6

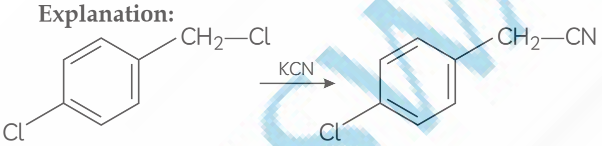
CHAPTER

Haloakanes and Haloaranes

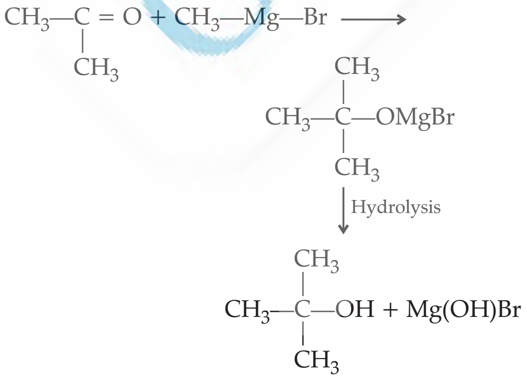
Level - 1 CORE SUBJECTIVE QUESTIONS

MULTIPLE CHOICE QUESTIONS (MCQs) (1 Mark)

1. **Option (D) is correct.**
   Explanation: The boiling points in haloalkanes increases with increase in carbon chain length. However, branching generally decreases the boiling points due to reduced intermolecular forces like van der Waal's forces and dipole -dipole interactions.
   This explains why bromomethane with less carbon atoms and branching has the lowest boiling point and 1-bromobutane which has a straight chain structure has highest boiling point among the given compounds.
2. **Option (D) is correct.**
   Explanation: 1-Bromobutane has high boiling point because it is less satirically hindered from other given molecule.
3. **Option (B) is correct.**
   Explanation: The order followed is this $CH_3I < CH_3Br < CH_3F < CH_3Cl$, though F is most electronegative, the bond length is small as compared to C–Cl.
   Dipole moment is the product of the charge and the bond length.
   Hence, CH_3Cl has higher dipole moment though Cl is less electronegative than F.
4. **Option (C) is correct.**
   Explanation:



   substitution takes place where CN^- replaces Cl^-
5. **Option (B) is correct.**
   Explanation: Tertiary alcohol formed.



$$CH_3—\underset{\underset{CH_3}{|}}{C}=O + CH_3—Mg—Br \longrightarrow CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OMgBr \xrightarrow{\text{Hydrolysis}} CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OH + Mg(OH)Br$$

6. **Option (B) is correct.**
   Explanation: This is because the formation of a resonance stabilised carbocation makes it easier to remove Br^-.
7. **Option (C) is correct.**
   Explanation: $CH_3 — CH_2ONa + CH_3Cl \rightarrow CH_3—CH_2—O—CH_3 + NaCl$
8. **Option (C) is correct.**
   Explanation:
   $CH_2 = CH—X$
   The compound that contain sp^2 hybridised carbon bonaded to X is C_2H_3X also known as vinyl halide A C-C double bonding occurs between sp^2 hybrid carbon atoms.
9. **Option (C) is correct.**
   Explanation:
   $$2CHCl_3 + O_2 \xrightarrow{\text{Light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$
10. **Option (A) is correct.**
    Explanation: In three these structures, carbon is linked to four different groups. That's why three compounds are chiral which are I, II, III.
11. **Option (C) is correct.**
    Explanation: Enatiomers does not have same specific rotation. They are mirror images of each other.
12. **Option (C) is correct.**
    Explanation: $CH_3 —CH_2—Cl + KOH(alc.) \rightarrow CH_2 = CH_2 + KCl + H_2O$
13. **Option (B) is correct.**
    Explanation: $CH_3—Br + AgF \rightarrow CH_3—F + AgBr$ Swartz reaction
14. **Option (A) is correct.**
    Explanation: Racemisation occurs in $S_N{}^1$ reaction because carbocation are planar species that allow nucleophiles to attack from both sides.

ASSERTION-REASON QUESTIONS (1 Mark)

1. **Option (A) is correct.**

   Explanation: Gabriel phthalimide synthesis is used to prepare primary aliphatic amines not aromatic amines, through nucleophilic substitution with anion formed by phthalimide.

2. **Option (C) is correct.**

   Explanation: S_N2 reaction is a one-step reaction where the (attacking of nucleophile) and elemination of hologen occur simultaneously. And the nucleophile attacks the carbon atom from the side opposite to the leaving group, resulting in inversion of configuration.

3. **Option (C) is correct.**

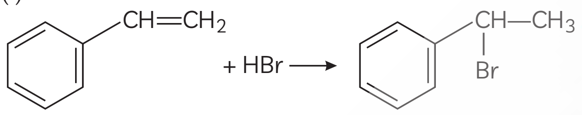
   Explanation: This is due to smaller size and higher electronegativity of chlorine. Bond energy of C—Cl bond is more then C-I bond.

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

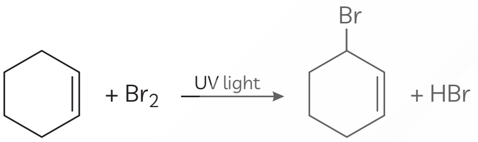
1. (i) $CH_3—CH_2—I$ undergo $S_N{}^2$ reaction faster because size of I is large, it will be released at a faster rate in the presence of incoming nucleophile.

