks

29. Ethyl bromide on reaction with moist silver gives ..... as the main product. The well known refrigerant freon has the structure ..... .
(a) Ethanol, CCl_2F_2
(b) Ethanoic acid, CCl_4
(c) Propanol, $CHCl_3$
(d) Propanoic acid, CH_4

30. In S_N1 mechanism ..... are involved as intermediate species. Formation of phenol from chlorobenzene is an example of ..... aromatic substitution.
(a) Anion, electrophilic
(b) Ethanoic acid, nucleophilic
(c) Carbocation, nucleophilic
(d) Carbanion, electrophilic

31. Bleaching powder, on treatment with ethanol or acetone gives ..... . This is an example of ..... reaction. Butane nitrile can be prepared by heating ..... with alcoholic KCN.
(a) Carbon tetrachloride, iodoform, ethanol
(b) Freon, haloform, *n*-ethyl chloride
(c) Iodine, iodoform, n-propanol
(d) Chloroform, haloform,. *n*-propyl chloride

32. Vinyl chloride on reaction with dimethyl copper gives ..... . The trade name of carbon tetrachloride is ..... .
(a) Propanol, pyrene
(b) Propene, pyrene
(c) Propane, pyrene
(d) Propyne, pyrimidine

33. BHC is commercially called ..... .Phenyl isocyanide is formed when chloroform is treated with ..... in the presence of alcoholic KOH.
(a) Gropanol, Chloroform
(b) Gammaxene, ethanol
(c) Gammaxene, aniline
(d) Gammaxene, benzene

34. Vinyl chloride is ..... reactive than aryl chloride. Preparation of chlorobenzene from benzene diazonium chloride and aqueous HCl is known as .....reaction.
(a) Less, Gattermann reaction
(b) Less, Sandmeyer's reaction
(c) More, Wurtz's reaction
(d) More, Wurtz-Fittig reaction.

35. In alkyl halides, due to greater polarity as well as higher molecular mass, as compared to the parent hydrocarbon, the intermolecular ..... and ..... of attraction are stronger in the halogen derivatives.
(a) dipole-dipole and Van der Waal's forces.
(b) Hydrogen bond and dipole-dipole forces.
(c) Van der Waal's and hydrogen bond forces.
(d) dipole-dipole and London forces.

36. Nucleophilic reactions are the most useful classes of organic reactions of alkyl halides in which halogens are bonded to ..... hybridized carbon.
(a) sp^2 (b) sp^3
(c) sp (d) none of the above

37. The spatial arrangement of four groups (valences) around a central carbon atom is tetrahedral and if all the substituents attached to that carbon are different, and then such a carbon is called .....
(a) Achiral (b) Chiral
(c) Asymmetric (d) Symmetric

Match the following

38. Match the columns:

Column I	Column II
1. Ammonical silver nitrate	(p) Tollen's reagent
2. DDT	(q) Insecticide
3. Freon	(r) Refrigerant
4. Iodoform	(s) Antiseptic
5. Grignard Reagent	(t) RMgX

(a) 1-(p), 2-(q), 3-(s),4-(t),5-(r)

(b) 1-(r), 2-(t), 3-(s),4-(q),5-(p)

(c) 1-(s), 2-(t), 3-(p),4-(q),5-(r)

(d) 1-(q), 2-(p), 3-(r),4-(s),5-(t)

Reaction based questions

39. Complete the following reaction and name the reaction :

..... + $3I_2$ + 4KOH → CHI_3 + CH_3COOK + 3KI + $3H_2O$

(a) CH_3COCH_3 , Iodoform reaction

(b) CH_3COOH, Haloform reaction

40. Complete the reaction:

$CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{Heat}]{\text{Acetone}}$

(a) CH_3CHCH_3Na (b) $CH_2CH_2CH_2I$

41. Complete the reaction:

$(CH_3)_3\,CBr + KOH \xrightarrow{\text{Ethanol, heat}}$

(a) $CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + KBr + H_2O$

(b) $CH_3-\underset{\displaystyle OH}{\overset{|}{CH}}-CH_2-CH_3 + KBr$

42. Complete the reaction:

$CH_3CH_2Br + KCN \xrightarrow{\text{Aq. Ethanol}}$

(a) $CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + KBr$

(b) $CH_3CH_2CN + KBr$

43. Complete the reaction:

$C_6H_5ONa + C_2H_5Cl \rightarrow$

(a) $CH_3CH_2CH_2Cl + NaCl + H_2O$

(b) $C_6H_5-O-C_2H_5 + NaCl$

44. In the reaction.

$2C_2H_5Br + 2Na \xrightarrow{\text{dry ether}}$

(i) The product formed will be:

(a) $C_2H_5 - C_2H_5 + 2NaBr$

(b) $C_2H_8 + HBr + NaBr$

(c) $CH_2CH_2 + 2HBr + 2NaBr$

(d) $C_2H_6 + 2NaBr + 2H_2O$

(ii) The above reaction is an example of :

(a) Sandmeyer's reaction

(b) The Wurtz reaction

(c) Aldol condensation

(d) Williamson's reaction

45. Which of the following poisonous gas is formed when chloroform is exposed to light and air ?

(a) Mustard gas (b) Carbon monoxide

(c) Phosgene (d) Chlorine

Assertion and Reason based questions

Directions: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

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

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

(c) If assertion is true, but reason is false.

(d) If both assertion and reason are false

46. **Assertion:** $(CH_3)_3\,C-O-CH_3$ give $(CH_3)_3\,C-I$ and CH_3OH on treatment with HI.

Reason: The reaction occurs by S_N1 mechanism.

47. **Assertion:** Hydrogen iodide readily reacts with alkenes to form alkyl halides.

Reason: Aqueous hydrohalogen acids are used to prepare alkyl halides from alkenes.

48. **Assertion:** $CHCl_3$ is stored in dark bottles.

Reason: $CHCl_3$ is oxidised in dark.

49. **Assertion:** CCl_4 is a fire extinguisher.

Reason: CCl_4 is insoluble in water.

50. **Assertion:** $CH_2=CH-CH_2-X$ is an example of allyl halides.

Reason: These are the compounds in which the halogen atom is bonded to an sp^2 hybridised carbon atom.

51. **Assertion:** Alkylbenzene is not prepared by Friedel-Crafts alkylation of benzene.

Reason: Alkyl halides are less reactive than aryl halides.

52. Assertion: Aryl halides cannot be prepared by replacement of hydroxyl group of phenol by halogen atom.

Reason: Phenols react with halogen acids violently.

53. Assertion: Exposure of ultraviolet rays to human causes the skin cancer, disorder and disrupt the immune system.

Reason: Carbon tetrachloride is released into air it rises to atmosphere and deplets the ozone layer.

54. Assertion: The boiling points of alkyl halides decrease in the order : RI > RBr > RCl > RF

Reason: The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

55. Assertion: Electron withdrawing groups in aryl halides increase the reactivity towards nucleophilic substitution.

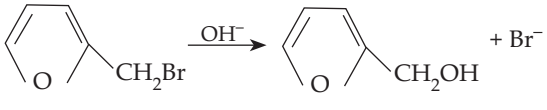
Reason: 2, 4-Dinitrochlorobenzene is less reactive than chlorobenzene.

Source based questions

Read the passage given below and answer the following questions:

56. Haloalkanes and alcohols are important starting materials in the synthesis of compounds having other functional groups. Primary haloalkanes react with hydroxide ion to give alcohols, although we will see that elimination reactions compete with substitution for secondary and tertiary halides.

When comparing alkanes and haloalkanes, we will see that haloalkanes have higher boiling points than alkanes containing the same number of carbons. London dispersion forces are the first of two types of forces that contribute to this physical property. London dispersion forces increase with molecular surface area. In comparing haloalkanes with alkanes, haloalkanes exhibit an increase in surface area due to the substitution of a halogen for hydrogen. The increase in surface area leads to an increase in London dispersion forces, which then results in a higher boiling point.



(i) Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechanism?

(a) Benzyl Chloride

(b) Ethyl chloride

(c) Chlorobenzene

(d) Isopropyl chloride

(ii) Which of the following is most reactive towards S_N1 reaction?

