



HALOALKANES - HALOARENES

Master the intricacies of Haloalkanes and Haloarenes with our targeted revision module designed for CBSE Class 12 Chemistry. This module is meticulously crafted to reinforce your understanding of key concepts, reactions, and applications in the realm of organic chemistry.

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Topic Coverage: The revision module comprehensively covers Haloalkanes and Haloarenes, delving into nomenclature, preparation methods, reaction mechanisms, and their diverse applications in organic synthesis – aligning with the CBSE Class 12 Chemistry curriculum.

Concise and Clear: The content is presented in a concise and clear manner, focusing on the most critical aspects of Haloalkanes and Haloarenes. It serves as an effective tool for quick revision before exams.

Important reactions: The module includes a compilation of important reactions and mechanisms, providing a quick reference for key transformations in Haloalkanes and Haloarenes.

Application-Based Questions: Engage in practice with a set of application-based questions to enhance your problem-solving skills and understand the real-world applications of organic reactions.

Concept Reinforcement: Reinforce your understanding of the underlying concepts through targeted explanations and examples, ensuring a solid foundation in Haloalkanes and Haloarenes.

Exam-Style Questions: Familiarize yourself with the types of questions that could appear in the CBSE Class 12 Chemistry exam. Solve exam-style questions to refine your exam-taking strategies.

Online Accessibility: The revision module is accessible online, allowing you to study anytime anywhere. This flexibility enables you to integrate revision seamlessly into your schedule.

HALOALKANES-HALOARENES
 REVISION MODULE
 CHEMISTRY CBSE-XII

POINTS TO

REMEMBER

1. **Haloalkanes or alkyl halides** are the compounds which have the general formula RX , where R is an alkyl or substituted alkyl group and X is a halogen (F, Cl, Br, I). Likewise, **Haloarenes or Aryl halides** are the compounds containing halogens attached directly to an aromatic ring. They have the general formula ArX (where Ar is phenyl, or substituted phenyl).



An alkyl halide
(Haloalkane)

R = Alkyl or substituted alkyl

X = F, Cl, Br, I



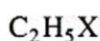
An aryl halide
(Haloarene)

Ar = Phenyl or substituted phenyl

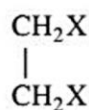
X = F, Cl, Br, I

Classification:

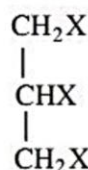
- (a) **Classification based on the number of halogen atoms:** These may be classified as mono, di, or polyhalogen compounds depending on whether they contain one, two or more halogen atoms in their structures. For example,



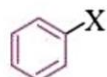
Monohaloalkane



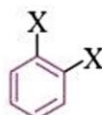
Dihaloalkane



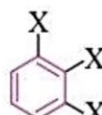
Trihaloalkane



Monohaloarene



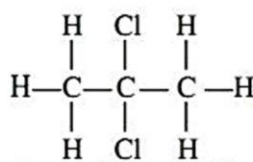
Dihaloarene



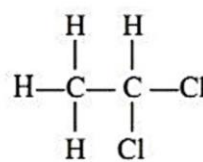
Trihaloarene

Dihalogen compounds may be further classified as discussed below:

- **Gem-dihalides:** The two halogen atoms are attached to the same carbon atom in gem-dihalides. For example,

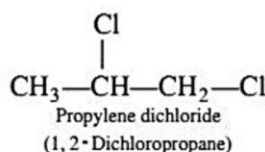
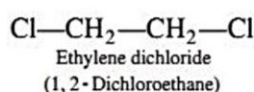


Isopropylidene chloride
(2,2-Dichloropropane)



Ethylidene chloride
(1,1-Dichloroethane)

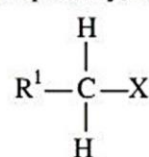
- **Vic-dihalides:** In these compounds, the two halogen atoms are attached to adjacent carbon atoms. For example,



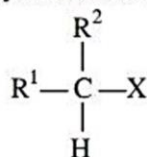
(b) Classification based on hybridisation of carbon atom:

- (i) Halogen compounds in which halogen is bonded to sp^3 hybridised carbon. This class includes:

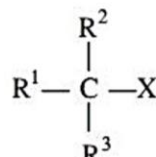
- (a) **Haloalkanes or alkyl halides:** They are the halogen compounds of saturated hydrocarbon. Their general formula is $\text{C}_n\text{H}_{2n+1}\text{X}$. They are further classified as primary haloalkane, secondary haloalkane or tertiary haloalkane according to whether the halogen atom is bonded to primary, secondary or tertiary carbon atom.



Primary haloalkane

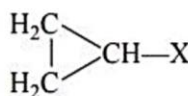


Secondary haloalkane

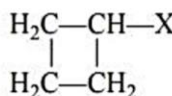


Tertiary haloalkane

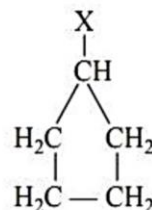
If in $\text{R}-\text{X}$, R is an alicyclic, *i.e.*, cyclic aliphatic hydrocarbons such as cyclopropane, cyclobutane, cyclopentane, etc., they are known as halocycloalkane or cycloalkylhalide. For example,



Halocyclopropane

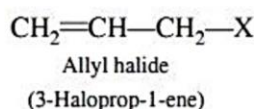


Halocyclobutane



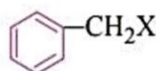
Halocyclopentane

- (b) **Allylic halides:** In these compounds, halogen is bonded to allylic carbon, *i.e.*, to the sp^3 hybridised carbon atom next to a carbon-carbon double bond. Examples are:

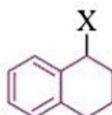


3-Halocyclohex-1-ene

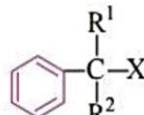
- (c) **Benzylic halides:** In these halides, the halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring, *i.e.*, to a benzylic carbon. For example,



Benzyl halide



1-Halo-1, 2, 3, 4 tetrahydro naphthalene

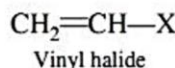


Dialkylbenzyl halide

Benzylic halides may be primary, secondary or tertiary.

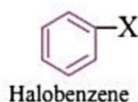
- (ii) Halogen compounds in which halogen is bonded to sp^2 or sp hybridised carbon.

- (a) **Vinyl halides:** In these halides, halogen is bonded to one of the carbon atoms of a vinyl carbon, *i.e.*, carbon-carbon double bond which is sp^2 hybridised. The examples are :



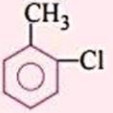
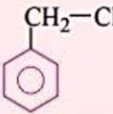
1-Halocyclohex-1-ene

(b) **Aryl halides:** In these halides, the halogen atom is directly bonded to carbon atom of aromatic ring. These are called haloarene or aryl halides, e.g., halobenzene.



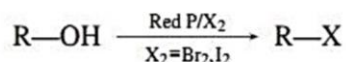
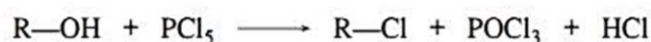
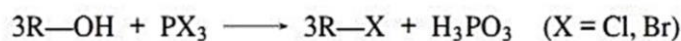
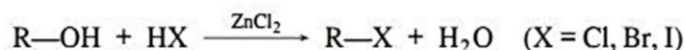
2. Common and IUPAC names of some halides:

Table 6.1: Common and IUPAC Names of Some Halides

Structure	Common Name	IUPAC Name
$\text{CH}_3\text{—Cl}$	Methyl chloride	Chloromethane
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—F}$	<i>n</i> -Propyl fluoride	1-Fluoropropane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—CH—Cl} \end{array}$	Isopropyl chloride	2-Chloropropane
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—Cl}$	<i>n</i> -Butyl chloride	1-Chlorobutane
$\begin{array}{c} \text{CH}_3\text{—CH}_2\text{—CH—CH}_3 \\ \\ \text{Cl} \end{array}$	sec-Butyl chloride	2-Chlorobutane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—CH—CH}_2\text{—Cl} \end{array}$	Isobutyl chloride	1-Chloro-2-methylpropane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—C—CH}_3 \\ \\ \text{Br} \end{array}$	<i>tert</i> -Butyl bromide	2-Bromo-2-methylpropane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—C—CH}_2\text{—Br} \\ \\ \text{CH}_3 \end{array}$	<i>neo</i> -Pentyl bromide	1-Bromo-2, 2-dimethylpropane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—CH—CH}_2\text{—CH}_2\text{—Cl} \end{array}$	Isopentyl chloride	1-Chloro-3-methylbutane
$\text{CH}_2\text{=CH—Cl}$	Vinyl chloride	Chloroethene
$\text{CH}_2\text{=CH—CH}_2\text{—Br}$	Allyl bromide	3-Bromoprop-1-ene
$\text{CH}_2\text{—Cl}_2$	Methylene chloride	Dichloromethane
CHCl_3	Chloroform	Trichloromethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
	<i>o</i> -Chlorotoluene	2-Chlorotoluene or 1-Chloro-2-methylbenzene
	Benzyl chloride	Chlorophenylmethane

3. Methods of Preparation of Haloalkanes

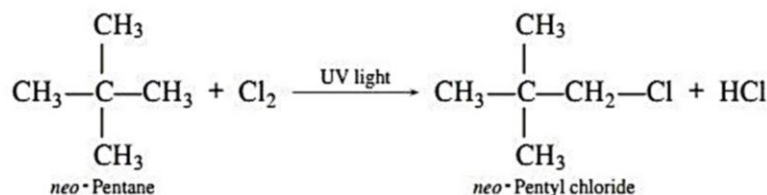
(a) **From alcohols:** Alkyl halides are best prepared from alcohols, which are easily accessible.



The reactions of primary and secondary alcohols with HX require the presence of the catalyst, $ZnCl_2$.

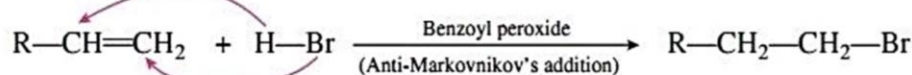
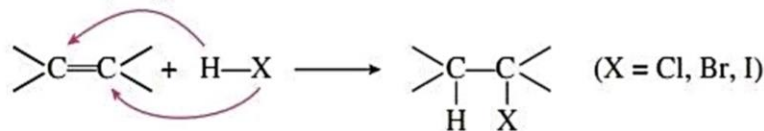
(b) **From hydrocarbons**

By free radical halogenation:

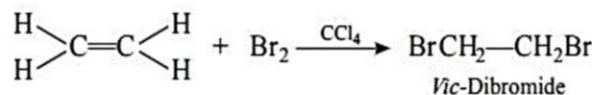


(c) **From alkenes**

(i) Addition of hydrogen halides

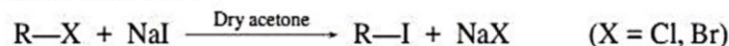


(ii) Addition of halogens

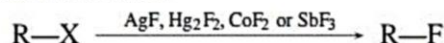


(d) **Halide exchange**

(i) By Finkelstein reaction



(ii) By Swarts reaction



4. Physical Properties of Haloalkanes

- (a) **Melting and boiling point:** Haloalkanes have higher boiling points as compared to those of corresponding alkanes. This is due to their polar nature and strong dipole-dipole interactions between their molecules.

The boiling points of haloalkanes are in the order $\text{RCl} < \text{RBr} < \text{RI}$. It is because with the increase in size and mass of the halogen atom the magnitude of van der Waals forces of attraction increases.

Among isomeric alkyl halides, the boiling point decreases with increase in branching in the alkyl group. This is due to the reason that with increase in branching, the molecule attains a spherical shape with less surface area. As a result, interparticle forces become weaker resulting in lower boiling point. For example, among isomeric butyl chlorides, the straight chain isomer, *n*-butyl chloride has the highest boiling point whereas *tert*-butyl chloride has the lowest boiling point.