   (ii) Butane < Chlorobutane < Bromobutane < Iodo butane. As the size and electronegativity of the halogen atoms increase in the order of Chlorine < Bromine < Iodine. Therefore, the strength of the dipole-dipole interactions also increases in that order, leading to a higher boiling point for 1-iodobutane as compared to other halobutanes..

2. (i)

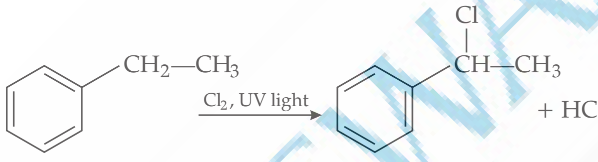


   (ii)



3. (i)  because of larger size of Iodine, I is released at faster rate as compared to Br.

   (ii)



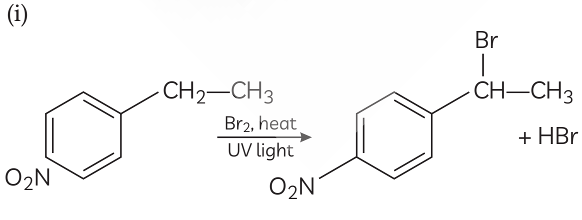
Ethyl benzene

1-Chloro-1-phenyl ethane (Major)

4. (i) $CH_3CH_2—I$ undergo $S_N{}^2$ reaction faster because I is a better leaving group because of its larger size, it will be released at a faster rate in the presence of incoming nucleophile.

   (ii) Chloroform is stored in closed dark coloured bottles to avoid the formation of phosgene -a poisonous gas formed due to action of light and air on chloroform.

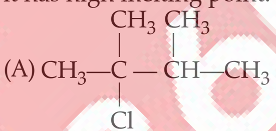
5. (i)



   (ii)

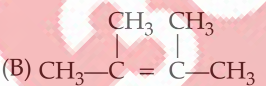
6. Boiling point depends on the intermolecular interaction and the dipole moment, Ortho has high dipole moment than meta and para. Hence, it has high boiling point. Para is very stable position and it is difficult to break bond due to the symmetry of compound, it is efficiently packed in solid state hence it has high melting point.

7. (A)



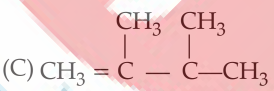
$$CH_3—\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}—\overset{\overset{CH_3}{|}}{C}H—CH_3$$

(B)



$$CH_3—\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}—CH_3$$

(C)



$$CH_3=\overset{\overset{CH_3}{|}}{C}—\overset{\overset{CH_3}{|}}{C}—CH_3$$

8. (i) The mechanism takes place in three steps

   Step I: Formation of protonated alcohol

$$CH_3—CH_2—\ddot{O}—H + H^+ \rightleftharpoons CH_3—CH_2—\overset{+}{O}\begin{matrix}H\\H\end{matrix}$$

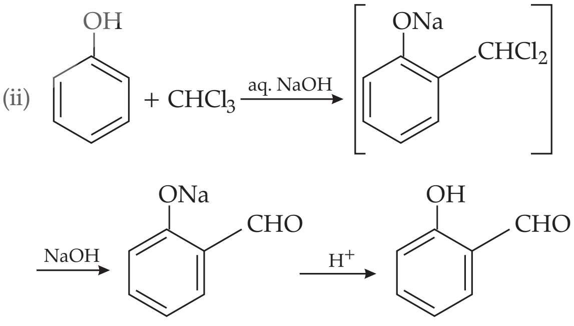
   Step II: Formation of carbocation

$$CH_3—CH_2—O\begin{matrix}H\\H\end{matrix} \rightleftharpoons CH_3—\overset{+}{C}H_2 + H_2O$$

   Step III: Elimination of a proton to form ethene.

$$CH_3—\overset{+}{C}H_2—O \xrightleftharpoons{Fast} CH_2 = CH_2 + H^+$$

   (ii)



Salicylaldehyde

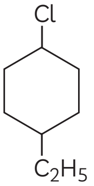
9. Option (ii) is halogenated exchange reaction

   Explanation: Hologen exchange reactions are those reactions in which one halide replaces another in option (ii) halogen (—X) is replaced by iodine. This reaction is named Finkelstein reaction.

10. (i) 2-Chloropropane < 1-chloropropane < 1-chlorobutane. The longer the carbon chain- the higher is the boiling point. Branching lowers the boiling point.

(ii) The nucleophile that can attack through two different sites are known as ambident nuecleophiles. For example: Cyanide ion is an ambident nucleophile. It can attack through either C atom or N atom to form alkyl cyanide or alkyl isocyanide.