(a) $C_6H_5CH(CH_3)Br$

(b) $C_8H_5CH_2Br$

(c) $C_6H_5CH(C_6H_5)Br$

(d) $C_6H_5C(CH_3)C_6H_5Br$

(iii) The addition of HBr is easiest in which one of the following substrates:

(a) $CH_2 = CHCl$ (b) $ClCH = CHCl$

(c) $CH_3\text{-}CH = CH_2$ (d) $(CH_3)_2C = CH_2$

(iv) Which among MeX, R-CH_2X, R_2CHX, R_3CX is most reactive towards S_N2 reaction:

(a) CH_3X (b) RCH_2X

(c) R_3CHX (d) R_3CX

(v) $(CH_3)_3CMgBr$ on reaction with D_2O produces:

(a) $(CH_3)_3CD$ (b) $(CH_3)_3COD$

(c) $(CH_3)_3CD$ (d) $(CD_3)_3OD$

57. Classical molecular dynamics simulations with a polarizable force field were used to study adsorption of gas-phase alkyl halides to the surface of liquid water and their hydration properties in the interfacial environment. A systematic investigation has been performed for a set of monosubstituted alkyl chlorides, bromides and iodides of the alkyl chain length from one to five carbon atoms ($CnH_{2n+1}X$, n = 1–5, X = Cl, Br, or I). All alkyl halides readily adsorb to the water surface and exhibit a strong preference for interfacial (partial) hydration. When adsorbed, the alkyl halide molecules reside primarily in the outermost region of the water–vapor interface. The (incomplete) hydration shell of the surface-adsorbed methyl halide species is centered on the methyl end of the molecule, with the halogen atom largely exposed and facing away from water into the gas phase.

Mark the correct choice as

(i) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(ii) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(iii) Assertion is correct statement but reason is wrong statement.

(iv) Both assertion and reason are wrong.

(a) **Assertion:** There is a retention of configuration in 1-Chloro-2-methylbutane obtained from 2-methylbutan 1-ol.

Reason: The reactions where retention of configuration is observed do not preserve the integrity of the spatial arrangement of reactant.

(b) **Assertion:** A mixture containing two enantiomeres in equal proportions will have zero optical rotation.

Reason: Rotation due to one isomer is cancelled by the rotation due to the other isomer.

(c) **Assertion:** Carbon-halogen bond in alkyl halide is a non-polar bond.

Reason: Halogen atoms are less electronegative than carbon.

(d) **Assertion:** Reaction of aryl chlorides with iodine need an oxidising agent to be added in order to get a smooth reaction.

Reason: Reactions with iodine are irreversible in nature.

(e) Assertion: To obtain pure alkyl halides from alcohols thionyl chlorides are the reagents of choice.

Reason: Thionyl chloride reacts with alcohols to give alkyl halide.

Answers

Multiple choice questions

1. (c) A mixture of mono-, di-, tri- and tetra-halogen derivatives

Explanation: When halogen reacts with an alkane in the presence of sunlight or heat leads to the formation of a haloalkane (alkyl halide). Depending on the proportion of the two reactants that are used, various products of different amount are produced. For example, in the case of methane (CH_4), a large excess of the hydrocarbon favours formation of methyl chloride as the primary product; whereas, an excess of chlorine favours formation of chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4). Similarly, in general a mixture of mono-, di-, tri- and tetra-halogen derivatives is formed.

2. (c) Nucleophilic substitution reactions

Explanation: Alkyl halides can undergo two major types of reactions - substitution and/or elimination. It is called substitution reaction because the electrophilic alkyl halide forms a new bond with the nucleophile which replaces the halogen at the alpha-carbon. Hence the correct answer would be Nucleophilic substitution reactions.

3. (b) A substitution reaction

Explanation: Alkyl halide converted into an alcohol by alkaline hydrolysis. This process occurs due to a substitution reaction where the −X atom is substituted by a −OH group.

Chemical Reaction: $R{-}X + NaOH \rightarrow R{-}OH + NaX$

Hence, it is an example of a substitution reaction.

4. (b) CH_3CH_2I

Explanation: The melting and boiling points of molecular compounds are generally quite low compared to those of ionic compounds. Ionic solids typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801°C and boils at 1413°C. So in this case CH_3CH_2I will react most readily by nucleophilic substitution.

5. (a) Both the compounds form same product on treatment with alcoholic KOH.

Explanation: Ethylene chloride and ethylidene chloride on treatment with alc. KOH show elimination reaction and form ethyne as the product and both these compounds form same products(ethane) on reduction.

