Class - 12 Chemistry (Haloalkanes and Haloarenes)

- 1. What is inversion of configuration?
 - a. secondary butyl chloride
 - b. w-butyI bromide
 - c. tert-butyl chloride
 - d. iso-butyl iodide
- 2. Bromomethane, Chloromethane, Dibromomethane. 1 Chloropropane, Isopropyl chloride, 1 Chlorobutaneare all
 - a. Completely soluble in organic solvents
 - b. Slightly soluble in organic solvents
 - c. Insoluble in organic solvents
 - d. Completely soluble in water
- 3. Triiodomethane (Iodoform) is
 - a. Pesticide
 - b. Refrigerant
 - c. antiseptic drug
 - d. degreasing agent
- 4. Reactions with iodine in preparation of aryl iodide from arenes require the presence of
 - a. diazonium salt
 - b. an oxidizing agent
 - c. a reducing agent
 - d. ZnCl₂ catalyst
- 5. Anisole reacts with a mixture of concentrated sulphuric and nitric acids to yield a mixture of ortho and paranitroanisole

$$OCH_3$$
 H_2SO_4
 HNO_3
 OCH_3
 OC

a. None of these

- b. minor product is orthonitroanisole
- c. major product is paranitroanisole
- d. ortho and para in equal amounts.
- 6. What is meant by axis of symmetry?
- 7. Give IUPAC names of:

$$CH_3 - CH - CH_2 - Cl$$

8. Give IUPAC name of:

$$CH_3-CH-CH_2-CH_2-Br \ |_{Br}$$

- 9. Give the structure of 1,3-dichloro -2-(bromomethyl) propane
- 10. Complete the following reaction equation:

i.
$$C_6H_5N_2^+Cl^+ + KI \rightarrow \dots$$

ii.
$$H = C + Br_2 \xrightarrow{CCl_4} \dots$$

- 11. Write the structure of the major organic product in the following reaction: $CH_3CH_2CH_2OH + SOCl_2 \rightarrow \\$
- 12. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.
- 13. Write the structural formula of the organic compounds A and B in the following sequence of reaction.

$$CH_3 - CH - CH_2 - CH_3 \xrightarrow{alc.KOH} {
m A} \ {
m A} \xrightarrow{Br_2} {
m B}$$

- 14. Point out the difference between:
 - i. Chirality and chiral centre.
 - ii. Diastereoisomers and Enantiomers.
- 15. 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?

Class - 12 Chemistry (Haloalkanes and Haloarenes) Solutions

1. (a) secondary butyl chloride

Explanation: Secondary butyl chloride is optically active because it has chiral carbon atom marked*

$$CH_3-\overset{*}{\overset{C}{\overset{H}{\cap}}}-CH_2^--CH_3$$

2. (a) Completely soluble in organic solvents

Explanation: These all are covalent compounds hence are soluble in organic solvents.

3. (c) antiseptic drug

Explanation: The compound finds small scale use as a disinfectant. Around the beginning of the 20th century it was used in medicine as a healing and antiseptic dressing for wounds and sores, although this use is now superseded by superior anticeptics.

4. (b) an oxidizing agent

Explanation: Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO₃, HIO₄) to oxidise the HI formed during iodination.

5. (c) major product is paranitroanisole

Explanation: OCH₃ is activator and o/p director out of which para is major product.

- 6. It is an imaginary axis around which if the compound is rotated by a minimum angle of rotation, it gives back the original molecule with same configuration.
- 7. 1-Chloropropan-2-ol
- 8. In writing the IUPAC name, we first count the number of C atoms in the longest C chain (parent chain) and assign the locants according to the functional groups attached. Here as we can see the longest chain contains 4 C and it is an alkane, so we name it butane. The -Br (bromo) group is attached at position 1 and 3. So the name of the compound is 1,3-dibromobutane.
- 9. We can understand from the name that the longest C chain contains 3 C (as it is propane). Also at positions 1 and 3, -Cl is attached and at position 2, bromomethyl group i.e. -CH₂Br is attached. So the structure of the given compound must be:

$$CH_2Br \ | \ CH_2-CH-CH_2 \ | \ Cl \ Cl$$

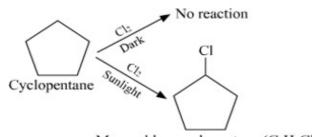
10. i.
$$C_6H_5N_2^+Cl^- + KI \rightarrow C_6H_5I + KCI + N_2$$