11. (i)

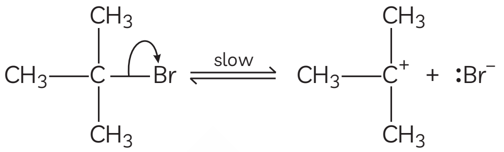


(ii) In the presence of sulphuric acid (H_2SO_4), KI produces I_2

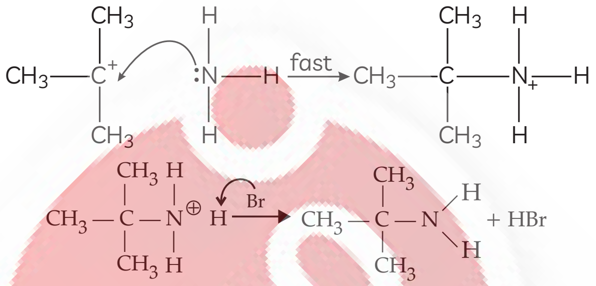
$2KI + H_2SO_4 \rightarrow I_2 + SO_2 + 2KOH$

As a result the reaction between alcohol and KI to produce alkyl iodide cannot occur. Therefore, sulphuric acid is not used during the reaction of alcohol.

12. The mechanism involves an initial ionisation of the haloalkane to form a carbocation:



This is followed by a very rapid attack by ammonia on the carbocation formed:



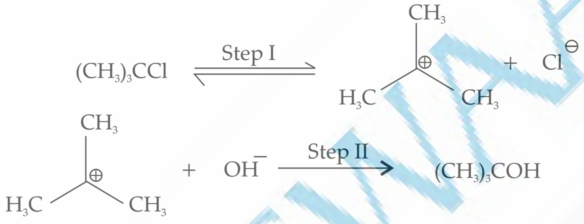
SHORT ANSWER TYPE QUESTIONS (3 Marks)

1. (i) CH_3CH_2CN (major), CH_3CH_2NC (minor)

(ii) $CH_3CH_2CHBrCH_3$, $CH_3CH_2CH_2CH_2Br$
(major) (minor)

(iii) $(CH_3)_2C = CHCH_3$, $(CH_3)_2CHCHCH_2$
(major) (minor)

2. "A" is $(CH_3)_3CCl$, the carbocation intermediate obtained in tertiary alkyl halide is most stable, making A most reactive of all possible isomers.



3. (i) Grignard reagent should be prepared under anhydrous conditions because they are highly reactive with water and produce alkanes and magnesium hydroxide preventing the required reaction from taking place.

(ii) In an aqueous solution, KOH almost completely ionises to give OH^- ions. OH^- ion is a strong nucleophile which leads the alkyl chloride to undergo a substitution reaction to form alcohol.

$R—Cl + KOH \rightarrow R—OH + KCl$

Alkyl chloride — Alcohol

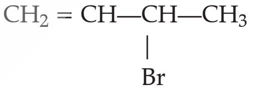
On the other hand an alcoholic solution of KOH contains alkoxide (RO^-) ion which is a strong base. Thus it can abstract a hydrogen from the β-carbon of the alkyl halide and form an alkene by eliminating a molecule of HX.

4. (i) Haloalkanes react with AgCN to form isocyanide as main product because AgCN is mainly covalent in nature which allow the nitrogen atom to act as a nucleophile and to donate an electron pair and form isocyanides.

(ii) Allyl chloride is highly reactive towards S_N1 reaction because it forms a stable carbocation that is stabilised by resonance.

(iii) Haloarenes are less reactive towards nucleophilic substitution reaction because the C-X bond in Aryl halide has a partial double bond character due to resonance. This makes it more difficult to subtitute halogen by nucleophile so haloarenes are less reactive.

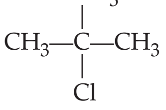
5. (i) (2)



$CH_2 = CH—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$

(ii) 2, 4, 6-Trinitro chlorobenzene is more reactive towards nucleophilic substitution as compared to chlorobenzene because electron withdrawing group NO_2 on ortho and para position increases the reactivity towards nucleophilic substitution due to stabilised carbanion by resonance.

(iii) 2-chloro-2-methyl propane has lowest boiling point because this isomer is highly branched resulting in the least surface area and therefore the lowest boiling point among all isomers.



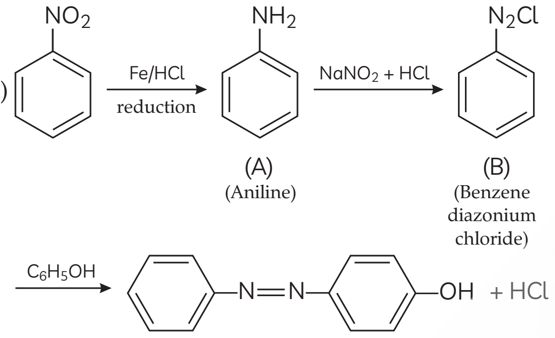
$CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}—CH_3$

6. (i)

$$CH_3CH_2Cl \xrightarrow[\substack{\text{Nucleophilic}\\ \text{Substitution}}]{KCN} \underset{\substack{(A)\\ \text{(propionitrile)}}}{CH_3CH_2CN} \xrightarrow[\text{(reduction)}]{LiAlH_4}$$

$$\underset{\substack{(B)\\ \text{(propylamine)}}}{CH_3CH_2CH_2NH_2} \xrightarrow{HNO_2} \underset{\substack{(C)\\ \text{(propionol)}}}{CH_3CH_2—CH_2—OH}$$

(ii)



(A) (Aniline)

(B) (Benzene diazonium chloride)