6. (d) 1-chloro-2, 2-dimethyl propane

Explanation: As per the IUPAC nomenclature, the numbering of the compound should begin with functional group and then lowest "Locant Rule" should be followed. Hence, the IUPAC name of the compound is 1-Chloro-2,2-dimethyl propane.

7. (b) CCl_2F_2

Explanation: Chlorofluorocarbons (CFCs) have significant potential to deplete ozone layer in the

Earth's atmosphere, which blocks the inflow of the harmful UV rays. CFCs causes depletion of stratospheric ozone layer and as a consequence it contributes to the global warming.

8. (c) NaCl

Explanation: Alkyl Chloride is an ionic compound which cannot displace –OH group by Cl. Rest all other reagents (HCl + $ZnCl_2$, $SOCl_2$, PCl_5) displaces -OH from alcohol and provide Cl.

9. (c) Methanamine (CH_3NH_2)

Explanation: Primary amine is obtained as a major product by taking large excess of ammonia. The reaction can be represented as:

$$CH_3Cl + NH_3 \rightarrow CH_3NH_2 + HCl$$

10. (c) Alcoholic KOH, chloroform, and primary amine

Explanation: Aliphatic and aromatic primary amines on heating with CCl_4 and alcoholic potassium hydroxide (alc. KOH) gives smelling alkyl isocyanides or carbylamines. So, Carbylamine test is performed in alcoholic KOH by heating a mixture of chloroform, and primary amine.

11. (b) Sodium formate

Explanation: Chloroform when heated with aqueous solution of caustic soda, first it produces formic acid which reacts further and form sodium formate.

$$CHCl_3 + 3NaOH \rightarrow CH(OH)_3 \xrightarrow{-H_2O}$$

$$HCOOH \xrightarrow{NaOH} HCOONa$$

12. (b) 3-Bromopentane

Explanation: $H_3\overset{5}{C}H_2\overset{4}{C}-\overset{3}{C}H(Br)-\overset{2}{C}H_2\overset{1}{C}H_3$

13. (b) Intramolecular dehydrohalogenation

Explanation: In ethyl alcohol, the attacking species is the ethoxide anion, which is a much stronger base than the hydroxide anion, so it directly extracts the beta hydrogen from ethyl bromide, followed by elimination of the bromide anion from the adjacent carbon atom to form ethene. So, it is an example of intramolecular dehydrohalogenation.

14. (a) The Wurtz reaction

Explanation: The wurtz reaction can be represented as:

$$C_2H_5Br + 2Na + C_2H_5Br \rightarrow C_4H_{10} + 2NaBr$$

15. (c) Alkyl halide

Explanation: Grignard reagents is prepared by the reaction of an alkyl or aryl halide with magnesium metal.

16. (b) S_N2 reaction.

Explanation: As primary alkyl halide is least sterically hindered among primary, secondary and tertiary alkyl halides, therefore primary alkyl halides undergo S_N2 reaction.

17. (b) Wurtz coupling reaction

Explanation: Wurtz-reaction

$$\underset{\text{Methyl bromide}}{CH_3Br} + 2Na + \underset{\text{Ethyl bromide}}{BrCH_2CH_3} \rightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} + 2NaBr$$

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + 2Na + \underset{\text{Ethyl bromide}}{BrCH_2CH_3} \rightarrow \underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + 2NaBr$$

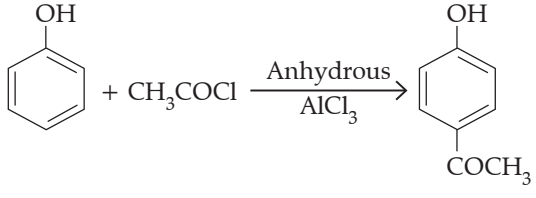
$$\underset{\text{Methyl bromide}}{CH_3Br} + 2Na + \underset{\text{Methyl bromide}}{BrCH_3} \rightarrow \underset{\text{Ethane}}{CH_3CH_3} + 2NaBr$$

18. (a) Its exposure causes cardiac damage

Explanation: Chloroform is harmful for the health. It can cause damages to the heart.