- (b) **Density:** Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.
- (c) **Solubility:** Haloalkanes and haloarenes are practically insoluble in water because they are not able to form intermolecular hydrogen bonds with water molecules. However, they are soluble in organic solvents.

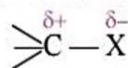
5. Chemical Properties of Haloalkanes

The chemical reactions of haloalkanes can be divided into following types:

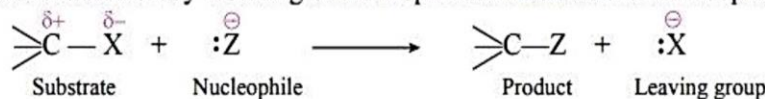
- (a) Nucleophilic substitution reactions
(b) Dehydrohalogenation or β -elimination reactions
(c) Reaction with metals

- (a) **Nucleophilic substitution reactions:** When an atom or group of atoms is replaced by a nucleophile, the reaction is called nucleophilic substitution reaction.

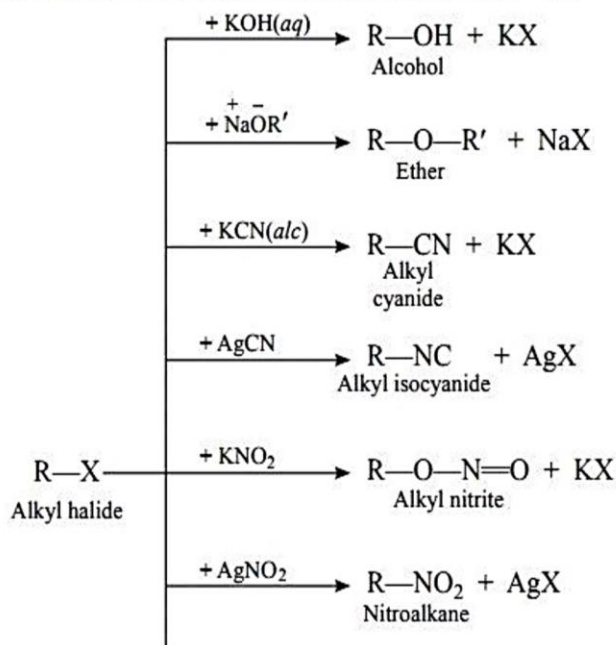
In haloalkanes, the halogen atom is attached to the carbon atom. As the halogen atom is more electronegative than carbon, the bond between carbon and halogen is polar in character.



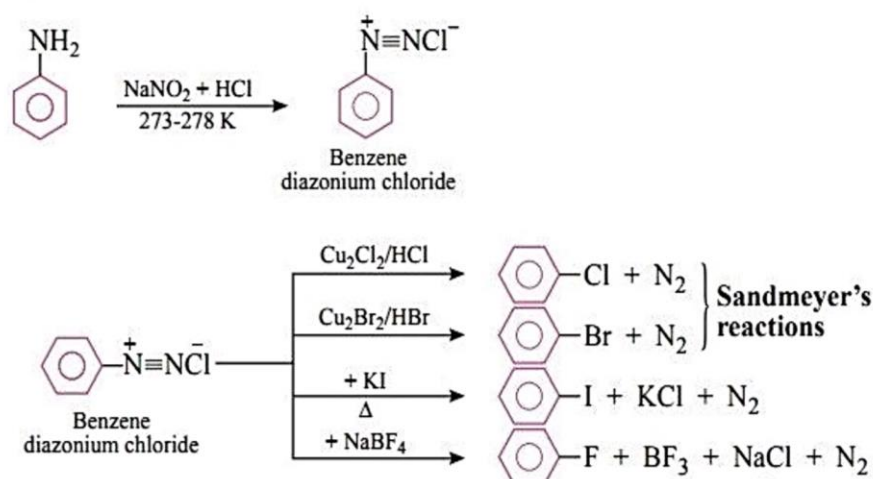
Due to the presence of partial positive charge on the carbon atom, the nucleophiles can attack on electron deficient carbon thereby resulting in the displacement of weaker nucleophile, the halide ion.



Nucleophilic Substitution of Alkyl halides (R—X)

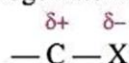


(b) From diazonium salts



7. Physical Properties of Haloarenes

- (a) **Melting and boiling points:** Boiling point of isomeric dihalobenzenes are very nearly same. However *p*-isomer have higher melting point as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho and meta isomers.
- (b) **Nature of C—X bond:** The C—X bond is polar as 'X' is more electronegative than carbon. The carbon has partial positive charge whereas halogen has slight negative charge because shared pair of electrons are more towards halogen atoms.



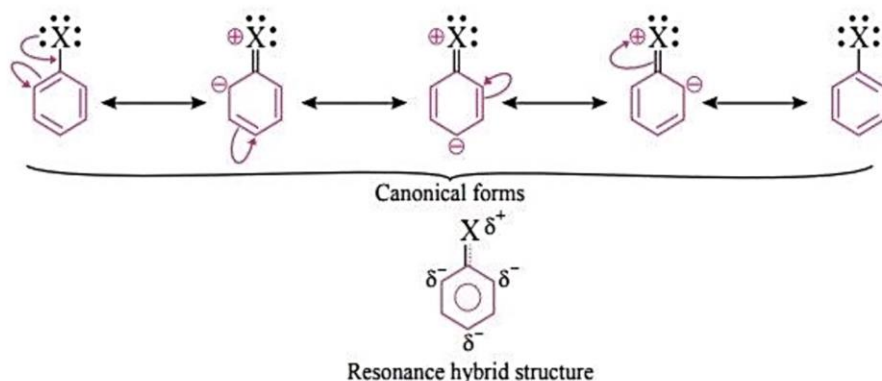
Dipole moment of CH_3Cl is higher than CH_3F due to greater bond length in C—Cl bond.

8. Chemical Properties of Haloarenes:

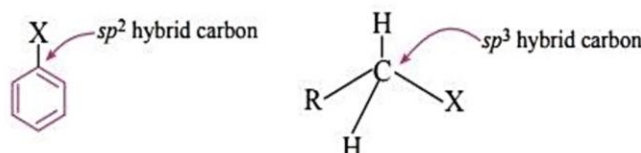
(a) Nucleophilic substitution reactions of haloarenes

Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

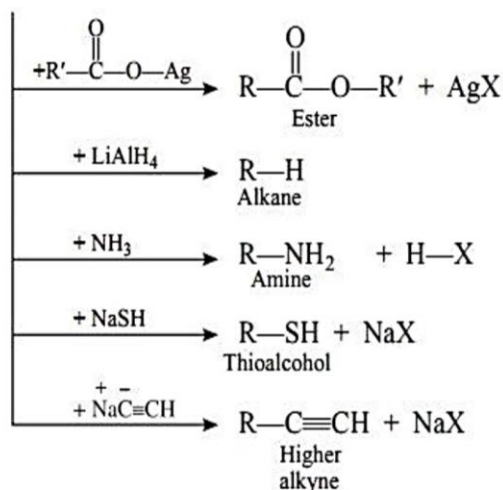
- (i) **Resonance effect:** In arylhalides C—X bond acquires a partial double bond character due to resonance. As a result C—X bond cleavage in aryl halides is difficult than alkyl halides and therefore they are less reactive towards nucleophilic substitution reaction.



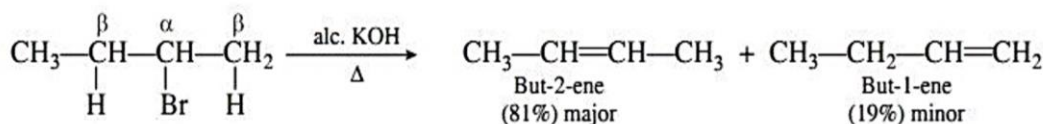
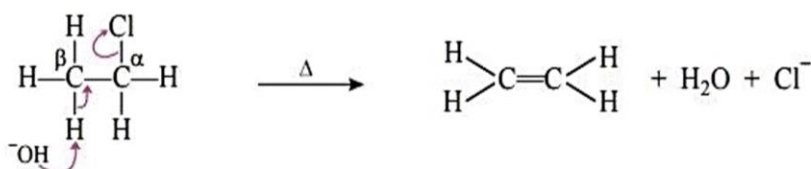
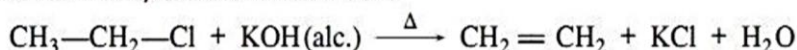
(ii) Difference in hybridisation:



- (iii) **Instability of phenyl cation:** In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore $\text{S}_{\text{N}}1$ mechanism is ruled out.

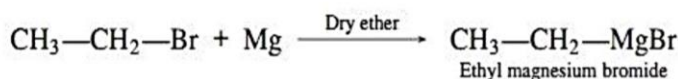
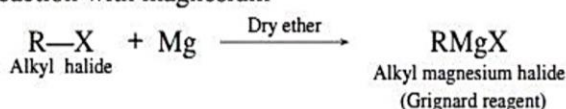


- (b) **Elimination reactions:** When haloalkane with β -hydrogen atom is heated with ethanolic potassium hydroxide, there is elimination of hydrogen atom from β -carbon atom and a halogen atom from α -carbon atom. As a result, an alkene is formed. Since β -hydrogen atom is involved in elimination, it is often called β -elimination reaction.

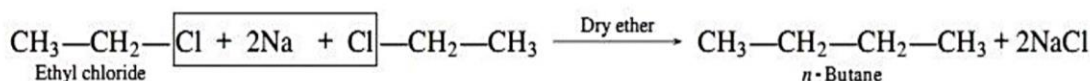
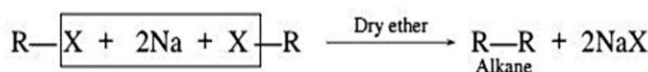


(c) Reaction with metals

(i) Reaction with magnesium

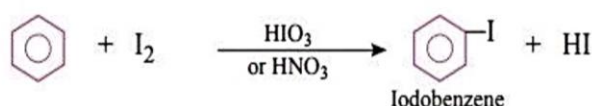
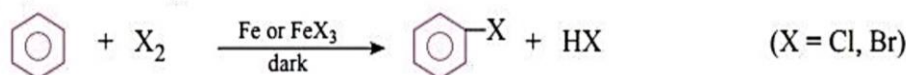


(ii) Reaction with sodium (Wurtz reaction)

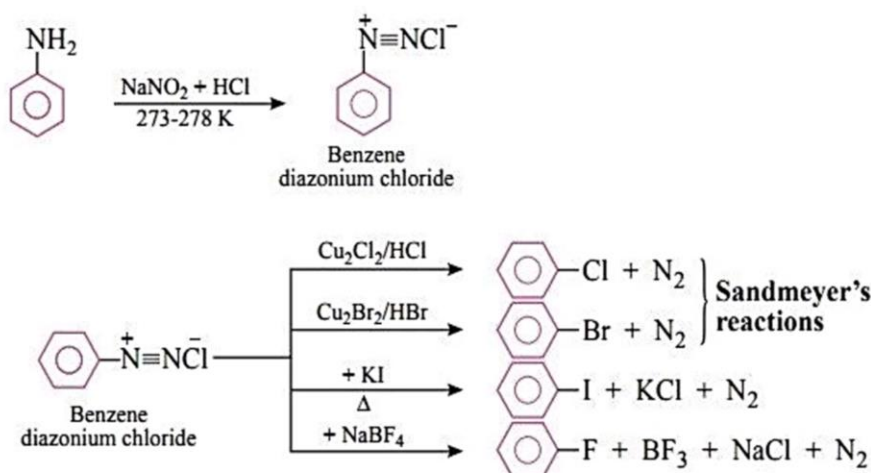


6. Preparation of Haloarenes

(a) By direct halogenation of benzene

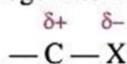


(b) From diazonium salts



7. Physical Properties of Haloarenes

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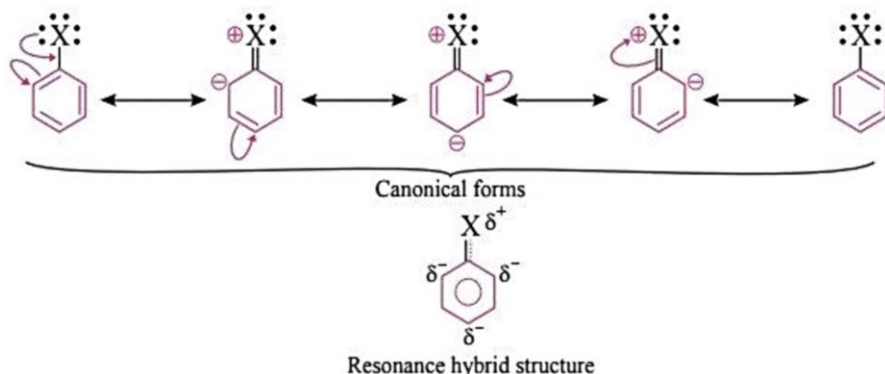
Dipole moment of CH_3Cl is higher than CH_3F due to greater bond length in C—Cl bond.