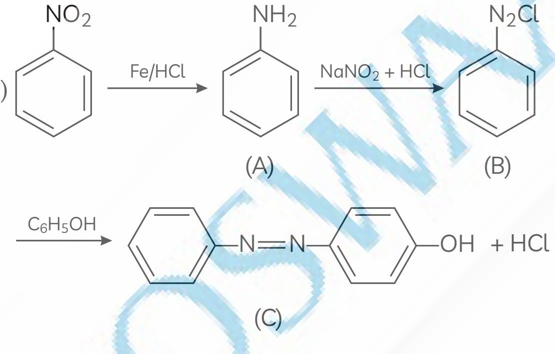
(C) (Diphenyl ether)

7. (i)

$$CH_3—CH_2—Br \xrightarrow{KCN} \underset{(A)}{CH_3CH_2CN} \xrightarrow{OH^-}$$

$$\underset{\substack{(B)\\ \text{Propionamide}}}{CH_3CH_2CONH_2} \xrightarrow[\substack{\text{Hoffman}\\ \text{bromide reaction}}]{NaOH + Br_2} \underset{\substack{(C)\\ \text{ethanamine}}}{CH_3CH_2NH_2}$$

(ii)



8. (i) The inductive-I effect of chlorine withdraws electron from benzene ring. Hence tends to destablise the intermediate carbocation formed during electrophitic substitution. This deactivates benzene ring towards electrophilic substitution. Conversely Cl donates it's lone pair electron to the aromatic ring and hence increases the electron density at ortho and para position through resonance effect. Thus, the lone pair of an electron on chlorine atom increase the density of electrons on o- and p-positions due to resonance directing the electrophiles to these two sites.

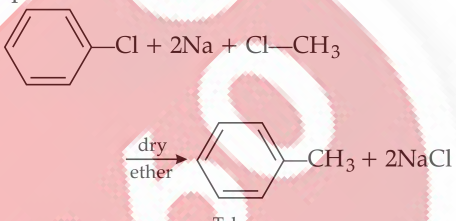
(ii) Racemic mixture is optically inactive because the rotation caused by one enantiomer is canceled by the rotation caused by the other enantiomer.

(iii) Allyl chloride is hydrolysed more readily than *n*-propyl chloride because the carbocation formed during hydrolysis is stabilised by reasonance in allyl chloride but not in *n*-propyl chloride.

9. (i) The hydrolysis of optically active 2-bromobutane with aqueous NaOH will result in formation of both (+) and (–) butan-2-ol as the reaction will proceed via- S_N1 mechanism.

The S_N1 reaction is a two step process that involve the formation of a carbocation. The —OH attacks the carbocation from either side, resulting in the formation of reacemic product 2-butanol. This racemic product is optically inactive.

(ii) When chlorobenzene and methyl chloride are treated with sodium metal in dry ether the product formed is toluene.



Toluene

10. (i) The dipole moment of chlorobenzene is less than cyclohexyl chloride as in chlorobenzene C—Cl bond is sp^2 hybridised where as in chloride the C—Cl bond is sp^3 hybridised. In chlorobenzene the lone pair of chlorine is delocalised with the benzene ring leading to partial double bond character of C—Cl bond and thus reducing the charge separation between C and Cl atoms and hence lowering the dipole moment.

That's why C—Cl bond in chlorobenzene is less polar and shorter as compared to cyclohexyl chloride.

(ii) Though alkyl halides are polar in nature, the dipole- dipole interactions of alkyl halides and water molecules are weaker than H-H intermolecular bonds in water. Hence, the alkyl halides are immisicible as they cannot overcome the intermolecular H-bonding in water.

(iii) As *n*-butyl bromide is straight chain, it has stronger van der Waals attraction forces between its molecules and consequently occupies more surface areas as compared to branched chain isomer. This increases the energy requirement to overcome the forces and hence higher boiling point is seen in *t*-butyl bromide.

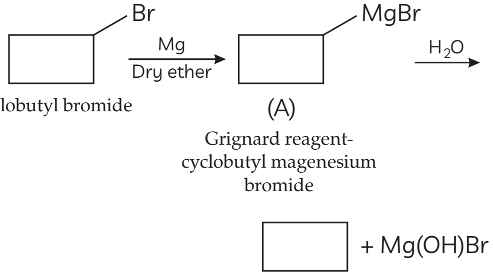
11. (i) The isomer of C_5H_{10} is cyclopentane. Since in cyclopentane all hydrogen atoms are equivalent, a single monochloro substituted product is formed in bright sunlight.

(ii) 1-Bromopentane < 2-Bromopentane < 2-Bromo-2-Methylbutane

(iii) *p*-dichlorobenzene As in S_N1 reaction the rate determining step is the formation of carbocation.

The more stable a carbocation is the faster the reaction will proceed. Hence, among the given compounds tertiary carbocation formed by 2-bromo-2-methylbutane is most stable hence the reaction is fastest with it followed by secondary and then primary whose reaction is slowest. A higher melting point than ortho and meta dichloro benzene isomers because it is more symmetrical and fits more closely in its crystal lattice.

(iv)



cyclobutyl bromide

(A)
Grignard reagent-
cyclobutyl magenesium
bromide

(B)
Cyclobutane

12. (i) Benzyl chloride in highly reactive towards S_N1 reaction because the benzyl carbocation that forms as an intermediate is stabilised by resonance with the benzene ring.