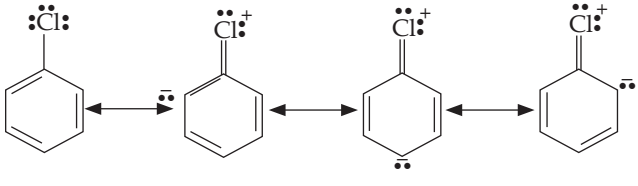
19. (b) An oxidative process

Explanation: Oxidation of the alkanes takes place during halogenation.

20. (c) 

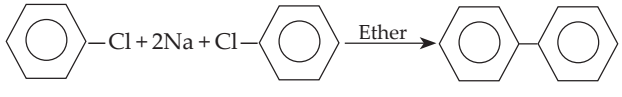
21. (a) Less reactive than benzyl chloride

Explanation: In chlorobenzene, the lone pairs present on Cl atom get involved in resonance with p electrons of benzene due to which C—Cl bond acquires double bond character, i.e. it becomes shorter and hence strong. Hence, reactivity decreases.



22. (a) Fittig reaction

Explanation: If only aryl halide reacts with sodium in presence of other, the reaction is called "Fitting" reaction.

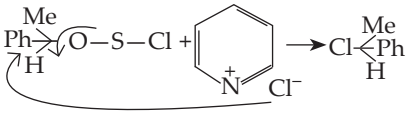


23. (b) CCl4 Reddish brown Colourless

Explanation: Addition of bromine in CCl4 to an alkene results in discharge of reddish-brown colour of bromine constitutes. It is an important method for detection of double bond in a molecule. The electrophilic addition results in the synthesis of vic-dibromides, which are colourless.

24. (b) Inversion of configuration

Explanation: Stronger nucleophilic Cl^- attacks from back and causes inversion of configuration.



25. (b) Wurtz coupling reaction

Explanation: Wurtz-reaction is a coupling reaction in organic chemistry, where two alkyl halides react with sodium metal in dry ether solution to form a higher alkane.

26. (c) Ethyne

Explanation: The gas obtained on heating iodoform with silver powder is ethyne. The reaction is as follows:

$$2CHI_3 + 6Ag \xrightarrow{\Delta} C_2H_2 + 6AgI$$

27. (c) A carbocation

Explanation: S_N1 reactions are unimolecular and the rate of such reactions depends only on the concentration of one reactant. S_N1 reactions happen in two steps:

- The leaving group leaves, and the substrate forms a carbocation which is an intermediate.
- The nucleophile attacks the carbocation, forming the product.

28. (i) (b) S_N2 mechanism

Explanation: Usually, primary alkyl halides and methyl halides undergo substitution by S_N2 mechanism. During the by S_N2 mechanism, bond breaking and bond formation takes place.

(ii) (c) Nucleophilic substitution reaction

Explanation: $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

In this reaction, nucleophile Br^- is replaced by another nucleophile OH^-. So, this is a nucleophilic substitution reaction.

Fill in the blanks

29. (a) Ethanol, CCl_2F_2

Explanation: Ethyl bromide on reaction with moist silver gives ethanol as the main product. The well known refrigerant freon has the structure CCl_2F_2.

30. (c) Carbocation, nucleophilic

Explanation: In S_N1 mechanism carbocation are involved as intermediate species. Formation of phenol from chlorobenzene is an example of nucleophilic aromatic substitution.

31. (d) Chloroform, haloform, *n*-propyl chloride

Explanation: Bleaching powder, on treatment with ethanol or acetone gives chloroform . This is an example of haloform reaction. Butane nitrile can be prepared by heating *n*-propyl chloride with alcoholic KCN.

32. (b) Propene, pyrene

Explanation: Vinyl chloride on reaction with dimethyl copper gives propene. . The trade name of carbon tetrachloride is pyrene .

33. (c) Gammaxene, aniline

Explanation: BHC is commercially called gammaxene. Phenyl isocyanide is formed when chloroform is treated with aniline in the presence of alcoholic KOH.

34. (a) Less, Gattermann reaction

Explanation: Vinyl chloride is less reactive than aryl chloride. Preparation of chlorobenzene from benzene diazonium chloride and aqueous HCl is known as Gattermann reaction.

35. (a) dipole-dipole and Van der Waal's forces.

Explanation: In alkyl halides, due to greater polarity as well as higher molecular mass, as compared to the parent hydrocarbon, the intermolecular dipole-dipole and Van der Waal's forces of attraction are stronger in the halogen derivatives.