8. Chemical Properties of Haloarenes:

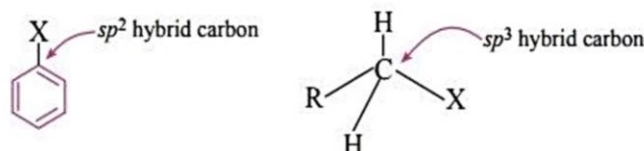
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(ii) Difference in hybridisation:

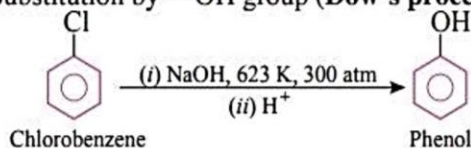


- (iii) **Instability of phenyl cation:** In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore $\text{S}_{\text{N}}1$ mechanism is ruled out.

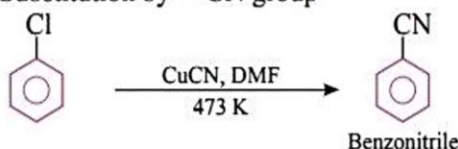
(iv) Because of the possible repulsion, it is less likely for the electron-rich nucleophile to approach electron-rich areas.

However, at high temperature and pressure several nucleophilic substitution reactions are carried out.

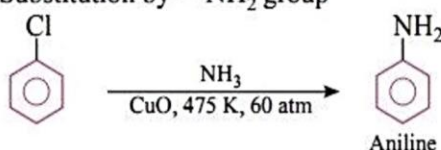
- Substitution by —OH group (Dow's process)



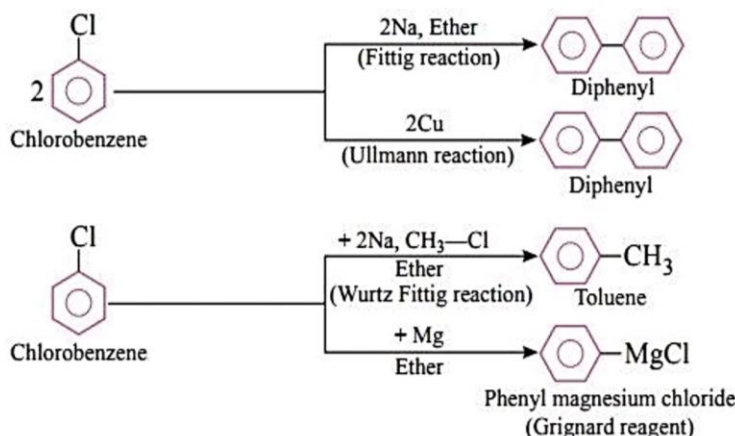
- Substitution by —CN group



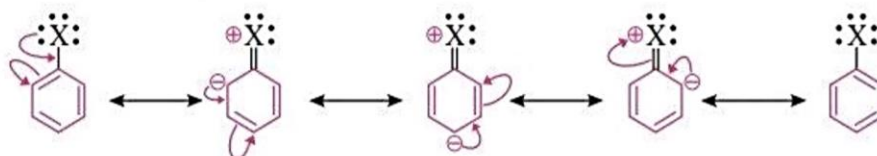
- Substitution by —NH₂ group



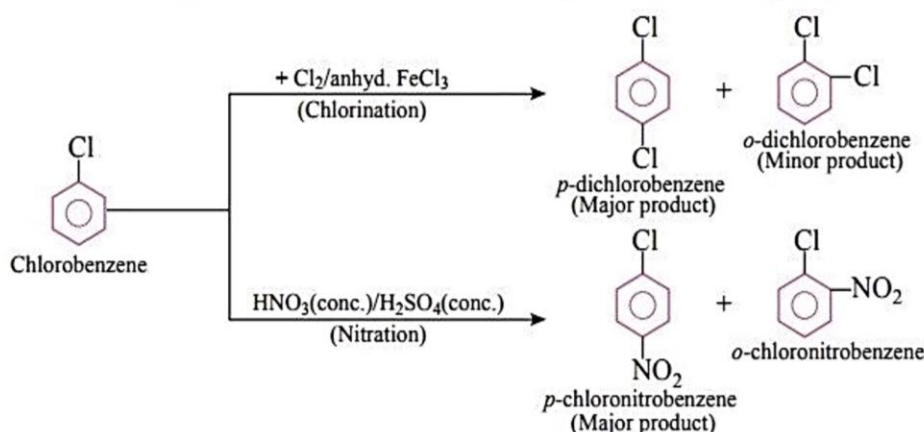
(b) Reactions with metals

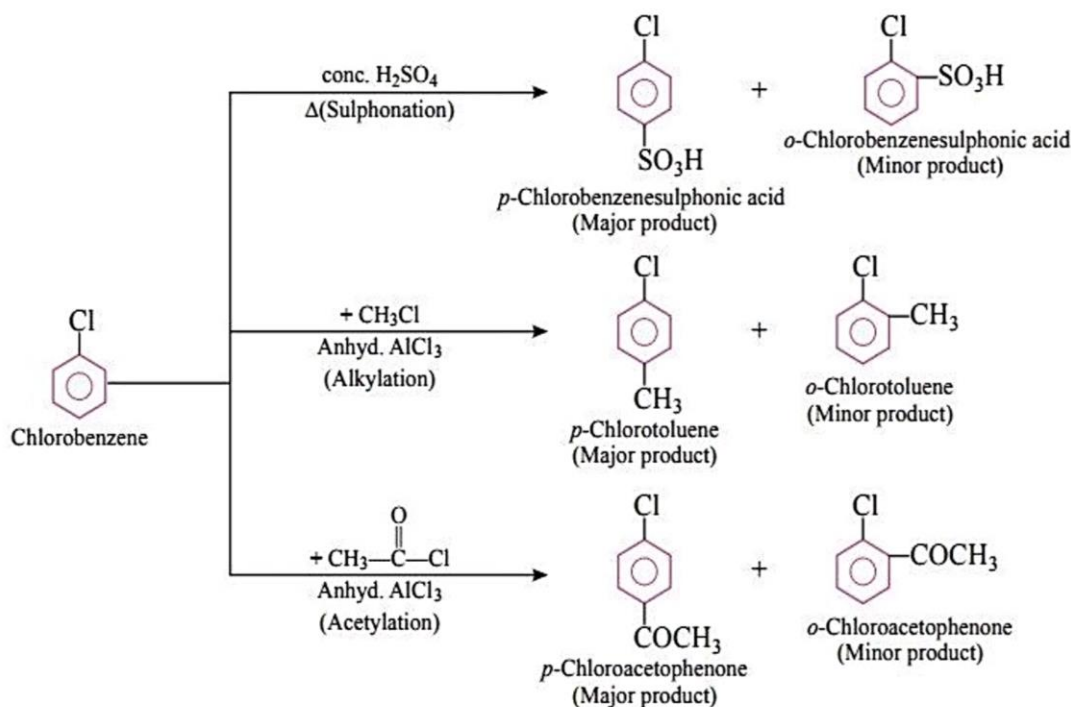


(c) Electrophilic substitution reactions of haloarenes



Due to resonance, the electron density increases more at ortho and para positions than at meta positions. Therefore, electrophilic substitution reactions take place at ortho and para positions.





9. (a) **Stereoisomerism:** Isomerism exhibited by two or more compounds with the same molecular and structural formulae but different spatial arrangements of atoms or groups in space is called stereoisomerism.
- (b) **Plane-polarised light:** The beam of light whose oscillations or vibrations are confined to one plane only is called plane-polarised light. It is obtained by passing a monochromatic light (light of single wavelength) through a Nicol prism.
- (c) **Optically active substances:** Those substances which rotate the plane of polarisation of plane-polarised light when it is passed through their solutions are called optically active substances. This phenomenon is called optical activity.
- (d) **Optical rotation:** The property of rotating the plane of polarisation either towards left or towards right is called optical rotation.
- (i) **Laevorotatory:** Those substances which rotate the plane of polarisation of light towards the left direction are called laevorotatory.
- (ii) **Dextrorotatory:** Those substances which rotate the plane of polarisation of light towards right are called dextrorotatory.

Currently, dextro and laevo rotations are represented by algebraic signs of (+) and (−), respectively.

- (e) **Specific rotation:** Specific rotation is defined as the number of degrees of rotation observed when the concentration of optically active substance is 1 g cm^{-3} and length of polarimeter tube is 1 decimetre (dm) for D-line of sodium vapour lamp at 25°C .

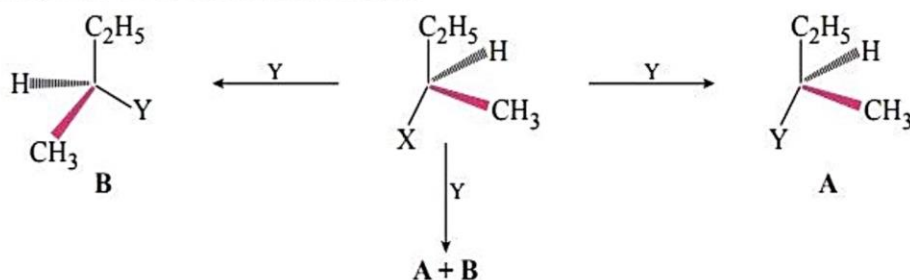
$$\text{Specific rotation } [\alpha] = \frac{\text{Observed rotation } (\alpha_{\text{obs}})}{\text{Length of tube (dm)} \times \text{Concentration of solution (g mL}^{-1}\text{)}}$$

While reporting $[\alpha]$, the wavelength of light used is given as subscript and the temperature (in degrees celsius) as a superscript. It is also customary to designate the solvent and concentration.

Thus, $[\alpha]_{\text{D}}^{25} = -2.25^\circ (\text{C}; 0.50 \text{ ethanol})$ means that α was measured at 25°C using sodium D-line and the sample concentration was 0.50 g/mL in ethanol.

- (f) **Asymmetric molecule:** If all the four substituents attached to carbon are different, the resulting molecule will lack symmetry. Such a molecule is called asymmetric molecule. Asymmetry of molecule is responsible for optical activity in such organic compounds.
- (g) **Chiral:** An object which is non-superimposable on its mirror image is said to be chiral. The property of being chiral is known as chirality.