11.
$$CH_3CH_2CH_2\ OH + SOCl_2 \rightarrow CH_3CH_2CH_2Cl + SO_2 + HCl_{1-Propanol}$$

12. 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_9Cl 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 (C_5H_{10}) The reactions involved in the question are:



Mono-chlorocyclopentane (C₅H₉Cl)

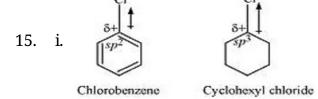
Thus A is but-2-ene and B is 2,3-dibromobutane

14. i. **Chirality**: Chirality is the property of a molecule, containing a carbon attached to four different groups, having a non-superimposable mirror image.

Chiral centre: The carbon which is attached to four different groups is called chiral centre.

ii. **Diastereoisomers:** Those pairs of stereoisomers which are not mirror images of each other. They differ in optical rotation.

Enantiomers: They are non-superimposable mirror images of each other. They have optical rotation equal in magnitude but opposite in sign.



In chlorobenzene, the Cl-atom is linked to a sp^2 hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to a sp^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 Cl-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 water-water 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.

$$RM rac{\delta - \ \delta + \ \delta -}{RM \ gX} + H_2O
ightarrow R - H + Mg(OH)X$$

Therefore, Grignard reagents should be prepared under anhydrous conditions.

Class - 12 Chemistry (Haloalkanes and Haloarenes)

- 1. Carbon tetra chloride has a dipole moment
 - a. $\mu = 0$
 - b. $\mu = 1$
 - c. $\mu = 2$
 - d. μ = 4
- 2. Dichloromethane (Methylene chloride) is
 - a. refrigerant
 - b. degreasing agent
 - c. pesticide
 - d. solvent
- 3. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with
 - a. SOCl₂ in presence of pyridine
 - b. PCl₃
 - c. Dry HCl in the presence of anhydrous ZnCl_2
 - d. PCl₅
- 4. Liver when chronically exposed to chloroform gets damaged because
 - a. chloroform is not metabolised in the liver
 - b. chloroform depresses central nervous system
 - c. chloroform develops sores in the liver
 - d. chloroform gets converted to carbonyl chloride which is a poison
- 5. To prepare alkanes containing odd number of carbon atoms, Wurtz reaction is not preferred because
 - a. a lot of reaction mixture goes wasted
 - b. a mixture of three different alkyl halides has to be used
 - c. a mixture of four different alkyl halides has to be used
 - d. a mixture of two different alkyl halides has to be used
- 6. Give the IUPAC name of the following compound:

$$CH_3-C_{egin{smallmatrix} | & C & = C-CH_2OH \ CH_3 & Br \ \end{bmatrix}}$$

- 7. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides.
 - $p ClC_6H_4CH_2 CH(CH_3)_2$
 - $m Cl CH_2C_6H_4CH_2C(CH_3)_3$
- 8. Name the following halide according to IUPAC system and classify it as alkyl, allyl, benzyl (primary, secondary, tertiary) vinyl or aryl halide. $\text{CH}_3 \, \text{CH}(\text{CH}_3) \text{CH}(\text{Br}) \, \text{CH}_3$
- 9. Give the structures of 2,3 dibromo 1 chloro -3- methylpentane
- 10. Write the structure of the major organic product in each of the: $CH_3 CH_2 CH_2Cl + NaI$ (in acetone)
- 11. Write the structure of the major organic product in the following reaction: $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{water}$
- 12. In the following pairs of halogen compounds, which would undergo ${\rm S}_{\rm N}2$ reaction faster?
 - i. CH₃CH₂CH₂Cl or (CH₃)₂CH-Cl
 - ii. $CH_3CH_2CH_2I$ or $CH_3CH_2CH_2Br$
- 13. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.
- 14. Mention the problems related to extensive use of DDT.
- 15. Give the IUPAC names of the following compounds:
 - i. $CH_3CH\left(Cl\right)CH\left(Br\right)CH_3$
 - ii. $CHF_2CBrClF$
 - iii. $ClCH_2C = CCH_2Br$
 - iv. $(CCl_3)_3CCl$
 - v. $CH_3C(p-ClC_6H_4)_2CH(Br)CH_3$
 - vi. $(CH_3)_3CCH = CCl(p C_6H_4I)$