36. (b) sp^3

Explanation: Nucleophilic reactions are the most useful classes of organic reactions of alkyl halides in which halogens are bonded to sp^3 hybridized carbon.

37. (b) Chiral

Explanation: The spatial arrangement of four groups (valences) around a central carbon atom is tetrahedral and if all the substituents attached to that carbon are different, and then such a carbon is called chiral

Match the following

38. (a) 1-(p), 2-(q), 3-(s),4-(t),5-(r)

Explanation: Amonical silver nitrate is Tollen's reagent. DDT (dichloro diphenyl trichloroethane) is an insecticide. Freon are low toxicity gases or liquids which are generally used as refrigerants and as aerosol. Iodoform is used as an antiseptic. RMgX is a grignard reagent.

Reaction based questions

39. (a) CH_3COCH_3 , Iodoform reaction

Explanation: When Iodine and sodium hydroxide are added to a compound that contains either a methyl ketone or a secondary alcohol with a methyl group in the alpha position, a pale yellow precipitate of iodoform or triiodomethane is formed.This reaction is known as iodoform reaction and it is used to test the presence of carbonyl compounds.

40. (b) $CH_2CH_2CH_2I$

Explanation: The given reaction is the Finkelstein reaction. In the given reaction, chloropropane reacrs with sodium iodide in the presence of acetone to form iodopropane and sodium chloride. The equation can be written as:

$$\underset{\text{1-Chloropropane}}{CH_3\,CH_2\,CH_2Cl} + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{Acetone, heat}} \underset{\text{1-Iodopropane}}{CH_2CH_2CH_2I} + NaCl$$

41. (a)

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + KBr + H_2O$$

Explanation: The given reaction is an example of dehydrohalogenation in which during a reaction a halogen and water is liberated. In the given reaction, 2-bromo-2-methyl propane reacts with KOH in the presence of ethanol to form 2-methyl propene and a molecule of KBr and H_2O is formed as the by-product.

42. (b) $CH_3CH_2CN + KBr$

Explanation: The given reaction is an example of nucleophilic substitution reaction. In the given reaction, bromoethane reacts with KCN in the presence of aqueous ethanol to form propane nitrile and potassium bromide. The reaction can be written as:

$$\underset{\text{Bromo ethane}}{CH_2CH_2Br} + KCN \xrightarrow[\text{(Nucleophilic substitution reaction)}]{\text{Aq. Ethanol}} \underset{\text{Propane nitrile}}{CH_3CH_2CN} + KBr$$

43. (b) $C_6H_5 - O - C_2H_5 + NaCl$

Explanation: The given reaction represents williamson's synthesis. In this reaction, an ether is formed from an organohalide and a deprotonated alcohol (alkoxide). In the given reaction, sodium phenoxide reacts with ethyl chloride to form phenetole and sodium chloride. The reaction can be written as:

$$\underset{\text{Sod. phenoxide}}{C_6H_5ONa} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} \xrightarrow[\text{Synthesis}]{\text{Williamson's}} \underset{\text{Phenetole}}{C_6H_5 - O - C_2H_5} + NaCl$$

44. (i) (a) $C_2H_5 - C_2H_5 + 2NaBr$

(ii) (b) The Wurtz reaction

Explanation of (i) and (ii) : Wurtz reaction is an chemical coupling reaction, in which sodium metal is reacted with two molecules of alkyl halide in the presence of ether in order to form a higher alkane along with a compound containing sodium and the halogen. The reaction is as follows:

$$2C_2H_5Br + 2Na \xrightarrow{\text{dry ether}} C_2H_5 - C_2H_5 + 2NaBr$$

45. (c) Phosgene

Explanation: When chloroform is exposed to air in the presence of light, it slowly oxidises and forms a poisonous gas called phosgene ($COCl_2$) and hydrochloric acid. The reaction is as follows:

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2\ (\text{phosgene}) + 2HCl$$

Since, chloroform gets oxidised by air in the presence of light, it is therefore, stored in dark coloured bottle completely filled so that air is kept out.

Assertion and Reason based questions

46. (a) For an S_N1 reaction, the formation of product is decided by the stability of the carbocation formed in the slowest step. The reaction between (CH_3)C-O-CH, and HI follows S_N1 mechanism. As tertiary butyl carbonium ion formed after the cleavage of C-O bond in the slowest step is more stable than methyl carbonium ion therefore, $(CH_3)_3$C-I and CH_3OH are formed as main products.