- (h) **Asymmetric carbon:** The carbon atom which is attached with four different groups of atoms is called asymmetric carbon. The molecule having asymmetric carbon atom is called asymmetric.
- (i) **Enantiomers:** The stereoisomers which are non-superimposable mirror images are called enantiomers. Enantiomers rotate the plane of polarised light to the same extent but in opposite direction.
- (j) **Racemic mixture:** An equimolar mixture of a pair of enantiomers is called racemic mixture. A racemic mixture is optically inactive due to external compensation.
- (k) **Racemisation:** The process of conversion of an enantiomer into racemic mixture is known as racemisation.
- (l) **Resolution of a racemic mixture:** Resolution is a process of separating a racemic mixture into its enantiomer constituents, i.e., dextro $d(+)$ and laevo-rotatory $l(-)$ substances.
- (m) **Meso compounds:** The compounds containing two or more chirality centres but possessing achiral molecular structure because of having plane of symmetry are called meso compounds. A meso compound is optically inactive due to internal compensation.
- (n) **Diastereomers:** The stereoisomers which are non-superimposable and do not bear a mirror-image relationship.
- (o) **Retention:** If in an optically active molecule the relative configuration of the atoms/groups around a chiral centre remains the same before and after the reaction, the reaction is said to proceed with retention of configuration.
- (p) **Inversion:** If the relative configuration of atoms/groups around a stereo centre in the product is opposite to that in reactant, the reaction is said to proceed with inversion of configuration.
- There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by Y in the following reaction:



If (A) is the only compound obtained, the process is called retention of configuration.

If (B) is the only compound obtained, the process is called inversion of configuration.

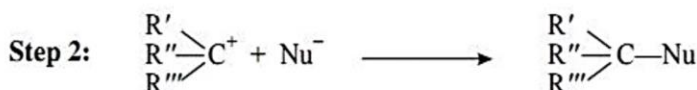
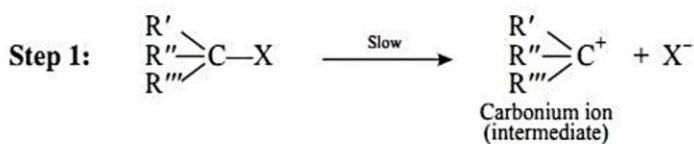
If a 50 : 50 mixture of the above two is obtained then the process is called racemisation and the product is optically inactive, as one isomer will rotate light in the direction opposite to another.

10. Mechanism of Nucleophilic Substitution in Alkyl Halides

The nucleophilic substitution reactions in alkyl halides can take place by either of two mechanisms: S_N1 and S_N2

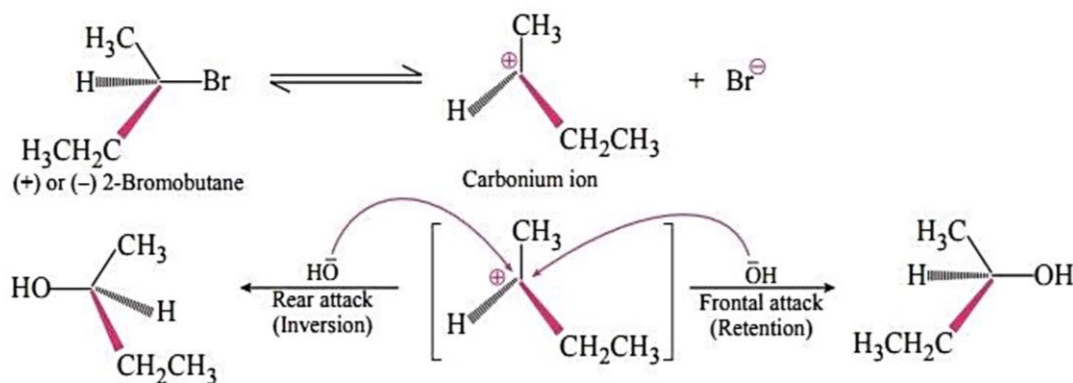
Substitution nucleophilic unimolecular (S_N1)

It takes place in two steps and the reaction is of first order. In the first step, alkyl halide undergoes slow heterolysis to produce carbonium ion (an intermediate) and a halide ion. In the second step, nucleophile rapidly combines with the carbonium ion to complete the substitution reaction.



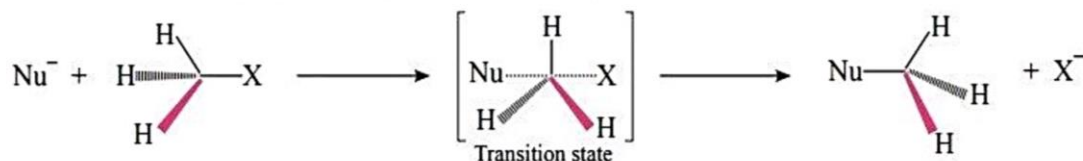
S_N1 reactions of optically active halides are accompanied by racemisation. This is because the carbonium formed in the slow step being sp^2 hybridised is planar (achiral) therefore, the attack of nucleophile on it can

occur from both the faces with equal ease giving a mixture containing two enantiomers in equal amounts. This may be illustrated by hydrolysis of optically active 2-bromobutane, which gives (±) butan-2-ol.



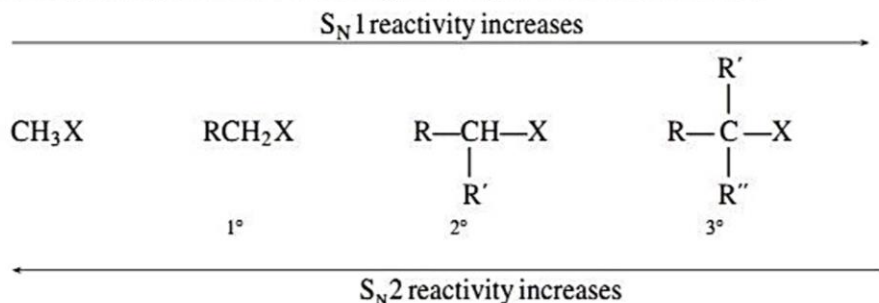
Substitution nucleophilic bimolecular (S_N2)

It takes place in one step and the reaction is of second order. In this process the nucleophile attacks the partially positive carbon of the C—X bond of the substrate, alkyl halide, from the back side of the C—X bond and the leaving group, X^- , departs simultaneously.

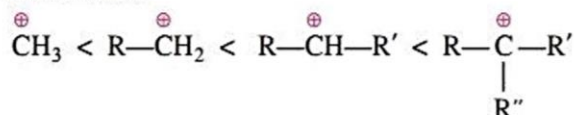


S_N2 reactions of optically active halides are accompanied by inversion of configuration. This is because the attack of nucleophile occurs from a direction opposite to the one from where the halogen atom leaves.

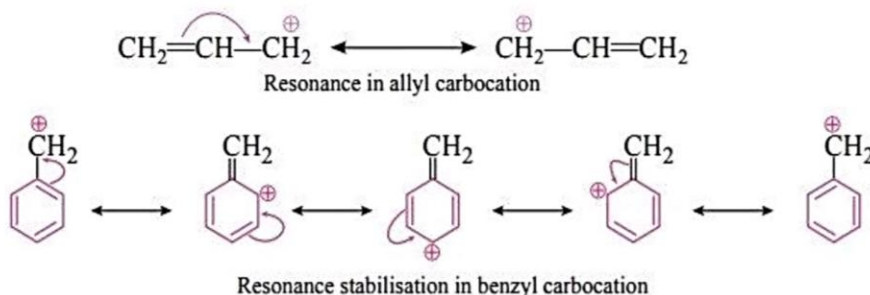
The order of reactivity of alkyl halides towards S_N1 and S_N2 reactions is as follows:



An alkyl group at the α -carbon, being bigger in size than H atom, tends to block the approach of the nucleophile to carbon due to steric hindrance in S_N2 mechanism and makes the reaction difficult to occur. In the S_N1 mechanism, a carbocation is formed in the first, slow step. The more stable the carbocation, more easily is the product formed. Tertiary alkyl halides undergo S_N1 reaction very fast because of the high stability of tertiary carbocation.



Primary allylic and benzylic halides show higher reactivity in S_N1 reactions than other primary halides. This is due to stabilisation of allylic and benzylic carbocation intermediates by resonance.

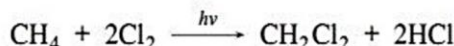


Thus, primary alkyl halides always react predominantly by S_N2 mechanism. Tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl halides may react by both the mechanisms without much preference. Polar solvents favour S_N1 and non-polar solvents favour S_N2 reactions.

11. **Polyhalogen Compounds:** Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture.

Some polyhalogen compounds are described as follows:

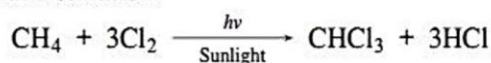
- (a) **Methylene chloride (Dichloromethane):** It is prepared industrially by the direct chlorination of methane.



Uses:

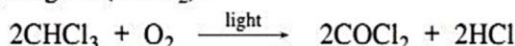
It is an effective solvent used in pharmaceutical and food industry.

- (b) **Chloroform (Trichloromethane):** It is manufactured by chlorination of methane followed by separation by fractional distillation.



Properties:

- (i) It is a sweet smelling liquid with boiling point 61°C .
(ii) It is stored in dark coloured bottles because it gets oxidised in the presence of sunlight to form a poisonous gas, phosgene (COCl_2).



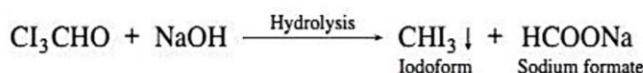
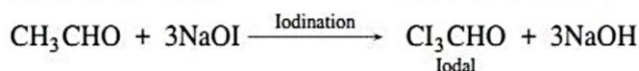
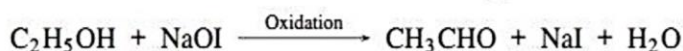
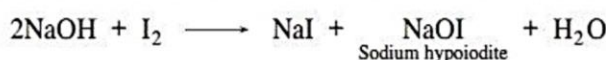
It is therefore stored in closed dark coloured bottles completely filled so that air is kept out. 1% ethanol is added so as to convert phosgene gas to diethyl carbonate which is non-volatile and non-toxic.



Uses:

- (i) It is widely used in industry as a solvent for fats, waxes, resins, rubber, etc.
(ii) It was once used as an anaesthetic agent in surgery and as flavouring agent in cough syrups but now it is not used because it forms phosgene gas which is poisonous.
(c) **Triiodomethane (Iodoform):** Iodoform is prepared by the action of iodine and alkali on ethyl alcohol or acetone.

Reactions involved in the preparation of iodoform from ethyl alcohol are:



The complete reaction may be written as:

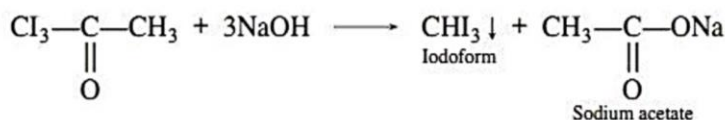


However, when sodium carbonate is used in place of sodium hydroxide then the complete reaction may be written as:

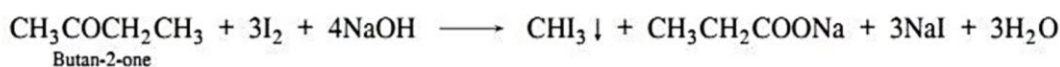
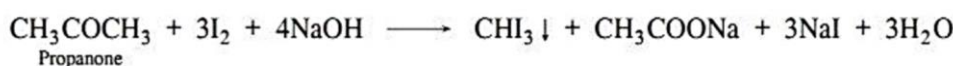
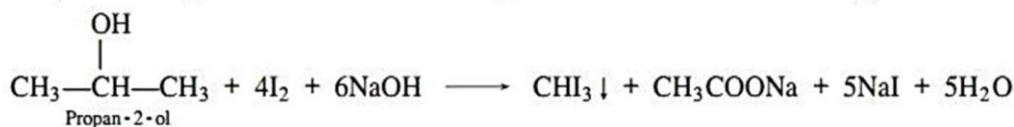
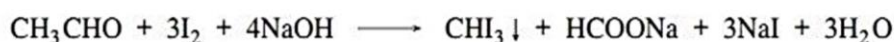


Reactions involved in the preparation of iodoform from acetone are:





The reaction of iodine and sodium hydroxide or iodine and sodium carbonate to give yellow precipitate of iodoform is called iodoform reaction.