(ii) Butan-2-ol has a chiral carbon atom with four different groups attached to the central carbon. As racemic mixtures cancel the optical activity of each other, such solution do not rotate the plane polarised light so they are optically inactive.

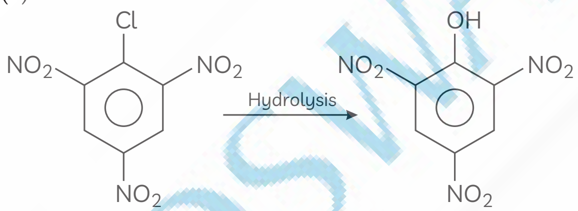
(iii) Chloroform is stored in dark-coloured bottles in the presence of ethanol to prevent the formation of a toxic substance called phosgene ($COCl_2$).

Chloroform ($CHCl_3$) undergoes slow oxidation in the presence of light and air to form phosgene, which is highly poisonous.

13. (i) $CH_3-Cl + NaI \xrightarrow{Acetone} CH_3I + NaCl$

Iodo methane

(ii)



2, 4, 6-trinitrophenol

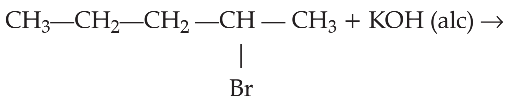
(iii) $CH_3-CH_2-CH_2-CH_2-Cl + KOH\ (alc.) \rightarrow$

(dehydrohalogenation)

$CH_3-CH_2-CH = CH_2 + H_2O$

Butene

14. (i)



$$CH_3-CH_2-CH_2-\underset{\substack{|\\Br}}{CH}-CH_3 + KOH\ (alc) \rightarrow$$

2-Bromopentane

$CH_3-CH_2-CH = CH-CH_3$

pent-2-ene

The product is formed according to Saytzeff's rule which predicts that the alkene with more alkyl groups attached to the double bond (the more substituted alkene) will be the major product of the elimination reaction.

(ii) CH_3-CH_2-Br because the reactivity order of S_N2 reaction is 1° > 2° > 3° because of the less steric hindrance in primary carbocation, the nucleophile can attack it with ease leading to inversion of configuration.

Tert alkyl halides are usually unreactive.

(iii) The resonance effect in chlorobenzene delocalises the lone pair of electrons on chlorine, giving the carbon-chlorine bond partial double bond character. It makes it stronger and more difficult to break.

Moreover, the *sp*^{2} hybridisation of the carbon atom bonded to chlorine makes it more electronegative and less susceptible to nucleophilic attack.

15. (i) Tertiary alkyl halides undergo S_N1 reaction faster than secondary or primary alkylhalide because teritiary carbocations are more stable than secondary or primary carbocation. The more stable carbocation intermediate the easier the compound undergoes S_N1 reaction.

(ii) Enantiomers are a pair of molecules that are mirror images of each other but cannot be on each other.

(iii) Chloroform is stored in dark-coloured bottles in the presence of ethanol to prevent the formation of a toxic substance called phosgene ($COCl_2$). Chloroform ($CHCl_3$) undergoes slow oxidation in the presence of light and air to form phosgene, which is highly poisonous:

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

Ethanol is added as a stabiliser. It reacts with any phosgene formed to convert it into non-toxic diethyl carbonate:

$COCl_2 + 2C_2H_5OH \rightarrow (C_2H_5O)_2CO + 2HCl$

Dark-coloured bottles block sunlight and minimise photochemical oxidation. Thus, storing chloroform with ethanol in dark bottles prevents the formation of phosgene and ensures safe storage.

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. (i) Both the reactions occur at the same rate as S_N1 reactions are independent of the concentration of the nucleophile.

(ii) The reaction (a) will be slower as Br^- is a better leaving group than Cl^-

(iii) Reaction (b) will not occur as the C-Cl bond has a partial double bond character due to reasonance.

2. (i) S_N2

Because in S_N2 reaction, the incoming neuclophile (I^-) interacts with the substrate (bromopropane) causing the C-Br bond to break and a new C-I bond to form. These two processes occur simultaneously in a single step without the formation of any intermediate.

The rate of reaction is determined by the concentrations of both the reactants.

(ii) Rate = $k\,[(CH_3)_3\,CBr]$ given S_N1.

Because S_N1 is a two step mechanism in which there is an intermediate carbocation formed.

The rate of reaction is determined only by the concentration of t-butyl bromide.

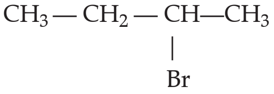
Level - 2 ADVANCED COMPETENCY FOCUSED QUESTIONS

MULTIPLE CHOICE QUESTIONS (MCQs) (1 Mark)

1. **Option (B) is correct.**

Explanation: According to Markovnikov's Rule:

$CH_3—CH_2—CH = CH_2 + HBr \rightarrow$



$$CH_3—CH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$$

2. **Option (C) is correct.**

Explanation: The leaving group play more important role in S_N^2 reaction. S_N^2 reaction is favoured by a good leaving group.

3. Option (B) is correct

Explanation: The iodoform test is used to detect Methyl ketones (compounds with the $–COCH_3$ group), and compounds that are oxidised to methyl ketones (like ethanol)

In this test, the compound is treated with iodine (I_2) and a base (NaOH or KOH). If a methyl ketone (or ethanol) is present, it gives a yellow precipitate of iodoform (CHI_3) — which is insoluble, yellow, and has a characteristic antiseptic smell. This yellow solid (CHI_3) makes the test easy to identify and confirms the presence of a methyl group attached to a carbonyl carbon or an ethanol structure.