Class - 12 Chemistry (Haloalkanes and Haloarenes) Solutions

1. (a) μ = 0

Explanation: CCl_4 is symmetrical hence dipole moment is zero.

2. (d) solvent

Explanation: Methylene chloride is an organic compound with the formula CH_2Cl_2 . This colorless, volatile liquid with a moderately sweet aroma is widely used as a solvent, as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent.

3. (a) SOCl₂ in presence of pyridine

Explanation: The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride. Thionyl chloride (SOCl₂) is preferred because the other two products SO₂ and HCl are escapable gases. Hence the reaction gives pure alkyl halides.

$$ROH + SOCl_2 \rightarrow RCl + SO_2(g) + HCl(g)$$

4. (d) chloroform gets converted to carbonyl chloride which is a poison

Explanation: Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene)

$$CHCl_3 + O_2 \rightarrow 2COCl_2 + 2HCl$$

5. (d) a mixture of two different alkyl halides has to be used

Explanation: Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as Wurtz reaction and is used for the preparation of higher alkanes containing even number of carbon atoms. Many side products are formed when two different alkyl halides are used. So this method is not preferred to prepare alkanes having odd number of C atoms.

6.
$$CH_3 - \overset{3}{\overset{1}{\overset{1}{C}}} = \overset{2}{\overset{1}{\overset{1}{\overset{1}{C}}}} - \overset{1}{\overset{1}{\overset{1}{C}}} OH$$

2 - bromo - 3 - methyl - but - 2 - en - 1 - ol

7. i. IUPAC name: 1-chloro-4-(2-methylpropyl)benzene, aryl halide

- ii. IUPAC name: 1-Chloromethyl-3-(2, 2-dimethylpropyl) benzene, 1° benzylic halide
- 8. IUPAC name: 2-Bromo-3-methylbutane
 It is a 2° alkyl halide because the halogen is attached to a secondary C.
- 9. As we can figure out the parent chain contains 5 C as it is a pentane. Also at position 1, -Cl is attached, at position 2 and 3, -Br is attached and at position 3 -CH₃ position is attached. So the structure of the compound must be

$$CH_3-CH_2-egin{pmatrix} CH_3\ -\ C\ -\ C\ -\ CH-CH-CH_2Cl\ Br & Br \end{pmatrix}$$

10.
$$CH_3CH_2CH_2Cl + NaI \xrightarrow{acetone} CH_3CH_2CH_2I + NaCl \xrightarrow{heat} 1-Iodopropane \begin{pmatrix} Finkelstein \\ reaction \end{pmatrix}$$

11.
$$CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{water} CH_3CH(OH)CH_2CH_3 + NaBr$$
2-Bromobutane

Butan - 2 - ol

- 12. i. $CH_3CH_2CH_2Cl$: It is primary halide and therefore undergoes S_N2 reaction faster.
 - ii. CH₃CH₂CH₂I: As iodine is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile as compared to Br.
- 13. Since the hydrocarbon gives only one monochloro compound, it indicates that all hydrogen atoms in the hydrocarbon are equivalent. Thus, the compound is cyclopentane with the molecular formula C_5H_{10} .