Physical properties:

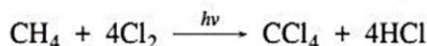
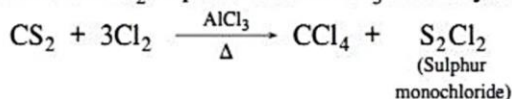
Iodoform is a yellow coloured solid having m.p. 392 K. It is insoluble in water but dissolves readily in organic solvents.

Uses:

It is used as an antiseptic for dressing wounds.

The haloform reaction is commonly used to distinguish between methyl ketones or methyl carbinols from other ketones and alcohols.

- (d) **Carbon tetrachloride (Tetrachloromethane):** It is prepared by chlorination of methane and by action of chlorine on CS_2 in presence of AlCl_3 as catalyst.



Properties:

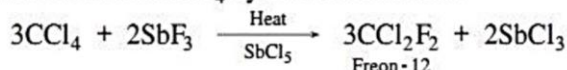
- CCl_4 is a colourless liquid with boiling point 350 K.
- It has a sickly sweet smell.

Uses:

It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and generally used as a solvent. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light-headedness, nausea and vomiting which can cause permanent damage to nerve cells. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer.

- (e) **Freon:** The chlorofluorocarbon compounds of methane and ethane are collectively called freons.

It is manufactured from CCl_4 by **Swarts reaction**.



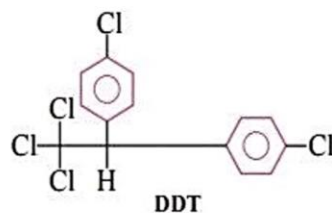
Properties:

- Dichlorodifluoromethane (CCl_2F_2 , Freon-12) is one of the most common freons in industrial use.
- They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquifiable gases.

Uses:

They have also been used extensively as propellants, for aerosols and foams to spray out deodorants, cleansers, hair spray, shaving creams. Use of freon is being reduced and banned because they are responsible for ozone layer depletion.

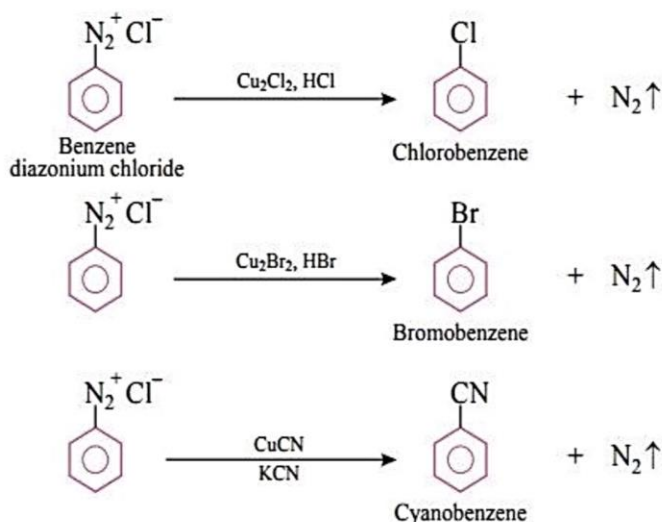
- (f) **DDT (*p,p'*-Dichlorodiphenyl trichloroethane):** It is a white powder insoluble in water, but soluble in oil. It is used as an insecticide. It results in pollution due to its extreme stability. It is non-biodegradable. Many species of insects developed resistance to DDT, and it was also discovered to have high toxicity in fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised rapidly by animals.



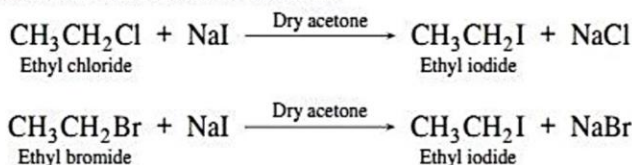
12. Important Name Reactions

(a) Sandmeyer's Reaction:

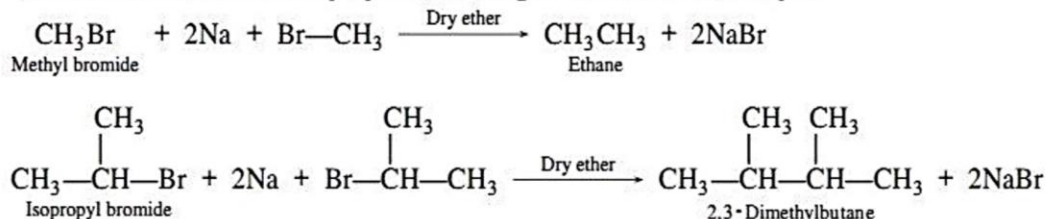
Benzene diazonium chloride is converted to chlorobenzene, bromobenzene, cyanobenzene on treatment with CuCl/HCl , CuBr/HBr and CuCN/KCN , respectively.



- (b) **Finkelstein Reaction:** Chloroalkanes or bromoalkanes are converted into corresponding iodoalkanes by treating with sodium iodide dissolved in acetone.

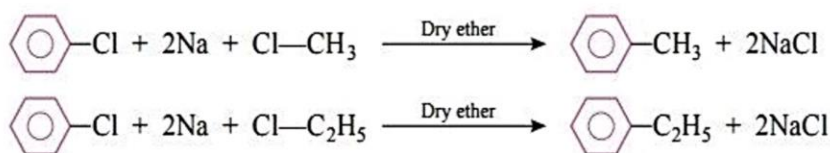


- (c) **Wurtz Reaction:** Alkyl halides react with metallic sodium in the presence of dry ether to form alkanes. This reaction is used for the preparation of higher alkanes. For example,

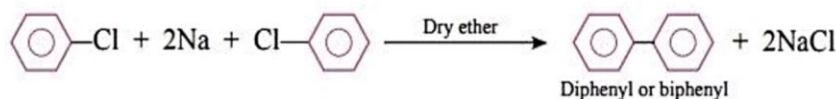


Wurtz reaction is only useful for the preparation of alkanes containing even number of carbon atoms and not for the alkanes containing odd number of carbon atoms.

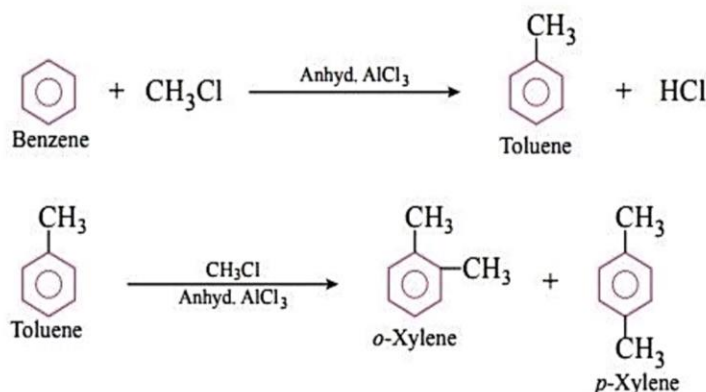
- (d) **Wurtz-Fittig Reaction:** Aryl halides when treated with alkyl halide and sodium in dry ether give alkylbenzenes.



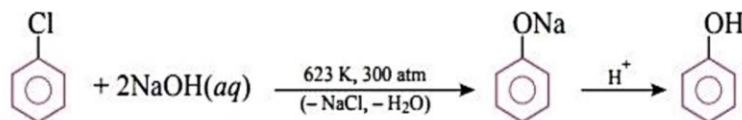
- (e) **Fittig's Reaction:** In this reaction two molecules of haloarene combine with metallic sodium in the presence of dry ether to give diphenyl or biphenyl.



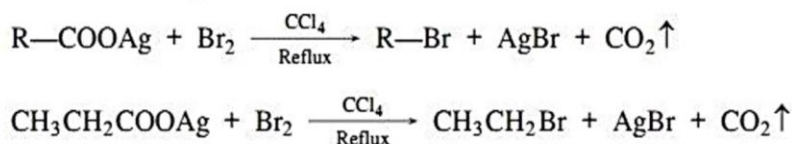
- (f) **Friedel-Crafts Alkylation:** Benzene and other aromatic compounds react with alkyl halides in the presence of anhydrous AlCl_3 to form alkyl benzene.



- (g) **Dow's Process:** When chlorobenzene is treated with an aqueous solution of NaOH at 623 K, 300 atm pressure sodium phenoxide is formed which on acidification gives phenol.

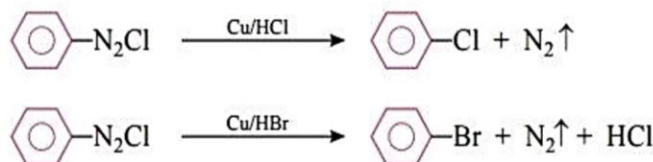


- (h) **Hunsdiecker's Reaction:** Bromoalkanes are obtained by this method by refluxing silver salts of fatty acids with Br_2 in CCl_4 .



This method can be employed to decrease the number of carbon atoms.

- (i) **Gatterman's Reaction:** The reaction of diazonium salts with 'Cu' powder in the presence of corresponding halogen acids is known as Gatterman's reaction.



13. Distinctions between Pairs of Organic Compounds Containing Halogen

Silver nitrate test: In this test, the halide is warmed with aqueous or alcoholic KOH . The solution is then acidified with dil. HNO_3 followed by addition of AgNO_3 solution.

Alkyl, benzyl and allyl halides give precipitate.

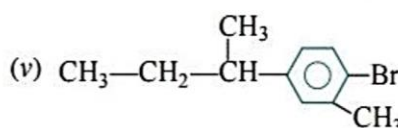
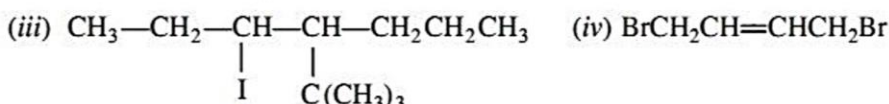
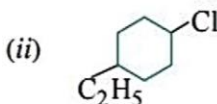
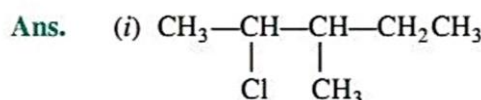
Aryl and vinyl halides do not give precipitate.

It may be noted that the precipitate formed should be insoluble in HNO_3 .

NCERT Intext Questions

Q. 1. Write the structures of the following compounds:

- (i) 2-Chloro-3-methylpentane (ii) 1-Chloro-4-ethylcyclohexane
(iii) 4-*tert*-Butyl-3-iodoheptane (iv) 1, 4-Dibromobut-2-ene
(v) 1-Bromo-4-*sec*-butyl-2-methylbenzene



Q. 2. Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans. H_2SO_4 cannot be used along with KI in the conversion of an alcohol to an alkyl iodide as it converts KI to corresponding HI and then oxidises it to I_2 .

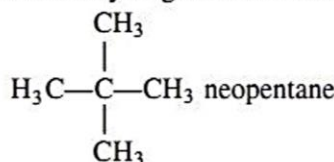
Q. 3. Write structures of different dihalogen derivatives of propane.

- Ans. (i) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (ii) $\text{ClCH}_2\text{CHClCH}_3$
(iii) $\text{Cl}_2\text{CHCH}_2\text{CH}_3$ (iv) $\text{CH}_3\text{CCl}_2\text{CH}_3$

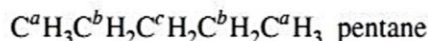
Q. 4. Among the isomeric alkanes of molecular formula C_5H_{12} , identify the one that on photochemical chlorination yields

- (i) A single monochloride [CBSE (F) 2017]
(ii) Three isomeric monochlorides
(iii) Four isomeric monochlorides

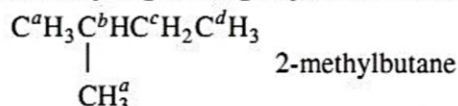
Ans. (i) All the hydrogen atoms are equivalent and replacement of any hydrogen will give the same product.