Thus, both assertion and reason are true and reason is the correct explanation of assertion.

47. (c) Halogen acids such as HCl, HBr and HI readily reacts with alkenes to form alkyl halides. Dry gaseous hydrohalogen acids are better electrophiles. In aqueous solution, H_2O. acting as nucleophile may produce alcohol. Thus, assertion is correct but reason is false.

48. (c) Chloroform is stored in dark bottles because it is slowly oxidised by air in the presence of light to an extremely poisonous gas `phosgene'. Thus, assertion is true but reason is false.

49. (b) CCl_4 is carbon tetrachloride and is used in fire extinguisher because it is a heavy non-combustible liquid. CCl_4 is insoluble in water due to absence of hydrogen atom that can form hydrogen bonding with water. Thus, both assertion and reason are true, but reason is not the correct explanation of assertion.

50. (c) $CH_2 = CH - CH_2 - X$ is an example of allyl halides.

Allyl halides are the compounds in which the halogen atom is bonded to an sp^3 hybridised carbon atom next to carbon-carbon double bond. Thus, assertion is true, but reason is false.

51. (b) The alkyl benzene is not prepared by Friedel -Craft's alkylation of benzene because the mono-alkyl product formed undergo alkylation to produce poly alkylated benzene. The reason the alkyl halides are less reactive than acyl halides is also correct but this is not the correct explanation of assertion

52. (c) Aryl halides cannot be prepared by replacing hydroxyl group of phenols because the carbon oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond. Thus, assertion is true but reason is false.

53. (b) The ozone layer is depleted as carbon tetrachloride rises into the atmosphere. As the ozone layer depletes, human beings are exposed to more UV radiation, which leads to an increase in skin cancer, eye disease, and disorder, as well as immune system disruption. Thus, both assertion and reason are true, but reason is not the correct explanation of assertion.

54. (b) The boiling point of the identical hydrocarbon component is determined by the atomic mass of the halogen atom. The boiling point of a halogen atom increases as its mass increases. As a result, the boiling point of halogen atoms lowers as the atomic mass of the halogen atom decreases. Thus, both assertion and reason are true, but reason is not the correct explanation of assertion.

55. (c) When electron withdrawing groups (nitro, cyano) are present at the ortho/para position, halobenzenes become reactive to nucleophile substitution reaction. This is evident by the fact that 2, 4-dinitrochlorobenzene requires milder hydrolysis condition than chlorobenzene. Thus, assertion is true, but reason is false.

Source based questions

56. (i) (a) Benzyl Chloride

(ii) (d) $C_6H_5C(CH_3)C_6H_5Br$

(iii) (d) $(CH_3)_2C = CH_2$

(iv) (a) CH_3X

(v) (a) $(CH_3)_3CD$

57. (a) (iii) Assertion is correct statement but reason is wrong statement.

(b) (i) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(c) (iv) Carbon-halogen bond in alkyl halide is a polar bond because halogen atoms are more electronegative than carbon. Thus, both assertion and reason are wrong.

(d) (iii) Reaction of aryl chlorides with iodine need an oxidising agent to be added in order to get a smooth reaction. However, reactions with iodine are reversible in nature. Thus, Assertion is correct statement but reason is wrong statement.

(e) (ii) To obtain pure alkyl halides from alcohols thionyl chlorides are the reagents of choice. Thionyl chloride reacts with alcohols to give alkyl halide. Thus, Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Word of Advice

1. Most of the students attempted the conversion of Chlorobenzene to biphenyl correctly, but a few students did not mention the required conditions, *i.e.,* dry ether, and heat for the reaction to take place.
2. Most of the students did not mention the reaction takes place in the presence of reagent, peroxide. Also, they did not mention that the addition of bromine to propene is according to anti-Markovnikov rule. .
3. Majority of the students were not able to write the complete balanced equations for the conversion of chlorobenzene to aniline. Also, they did not mentioned the name of the reagents and the condition required for the reaction to take place.
4. Some of the students did not mentioned the condition 'dry ether' while writing Wurtz-Fittig reaction.
5. During the course of a SN_1 reaction, the intermediate species formed is 'a carbocation' but some of the students wrote 'a carboanion' which was incorrect