- 14. i. Many species of insects developed resistance to DDT.
 - ii. It was also discovered to have a high toxicity towards fish.
 - iii. The chemical stability of DDT and its fat solubility compounded the problem.
 - iv. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored

in the fatty tissues.

v. If ingestion continues at a steady rate, DDT builds up within the animal over time.

(i)

2-Bromo-3-chlorobutane

(ii)

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

(iii)

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

1-Bromo-4-chlorobut-2-yne

(iv)

 $\hbox{2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane}\\$

(v)

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

(vi)

$$CI - \frac{1}{C} = \frac{2}{C}H - \frac{3}{C} - \frac{4}{C}CH_3$$
 $CI - \frac{1}{C} = \frac{2}{C}H - \frac{3}{C} - \frac{4}{C}CH_3$
 $CI - \frac{1}{C} = \frac{2}{C}H - \frac{3}{C} - \frac{4}{C}CH_3$
 $CI - \frac{1}{C} = \frac{2}{C}H - \frac{3}{C} - \frac{4}{C}CH_3$

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

Class - 12 Chemistry (Haloalkanes and Haloarenes)

- 1. The most common freons in industrial use is manufactured by
 - a. Swarts reaction
 - b. Fittig reaction
 - c. Sandmeyer reaction
 - d. Wurtz reaction
- 2. A mixture containing two enantiomers in equal proportions
 - a. will be called a racemic mixture
 - b. will be called a racemic mixture and will have a zero optical rotation.
 - c. will have inverted configuration
 - d. will have zero optical rotation
- 3. In the reaction, $R X + NaoR' \rightarrow ROR' + X$ (ve ion) The main product formed is
 - a. Ether
 - b. Alcohol
 - c. Ester
 - d. Amine
- 4. Hydrocarbons are prepared from Grignard reagent by
 - a. by reacting them with sodium
 - b. by reacting them with water
 - c. by exposing them to Magnesium
 - d. by exposing them to diethyl ether
- 5. In alkyl halide
 - a. All of these
 - b. the carbon atom of C-halogen bond bears a partial positive charge
 - c. the halogen atom bears a partial negative charge
 - d. the carbon-halogen bond of alkyl halide is polarised
- 6. Write the structural formula of p-Bromochlorobenzene.
- 7. Name the following halide according to IUPAC system and classify it as alkyl, allyl, benzyl (primary, secondary, tertiary) vinyl or aryl halide.

- 8. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure?
- 9. How is chlorobenzene prepared by
 - a. direct chlorination
 - b. diazotization method?
- 10. How will you bring the following conversion? Ethane to bromoethene
- 11. Write the structure of the major organic product in the following reaction:

$$(CH_3)_3 CBr + KOH \xrightarrow{ethanol}_{heat}$$

- 12. A compound 'A' contains carbon and hydrogen only and has molecular mass of 72. Its photo chlorination gives a mixture containing only one monochloro and two dichloro hydrocarbons. Deduce the structure of A and the chlorinated products.
- 13. p-Dichlorobenzene has higher m.p. and lower solubility than those of o- and misomers. Discuss.
- 14. Discuss the mechanism of $S_N 1$ reaction of haloalkanes.
- 15. 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.

Class - 12 Chemistry (Haloalkanes and Haloarenes) Solutions

1. (a) Swarts reaction

Explanation: The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction

2. (b) will be called a racemic mixture and will have a zero optical rotation.

Explanation: Enantiomers are chiral molecules that are *mirror images* of one another. Furthermore, the molecules are *non-superimposable* on one another. This means that the molecules cannot be placed on top of one another and give the same arrangement of atoms in space. If they are present in equal proportions, the mixture is called a racemic mixture and it is optically inactive, as one isomer will rotate light in the direction opposite to another.

3. (a) Ether

Explanation: This is normal substitution reaction.