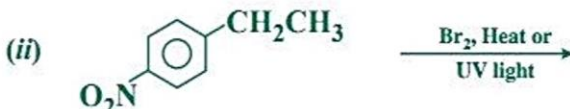
(ii) The equivalent hydrogens are grouped as *a*, *b* and *c*. The replacement of equivalent hydrogens will give the same product.

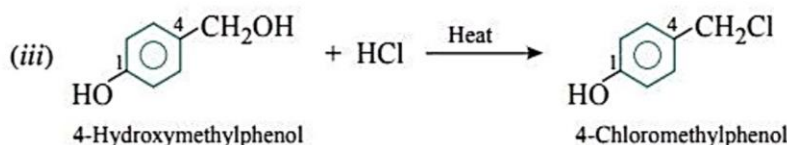
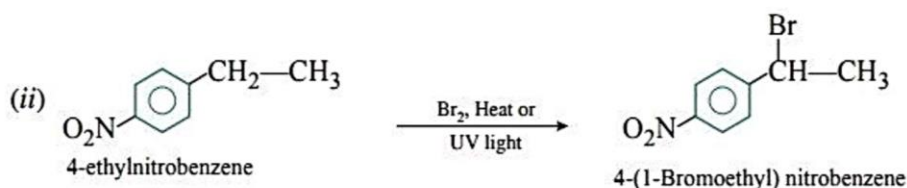
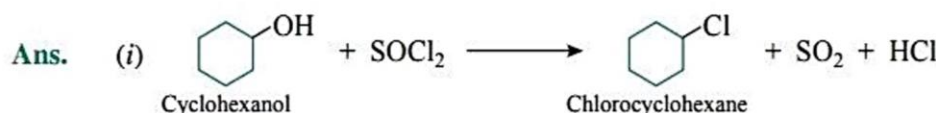


(iii) Similarly the equivalent hydrogens are grouped as *a*, *b*, *c* and *d*. Thus, four isomeric products are possible.

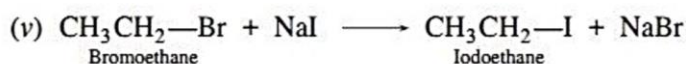
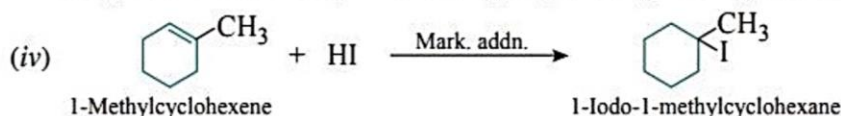


Q. 5. Draw the structures of major monohalo product in each of the following reactions:

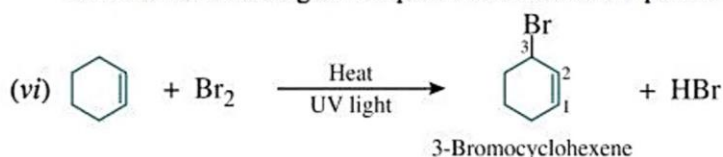




Only alcoholic but not phenolic OH groups are replaced by Cl on heating with HCl.



Iodide ion is a strong nucleophile and hence it displaces bromide ion.



Q. 6. Arrange each set of compounds in the order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

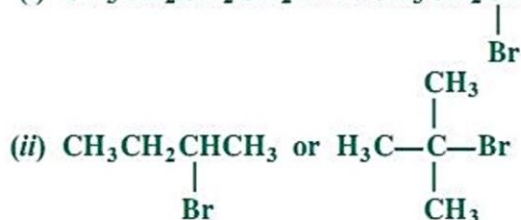
(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

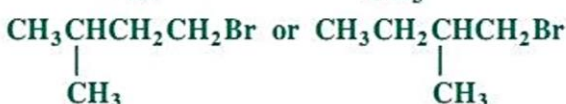
Ans. (i) Chloromethane < Bromomethane < Dibromomethane < Bromoform. Boiling point increases with increase in molecular mass.

(ii) Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane. Isopropyl chloride being branched has lower b.p. than 1-Chloropropane.

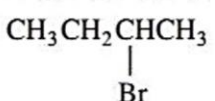
Q. 7. Which alkyl halide from the following pairs would you expect to react more rapidly by an $\text{S}_{\text{N}}2$ mechanism? Explain your answer.

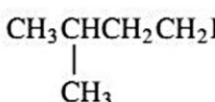
(i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ or $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$



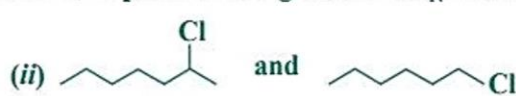
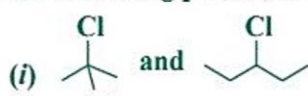
(iii) 


Ans. (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ Being primary halide, there won't be any steric hindrance.


(ii)  Being a secondary halide, there will be less crowding around α -carbon than tertiary halide.

(iii)  The presence of methyl group closer to the halide group will increase the steric hindrance and decreases the rate.

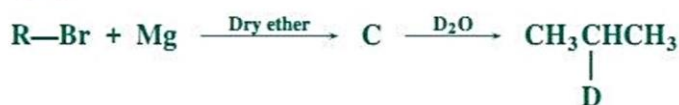
Q. 8. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

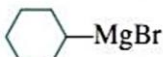



Ans. (i)  2-Chloro-2-methylpropane as the tertiary carbocation is more stable than secondary carbocation.

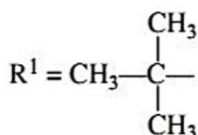
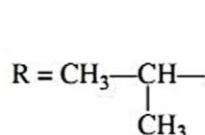
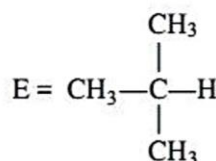
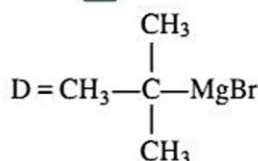
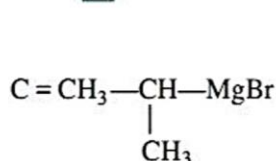
(ii)  2-Chloroheptane as the secondary carbocation is more stable than primary carbocation.

Q. 9. Identify A, B, C, D, E, R and R^1 in the following:



Ans. A = 

B = 



NCERT Exercises

Q. 1. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides.



Ans. (i) 2-Chloro-3-methylbutane; 2° alkyl halide
(ii) 3-Chloro-4-methylhexane; 2° alkyl halide
(iii) 1-Iodo-2, 2-dimethylbutane; 1° alkyl halide
(iv) 1-Bromo-3,3-dimethyl-1-phenylbutane; 2° benzylic halide
(v) 2-Bromo-3-methylbutane; 2° alkyl halide
(vi) 1-Bromo-2-ethyl-2-methylbutane; 1° alkyl halide
(vii) 3-Chloro-3-methylpentane; 3° alkyl halide
(viii) 3-Chloro-5-methylhex-2-ene; vinylic halide

- (ix) 4-Bromo-4-methylpent-2-ene; allylic halide
(x) 1-Chloro-4-(2-methylpropyl) benzene; aryl halide
(xi) 1-Chloromethyl-3-(2, 2-dimethylpropyl) benzene; 1° benzylic halide
(xii) 1-Bromo-2-(1-methylpropyl) benzene; aryl halide

Q. 2. Give the IUPAC names of the following compounds:

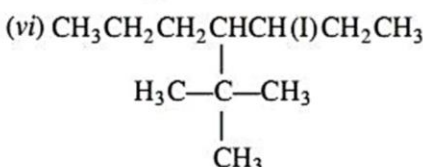
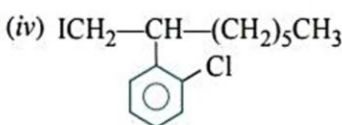
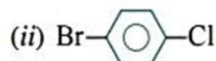
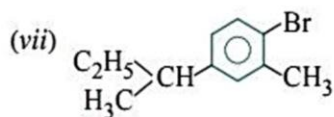
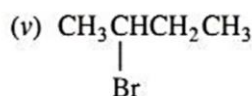
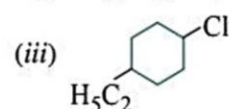
- (i) $\text{CH}_3\text{CH}(\text{Cl})\text{CH}(\text{Br})\text{CH}_3$ (ii) $\text{CHF}_2\text{CBrClF}$
(iii) $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Br}$ (iv) $(\text{CCl}_3)_3\text{CCl}$
(v) $\text{CH}_3\text{C}(\text{p-ClC}_6\text{H}_4)_2\text{CH}(\text{Br})\text{CH}_3$ (vi) $(\text{CH}_3)_3\text{CCH}=\text{C}(\text{Cl})\text{C}_6\text{H}_4\text{I-p}$

- Ans.** (i) 2-Bromo-3-chlorobutane
(ii) 1-Bromo-1-chloro-1, 2, 2-trifluoroethane
(iii) 1-Bromo-4-chlorobut-2-yne
(iv) 2-(Trichloromethyl)-1, 1, 1, 2, 3, 3, 3-heptachloropropane
(v) 2-Bromo-3, 3-Bis (4-chlorophenyl) butane
(vi) 1-Chloro-1-(4-iodophenyl)-3, 3-dimethylbut-1-ene

Q. 3. Write the structures of the following organic halogen compounds:

- (i) 2-Chloro-3-methylpentane (ii) *p*-Bromochlorobenzene
(iii) 1-Chloro-4-ethylcyclohexane (iv) 2-(2-Chlorophenyl)-1-iodooctane
(v) 2-Bromobutane (v) 4-*tert.* Butyl-3-iodoheptane
(vii) 1-Bromo-4-*sec.* butyl-2-methylbenzene
(viii) 1, 4-Dibromobut-2-ene

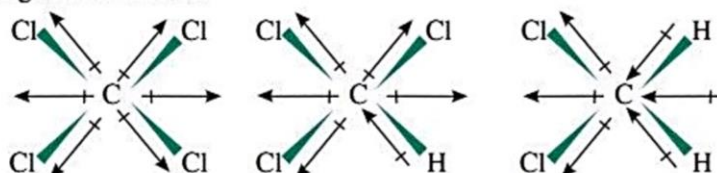
- Ans.** (i) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHClCH}_3$



Q. 4. Which one of the following has the highest dipole moment?

- (i) CH_2Cl_2 (ii) CHCl_3 (iii) CCl_4

Ans. The three-dimensional structures of the three compounds along with the direction of dipole moment in each of their bonds are given as follows:



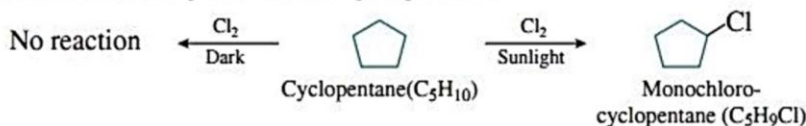
CCl_4 being symmetrical has zero dipole moment. In CHCl_3 , the resultant of two C—Cl dipoles is opposed by the result of C—H and C—Cl bond. As the latter resultant is expected to be smaller than the former, CHCl_3 has a finite dipole (1.03 D) moment.

In CH_2Cl_2 , the resultant of two C—Cl dipole moments is reinforced by the resultant of two C—H dipoles, hence, CH_2Cl_2 (1.62 D) has a dipole moment higher than that of CHCl_3 .

Therefore, CH_2Cl_2 has the highest dipole moment.