4. Option (C) is correct

Explanation: The S_N1 (unimolecular nucleophilic substitution) reaction proceeds via formation of a carbocation intermediate. Stability of this carbocation is the key factor in determining the rate. 2-Chloro-2-methylpropane (tert-butyl chloride) is a tertiary halide that forms a tertiary carbocation, which is highly stable due to +I and hyperconjugation effects. It undergoes S_N1 most readily.

5. Option (C) is correct

Explanation: When a haloalkane (R–X) is heated with aqueous KOH, the halogen ($X^–$) is replaced by a hydroxyl group ($OH^–$), forming an alcohol. This is an example of a nucleophilic substitution reaction, where $OH^–$ (from aqueous KOH) acts as a nucleophile. $X^–$ (halide) is a leaving group.

6. Option (D) is correct

Explanation: Hydrolysis of haloalkanes involves nucleophilic substitution, where the halogen atom is replaced by an –OH group. C_6H_5Cl does not undergo hydrolysis easily due to resonance stabilisation and partial double bond character of the C–Cl bond in the benzene ring.

ASSERTION-REASON QUESTIONS (1 Mark)

1. Option (A) is correct

Explanation: Assertion is true. Tertiary alkyl halides undergo S_N1 reactions faster because the rate-determining step involves the formation of a carbocation, and tertiary carbocations form more readily.

Reason is also true. Tertiary carbocations are more stable due to +I (inductive) and hyperconjugation effects from three alkyl groups around the positively charged carbon.

2. Option (A) is correct

Explanation: Assertion is true. Chlorobenzene is resistant to nucleophilic substitution under normal conditions due to the stability of the aromatic ring and lack of easy leaving group behaviour.

Reason is also true. The C–Cl bond in chlorobenzene shows partial double bond character because of resonance between the lone pair on chlorine and the aromatic ring. This strengthens the bond and makes it less reactive toward nucleophilic substitution.

3. Option (C) is correct

Explanation: Assertion is true. The S_N^2 reaction involves a single-step backside attack by a nucleophile. Methyl halides, having minimal steric hindrance around the carbon attached to the halogen, react fastest via the S_N^2 mechanism.

Reason is false. S_N^2 reactions do not involve carbocation formation at all. That's a feature of S_N^1 reactions.

4. Option (A) is correct

Explanation: Assertion is true. Haloalkanes that possess β-hydrogen atoms (hydrogen atoms attached to the β-carbon, i.e., the carbon adjacent to the one bearing the halogen) can undergo β-elimination (or E_2 reaction) to form alkenes.

Reason is also true. In E_2 elimination, a base abstracts the β-hydrogen while the leaving group (halide ion) departs from the α-carbon simultaneously, forming a double bond (alkene).

5. Option (A) is correct

Explanation: Assertion is true. Aryl halides (like chlorobenzene) are significantly less reactive towards nucleophilic substitution reactions compared to alkyl halides.

Reason is also true. In aryl halides, the halogen atom is attached to an sp^2 hybridised carbon of the aromatic ring. Due to resonance, the lone pair on the halogen overlaps with the π-system of the benzene ring, giving the C–X bond partial double bond character, making it stronger and harder to break.

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. Chloroform is stored in dark bottles to prevent light-induced formation of poisonous phosgene, and ethanol is added to neutralise any phosgene that may form.
2. Carbon tetrachloride (CCl_4) is no longer used as a fire extinguisher despite being non-flammable because of the following serious health and safety concerns:
   (1) Toxic Gases on Heating: When CCl_4 is exposed to high temperatures, such as in a fire, it decomposes and forms highly toxic gases like:
   $CCl_4 \xrightarrow{\text{heat}} \text{Phosgene } (COCl_2), Cl_2, HCl$
   Phosgene ($COCl_2$) is a deadly poisonous gas once used in chemical warfare.
   (2) Health Hazards: Inhalation of vapours or breakdown products can cause severe respiratory irritation, liver and kidney damage, and central nervous system depression.
   (3) Environmental Concerns: CCl_4 is a volatile organic compound (VOC) and contributes to ozone layer depletion.
3. The iodoform reaction is a valuable forensic tool because it is highly specific, easily observable, and can confirm the presence of ethanol or methyl ketones—substances commonly encountered in criminal investigations.
4. The partial double bond character in chlorobenzene enhances its thermal and chemical stability, making it a reliable industrial solvent for high-temperature and reactive systems where chemical inertness is crucial.
5. Fluorinated compounds are ideal for non-stick cookware due to their non-stick properties, thermal and chemical stability, and non-reactive nature, ensuring safe, efficient, and long-lasting cooking surfaces.