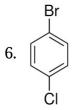
4. (b) by reacting them with water

Explanation: Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons. Thus Grignard reagent abstracts acidic hydrogen from H_2O forming alkane.

$$RMgX + H_2O \rightarrow RH + Mg(OH)X$$

5. (a) All of these

Explanation: Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



7. IUPAC name: 1-Chloro-4-(2 methylpropyl)benzene
It is an aryl halide because it contains a benzene ring.

8.
$$CH_3 - \star CH - CH_2 - CH_3$$

$$Cl$$
2 - Chlorobutane

Here the $\star C$ is the chiral center attached to 4 different groups.

9. a. by direct chlorination-

b. by diazotization method-

$$C_6H_5NH_2 \xrightarrow[0-5^o]{NaNO_2,HCl} C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Cl_2} C_6H_5Cl + N_2$$

10.
$$\text{CH}_3\text{-CH}_3 \xrightarrow{Br_2/UV light} \text{CH}_3\text{-CH}_2\text{Br} + \text{HBr} \xrightarrow{alc.KOH} \text{CH}_2 = \text{CH}_2 \xrightarrow{Br_2/CC l_4} \text{Br-CH}_2\text{-CH}_2\text{-Br} \xrightarrow{alc.KOH} \text{CH}_2 = \text{CH}_2 = \text{CH}_2 = \text{CH}_2$$

First ethane is treated with Br_2 in presence of UV light to give Bromoethane which when treated with alc. KOH gives ethene and HBr. Ethene on treating with Br_2 in presence of CCl_4 gives 1, 2-dibromoethane which on treating with alc. KOH gives CH_2 =CH-Br (Bromoethene)

12. A is C_5H_{12} (mol. wt. 72) Since its gives one mono chloro and two dichloro derivatives on photochemical chlorination, it is

$$CH_3-igcap _{CH_3}^{CH_3}-CH_3 \ _{CH_3}$$

neo-pentane

The reactions are

monochloro derivative

dichloro derivatives

$$CH_{3} = CH_{3} - CH_{2}Cl \ CH_{3} - CH_{2}Cl + CH_{3} - CH_{2}Cl + CH_{1} - CHCl_{2} + 2HCl \ CH_{3} - CH_{3$$

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.

14. Tertiary halides undergo nucleophilic substitution through $S_N 1$ mechanism. It is a two step mechanism. First step involves formation of carbocation by loss of halide ion.

1st Step:

$$CH_3 - CH_3 \stackrel{CH_3}{\overset{}{\stackrel{}{\longrightarrow}}} CH_3 \stackrel{CH_3}{\overset{}{\stackrel{}{\longrightarrow}}} CH_3 - CH_3 + Cl^-$$

2nd Step: Second step involves attack of nucleophile which can happen from either side of the plane of the molecule

Thus, the compound which gives the most stable carbocation on losing the halide ion will preferably undergo nucleophilic substitution by $S_{\rm N}1$ mechanism.

In the given compound, there are one type of β hydrogen atoms are present. Thus, dehydrohalogenation of this compound gives only one alkene.

ii.
$$CH_3$$

$$C_2H_5ONa/C_2H_5OH$$

$$CH_3$$

In the given compound, there are two different sets of equivalent -hydrogen atoms labelled as a and b. Thus, dehydrohalogenation of the compound yields two alkenes.

CH₃ — CH₂ — CH₃
$$\xrightarrow{\text{C}_2\text{H}_5\text{ONa/C}_2\text{H}_5\text{OH}}$$
 — CH₃ — C — CH — CH₃ $\xrightarrow{\text{CH}_3}$ — CH₃ $\xrightarrow{\text{CH}_3}$ — CH₃ $\xrightarrow{\text{CH}_3}$ $\xrightarrow{\text{CH}_3}$ — CH₂ — CH₂ — CH₂ — CH₃ $\xrightarrow{\text{CH}_3}$ — CH₂ — CH₂ — CH₃ $\xrightarrow{\text{CH}_3}$ \xrightarrow

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.

2, 2, 3 - triamethyl - 3 bromopentane

In the given compound, there are two different sets of equivalent β -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.