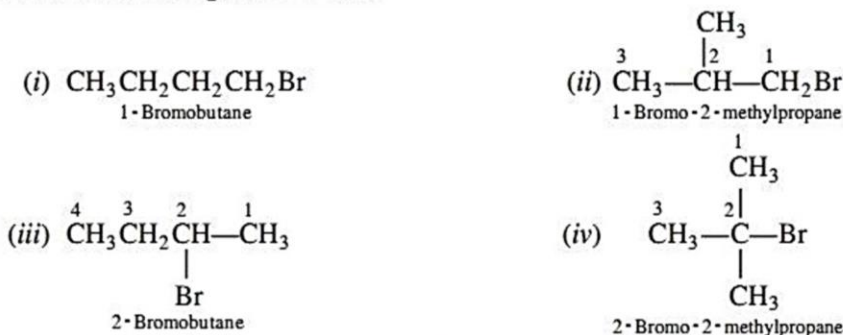
Q. 5. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound, C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

- Ans.** (i) The hydrocarbon with molecular formula C_5H_{10} can be either a cycloalkane or an alkene.
(ii) Since the hydrocarbon does not react with Cl_2 in the dark, it cannot be an alkene but must be a cycloalkane.
(iii) As the cycloalkane reacts with Cl_2 in the presence of bright sunlight, to give a single monochloro compound, C_5H_9Cl , therefore all the ten hydrogen atoms of the cycloalkane must be equivalent. Therefore, the cycloalkane is cyclopentane.

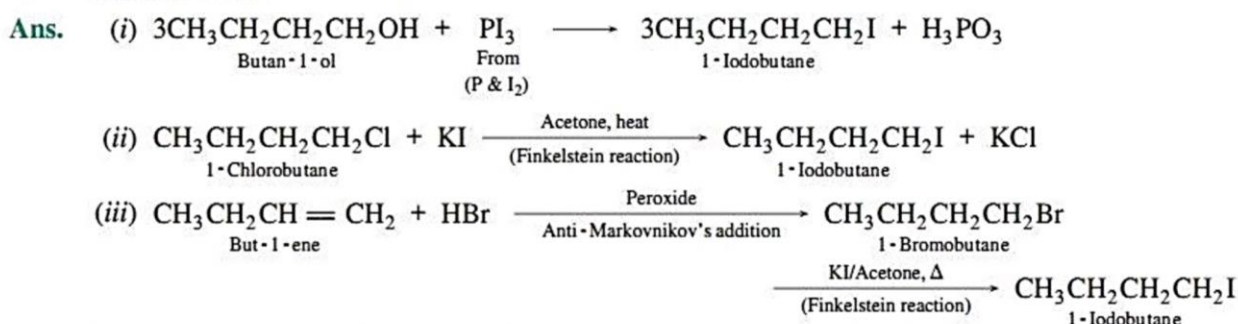


Q. 6. Write the isomers of the compound having formula C_4H_9Br .

Ans. It has the following four isomers:



Q. 7. Write the equations for the preparation of 1-iodobutane from (i) butan-1-ol (ii) 1-chlorobutane, and (iii) but-1-ene.



Q. 8. What are ambident nucleophiles? Explain with an example.

Ans. The nucleophiles which can attack through two different sites are called ambident nucleophiles. For example, cyanide ion is a resonance hybrid of the following two structures:



It can attack through carbon to form cyanides and through N to form isocyanides or carbylamines.

Q. 9. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ?

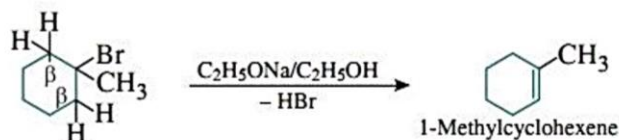
- (i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

- Ans.** (i) Since I^- ion is a better leaving group than Br^- ion, hence, CH_3I reacts faster than CH_3Br in S_N2 reaction with OH^- ion.
(ii) On steric grounds, 1° alkyl halides are more reactive than $tert$ -alkyl halides in S_N2 reactions. Hence, CH_3Cl will react at a faster rate than $(CH_3)_3CCl$ in a S_N2 reaction with OH^- ion.

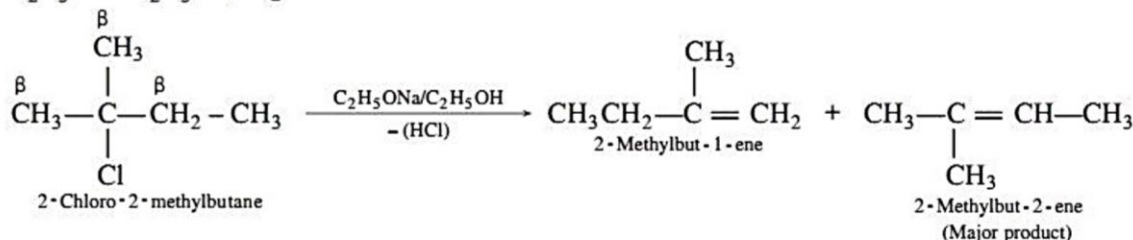
Q. 10. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.

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

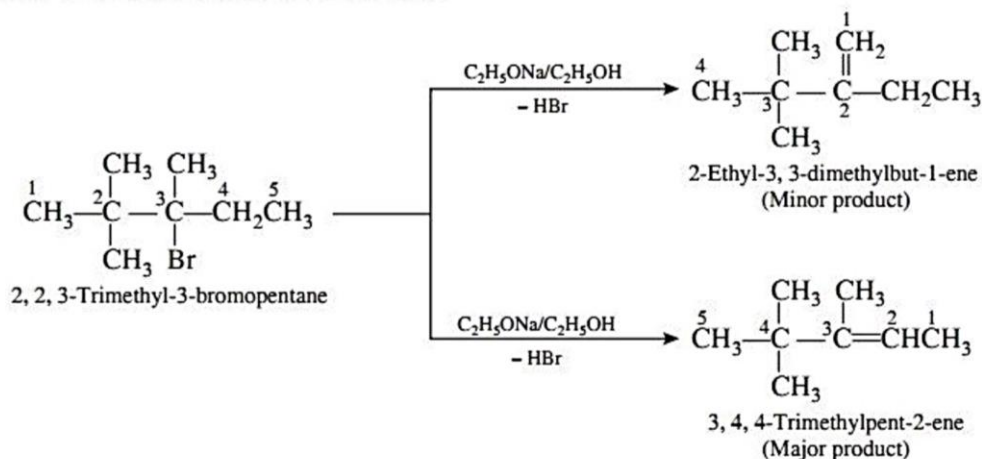
- Ans.** (i) In 1-bromo-1-methylcyclohexane, the β -hydrogens on either side of the Br atom are equivalent, therefore, only 1-alkene is formed.



- (ii) All β -hydrogens in 2-chloro-2-methylbutane are not equivalent, hence on treatment with $\text{C}_2\text{H}_5\text{ONa/C}_2\text{H}_5\text{OH}$, it gives two alkenes.

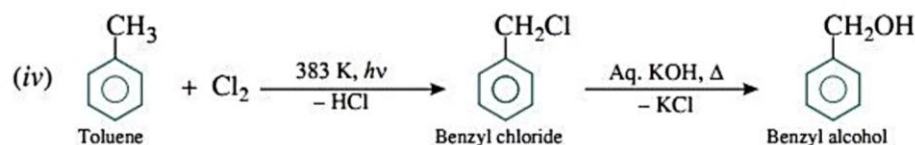
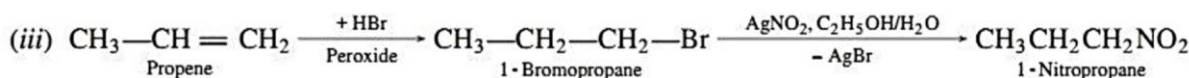
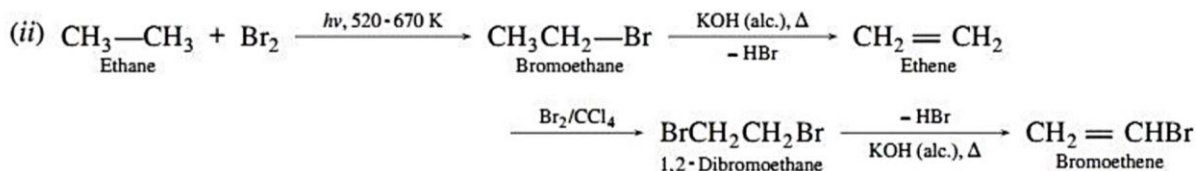
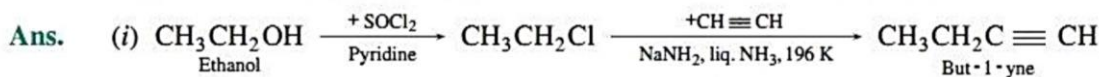


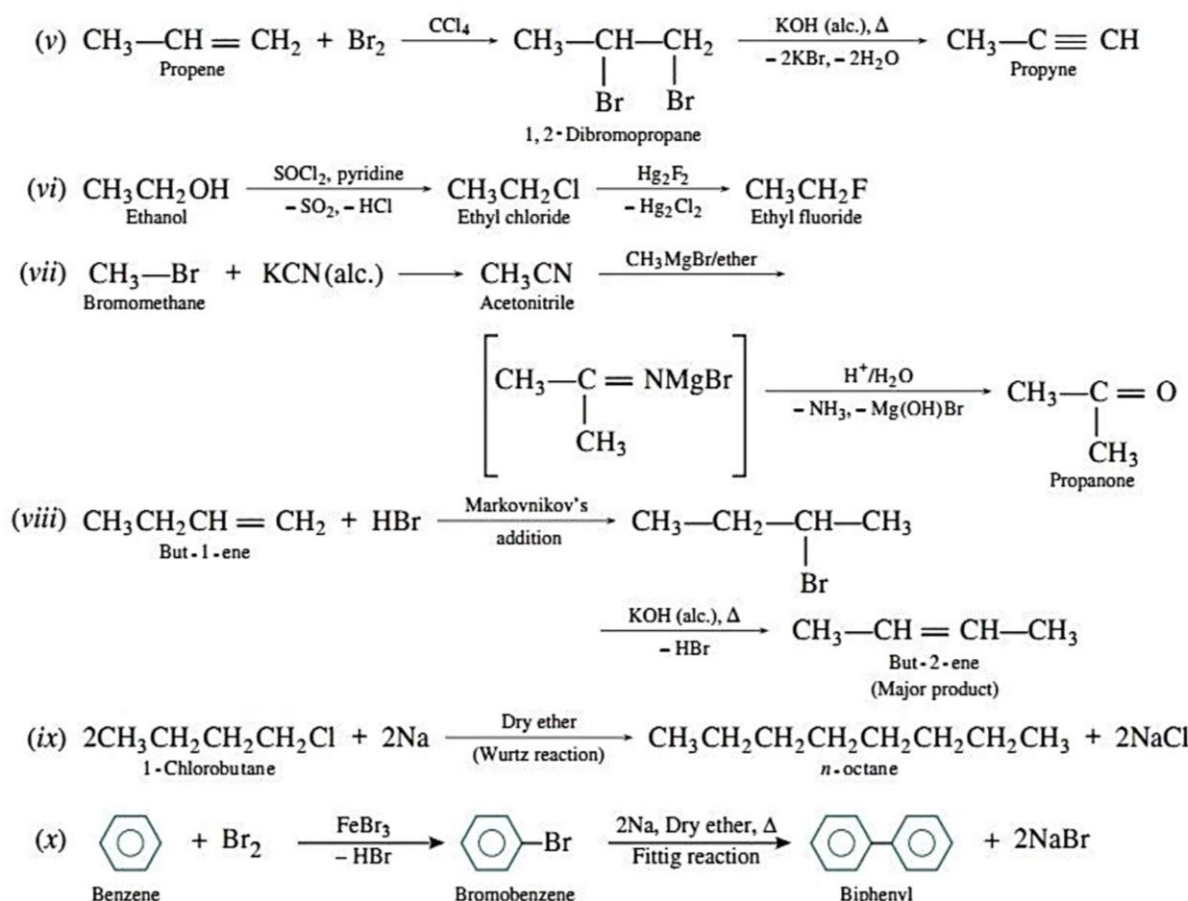
- (iii) 2, 2, 3-Trimethyl-3-bromopentane has two different sets of β -hydrogen and therefore, in principle, can give two alkenes (I and II). But according to Saytzeff rule, more highly substituted alkene (II), being more stable is the major product.