SHORT ANSWER TYPE QUESTIONS (3 Marks)

1. (i) CCl_2F_2 decomposes under UV light to give free radical chlorine which reacts with ozone and destroys the ozone layer.
   (ii) Compounds Q and S are suitable for refrigerant due to their less boiling point.
2. (p) Substitution; In polar solvent, substitution predominates for primary haloalkanes with ^{-}OH ions.
   (q) Elimination; In a less polar solvent like alcohol, elimination predominates for tertiary haloalkanes with ^{-}OH ions.
   (r) Elimination; elimination predominates due to steric effect as the base used is bulky group.
3. Haloalkanes are widely used in medicine as volatile general anesthetics. These compounds depress the central nervous system (CNS), leading to loss of sensation and consciousness, which is essential during surgical procedures.
   Haloalkanes, when inhaled, interact with neuronal membranes in the brain, altering the transmission of nerve impulses and inducing unconsciousness. Their lipid solubility allows them to easily cross the blood-brain barrier and act quickly.
   Halothane ($C_2HBrClF_3$) is a commonly used haloalkaneanesthetic.
   The advantages of Halothene over older anesthetics are:
   (1) Non-flammable: Unlike ether, halothane is non-explosive and safer to use in operation theatres.
   (2) Rapid induction and recovery: Patients go under and recover from anesthesia faster.
   (3) Better control: Halothane provides more predictable depth of anesthesia.
   (4) Non -irritating for respiratory tract as opposed to older anaesthetics.
4. The environmental concerns of chlorofluorocarbons (CFCs) in refrigeration are:
   (1) Ozone Layer Depletion: CFCs are highly stable compounds used historically in refrigeration and air-conditioning. Once released, they rise to the stratosphere, where UV radiation breaks them down, releasing chlorine free radicals (Cl).These radicals catalytically destroy ozone (O_3) molecules, which protect Earth from harmful ultraviolet (UV) rays.
   (2) Increased UV Radiation: Due to ozone thinning, especially the "ozone hole" over Antarctica, more UV-B radiation reaches Earth, leading to skin cancer, eye cataracts, suppressed immune systems, and damage to marine life and plants.
   (3) Global Warming Potential (GWP): CFCs are also potent greenhouse gases, trapping heat in the atmosphere and contributing to climate change.
   Alternatives and Their Impact:
   (1) Hydrochlorofluorocarbons (HCFCs): Less stable than CFCs, break down earlier in the atmosphere. It is still ozone-depleting, but less harmful and considered a transitional replacement.
   (2) Hydrofluorocarbons (HFCs): Do not contain chlorine, so they do not deplete ozone. Used widely as CFC substitutes in modern refrigeration. Still have high GWP, but safer for the ozone layer.
   (3) New-generation refrigerants (e.g., HFOs, CO_2, ammonia): Hydrofluoroolefins (HFOs) have very low GWP and zero ozone depletion. Natural refrigerants like CO_2 and ammonia are environmentally benign and used increasingly in sustainable systems.
5. The structure of aryl halides significantly influences their chemical behaviour in water purification processes, particularly in terms of reactivity, persistence, and environmental impact.
   (1) Low Reactivity Due to Resonance: In aryl halides (like chlorobenzene), the halogen is bonded to an aromatic ring, where the lone pair of electrons on the halogen delocalises into the π-system of the ring. This creates a partial double bond character in the C–X bond (X = halogen), making it stronger and less reactive than in alkyl halides. As a result, aryl halides are resistant to hydrolysis or breakdown in water.

(2) Persistence as Pollutants: Due to their stability, aryl halides (especially chlorinated aromatic compounds) can persist in water bodies and are not easily degraded by natural processes. This structural stability makes a target of removal in water treatment.

(3) Use in Adsorption or Chemical Sensors: Certain modified aryl halides (e.g., with functional groups) are used in chemical sensors or membranes to detect or bind specific pollutants. Their aromatic ring structure provides a stable backbone, allowing the attachment of chelating or reactive sites that assist in removing heavy metals or organic toxins.

(4) Limited Direct Role but Important in Designing Materials: While pure aryl halides are not directly used for water purification, they are part of larger polymeric materials or functionalised compounds designed for selective pollutant binding, membrane filtration, and advanced oxidation processes.

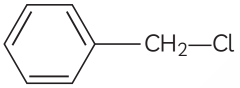
CASE BASED QUESTIONS (2 Marks)

1. (i) Racemisation occurs in S_N1 reaction because the nucleophile attacks the carbocations intermediate from both sides and forms an equal mixture (i.e. 50%-50%) of enantiomers.

(ii) A molecules's polarity is determined by the electronegativity difference between its constituents atoms. In ethanol, the electronegativity difference between carbon (C) and oxygen (O) is smaller than that between oxygen (O) and hydrogen (H) in water. As result the polarity of ehtanol is lower than that of water

(iii) (a) (1) $CH_3—CH_2—I$

It is because I^- is a better leaving group than Cl^-

(2) 

It is because Cl^- is linked to sp^3 hybridised carbon atom.

(b) (1) 1-Bromopentane < 2-Bromopentane < 2-Bromo-2-methyl butane

(2) 1-Bromo-3-methyl butane < 2-Bromo-3-methylbutane < 2-Bromo-2-methylbutane.

2. (i) 

Grignard's reagen-Phenyl magnesium bromide

(ii) (1) $CH_2 = CH — CH_2 — Cl$

As it forms a stable allylic carbocation due to resonance.

(2) $(CH_3)_3\,C—Cl$

In S_N1 reaction the rate determining step is formation of carbocation and a tert-carbocation is stabler hence reaction is faster with it.

(iii) (a) (1) By using Finkelstein reaction

$$CH_3CH_2CH_2CH_2Cl + NaI \xrightarrow[\text{Acetone}]{CH_3OH} CH_3CH_2—CH_2—CH_2I + NaCl$$

(2) By using peroxide

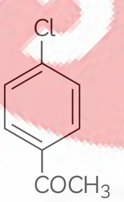
$$CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}} CH_3CH_2CH_2CH_2Br$$

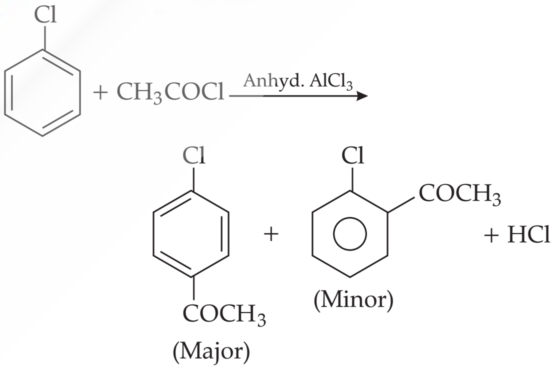
$$CH_3CH_2CH_2CH_2 — Br + NaI \xrightarrow[\text{acetone}]{\text{Dry}} CH_3CH_2CH_2CH_2—I + NaBr.$$

OR

(b) (1) $CH_3 — CH = CH_2$

$$CH_3—\underset{\underset{Br}{|}}{CH}—CH_3 + KOH \xrightarrow[\text{heat}]{\text{Ethanol}} CH_3—CH = CH_2 + KBr + H_2O$$

(2) 



LONG ANSWER TYPE QUESTIONS (5 Marks)

1. (i) Haloalkanes, such as bromoalkanes, are reactive intermediates that can undergo a wide range of reactions (especially nucleophilic substitution). The carbon-halogen bond is polar, making the carbon susceptible to attack by nucleophiles. This allows easy transformation into alcohols, amines, nitriles, and other functional groups—key steps in synthesising complex drug molecules.

(ii) **To alcohols:** Bromoalkanes react with aqueous KOH or NaOH to undergo nucleophilic substitution forming alcohols:

$R – Br + OH – \rightarrow R – OH + Br–$

To amines: They react with excess ammonia or amines to give primary, secondary, or tertiary amines:

$R – Br + NH_3 \rightarrow R\text{-}NH_2 + HBr$

(iii) The precautions to be taken during large-scale handling of haloalkanes are:

(1) Ventilation and closed systems to prevent inhalation exposure.

(2) Protective gear (gloves, masks, goggles) due to toxicity and skin absorption.

(3) Proper storage away from heat and light to avoid decomposition.

(4) Waste treatment systems to prevent release into the environment, as some haloalkanes can be carcinogenic or ozone-depleting.

(iv) (1) C – I > C – Br > C – Cl > C – F in terms of bond strength (weaker bonds = more reactive).

(2) Iodoalkanes react fastest in nucleophilic substitution due to weaker C–I bonds, while fluoroalkanes are least reactive.

(3) Electron-withdrawing nature of halogens also affects carbocation stability in S_N1 reactions.

(v) The green alternatives that are being researched to reduce environmental harm are:

(1) Use of greener solvents (like water, ethanol, or ionic liquids) in place of toxic organic solvents.

(2) Biocatalysts or enzymes to replace harsh chemical reagents.

(3) Microwave-assisted synthesis to reduce energy consumption.

(4) Fluorine-free or biodegradable reagents to replace harmful haloalkanes.

(5) Adoption of flow chemistry for better safety and atom economy in synthesis

2. (i) DDT (Dichloro Diphenyl Trichloroethane) was highly effective due to its long residual action, lipophilic nature (easily penetrates insect cuticles), and neurotoxic effect on pests. It interfered with nerve impulse transmission in insects, leading to paralysis and death.

(ii) DDT is non-biodegradable, bioaccumulative, and highly persistent in ecosystems. It enters the food chain, causing biomagnification—especially in birds (e.g., thinning of eggshells in birds like eagles and falcons), leading to population declines. It also poses health risks to humans (possible carcinogen, endocrine disruptor).

(iii) The structural features of DDT that contribute to its persistence in soil are:

(1) Contains multiple chlorine atoms, making it resistant to microbial degradation.

(2) Has aromatic rings which are chemically stable and degrade very slowly.

(3) Highly non-polar, making it poorly soluble in water and hence not easily washed away from soil.

(iv) Pyrethroids (e.g., permethrin) are commonly used today. They are synthetic analogs of natural pyrethrins derived from chrysanthemum flowers and are less toxic to humans and biodegradable.

(v) Eco-friendly pesticides are designed to:

(1) Break down easily in the environment (biodegradable functional groups)

(2) Have selective toxicity (affect pests but not humans/wildlife)

(3) Avoid bioaccumulation (low lipophilicity or persistent halogens)

(4) Use natural product mimics (e.g., neem-based or pheromone-based agents)

(5) Chemists use structure–activity relationships (SARs) to tweak functional groups for efficacy, safety, and degradation profiles.

(6) Solubility- water solubility due to presence of polar functional groups(-OH and -COOH) will ensure that they are run off with water and not bound to the soil particles.

◆