Q. 11. How will you bring the following conversions?

- (i) Ethanol to but-1-yne
 (ii) Ethane to bromoethene
 (iii) Propene to 1-nitropropane
 (iv) Toluene to benzyl alcohol
 (v) Propene to propyne
 (vi) Ethanol to ethyl fluoride
 (vii) Bromomethane to propanone
 (viii) But-1-ene to but-2-ene
 (ix) 1-Chlorobutane to *n*-octane
 (x) Benzene to biphenyl

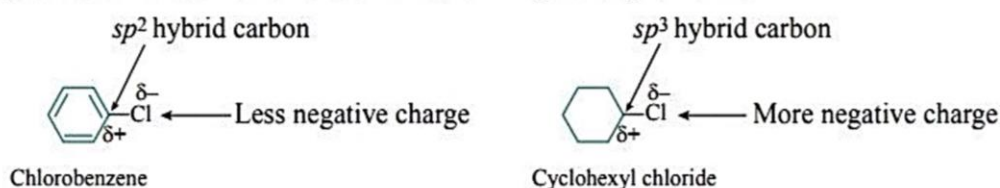




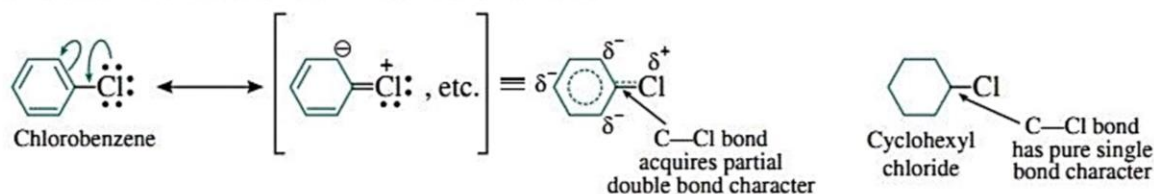
Q. 12. Explain why

- the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
- alkyl halides, though polar, are immiscible with water?
- Grignard reagents should be prepared under anhydrous conditions?

Ans. (i) Due to greater s -character, sp^2 hybrid carbon atom is more electronegative than sp^3 hybrid carbon atom. Therefore, the sp^2 hybrid carbon of C—Cl bond in chlorobenzene has less tendency to release electrons to Cl than an sp^3 hybrid carbon of cyclohexyl chloride. As a result, the magnitude of negative charge is less on Cl atom of chlorobenzene than in cyclohexyl chloride.



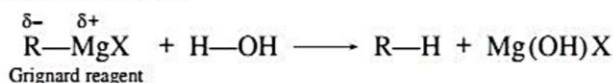
Further, due to resonance the C—Cl bond in chlorobenzene acquires partial double bond character whereas the bond in cyclohexyl chloride is a pure single bond. In other words, C—Cl bond in chlorobenzene is shorter than in cyclohexyl chloride.



As dipole moment is a product of charge and distance. Therefore, dipole moment of chlorobenzene is less than that of cyclohexyl chloride.

- Alkyl halides, though polar, are immiscible in water because they are unable to form hydrogen bonds with water molecules.

- (iii) Grignard reagents are very reactive. They react with moisture present in the apparatus or the starting materials to give hydrocarbons.

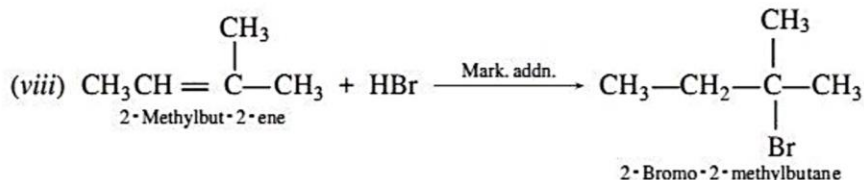
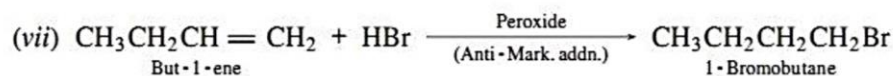
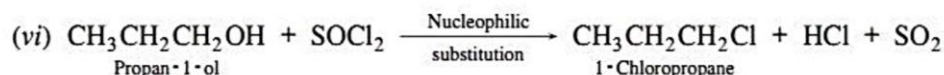
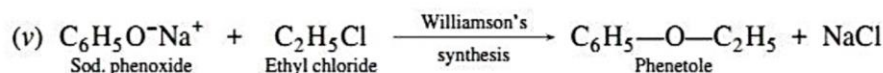
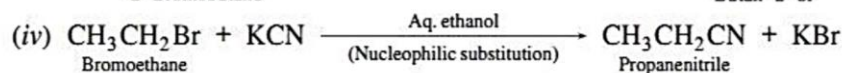
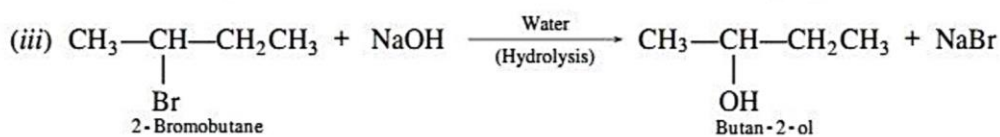
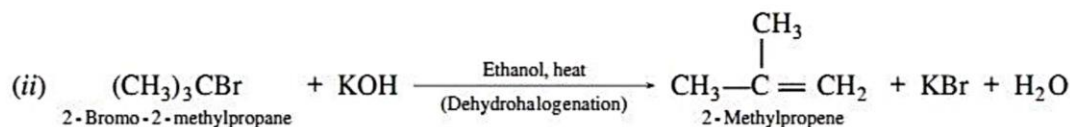
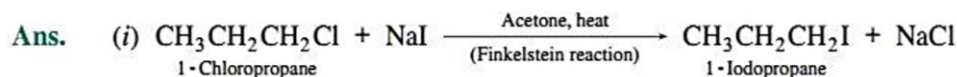
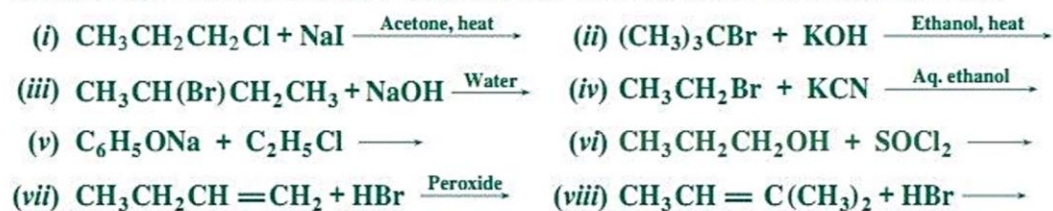


Hence, Grignard reagent must be prepared under anhydrous conditions.

- Q. 13.** Give the uses of Freon-12, DDT, carbon tetrachloride and iodoform.

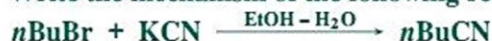
Ans. Refer to Points to remember 11.

- Q. 14.** Write the structure of the major organic product in each of the following reactions:



- Q. 15.** Write the mechanism of the following reaction:

[HOTS]



Ans. The above reaction is an $\text{S}_{\text{N}}2$ reaction.



CN^- ion is an ambident nucleophile so it can attack the carbon atom of C—Br bond in $n\text{-BuBr}$ through C or N. As C—C bond is stronger than C—N bond, therefore attack occurs through C to form $n\text{-BuCN}$.



Q. 16. Arrange the compounds of each set in order of reactivity towards S_N2 displacement:

[CBSE Delhi 2011]

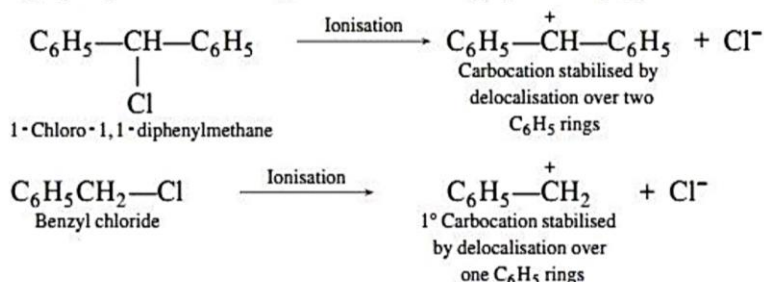
- (i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane.
- (ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane.
- (iii) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

Ans. The reactivity in S_N2 reactions depends upon steric hindrance; more the steric hindrance, slower the reaction.

- (i) Due to steric reasons, the order of reactivity in S_N2 reactions follows the order: $1^\circ > 2^\circ > 3^\circ$, therefore, order of reactivity of the given alkyl bromides is as follows:
1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylpentane.
- (ii) Due to steric reasons, the order of reactivity of alkyl halides in S_N2 reactions follows the order: $1^\circ > 2^\circ > 3^\circ$, therefore, the order of reactivity of the given alkyl bromides is as follows:
1-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 2-Bromo-2-methylbutane.
- (iii) As in case of 1° alkyl halides, steric hindrance increases in the order: n -alkyl halides, alkyl halide with a substituent at any position other than the β -position, one substituent at the β -position, two substituents at the β -position. Therefore, the reactivity decreases in the same order. Hence, the reactivity of the given alkyl bromides decreases in the order:
1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2, 2-dimethylpropane.

Q. 17. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$ which is more easily hydrolysed by aqueous KOH?

Ans. $C_6H_5CH_2Cl$ is a 1° alkyl halide while $C_6H_5CHClC_6H_5$ is a 2° alkyl halide.



In S_N1 reactions the reactivity depends upon the stability of carbocations. Since the carbocation $C_6H_5\overset{+}{CH}C_6H_5$ (where the +ve charge is delocalised over two C_6H_5 rings) derived from $C_6H_5CHClC_6H_5$ is more stable than the carbocation, $C_6H_5\overset{+}{CH_2}$ (where +ve charge is delocalised over one C_6H_5 ring) derived from $C_6H_5CH_2Cl$, therefore, $C_6H_5CHClC_6H_5$ gets hydrolysed more easily than $C_6H_5CH_2Cl$ under S_N1 conditions.

Although, under S_N2 conditions, the reactivity depends on steric hindrance, therefore, under S_N2 conditions, $C_6H_5CH_2Cl$ gets hydrolysed more easily than $C_6H_5CHClC_6H_5$.

Q. 18. *p*-Dichlorobenzene has higher m.p. than those of *o*- and *m*-isomers. Discuss.

Ans. The *p*-isomer being more symmetrical fits closely in the crystal lattice and thus has stronger intermolecular forces of attraction than *o*- and *m*-isomers. As during melting, the crystal lattice breaks, therefore, a larger amount of energy is needed to melt the *p*-isomer than the corresponding *o*- and *m*-isomers. In other words, the melting point of the *p*-isomer is higher than the corresponding *o*- and *m*-isomers.

Q. 19. How the following conversions can be carried out?

- | | |
|--|--|
| (i) Propene to propan-1-ol | (ii) Ethanol to but-1-yne |
| (iii) 1-Bromopropane to 2-bromopropane | (iv) Toluene to benzyl alcohol |
| (v) Benzene to 4-bromonitrobenzene | (vi) Benzyl alcohol to 2-phenylethanoic acid |
| (vii) Ethanol to propanenitrile | (viii) Aniline to chlorobenzene |
| (ix) 2-Chlorobutane to 3, 4-dimethylhexane | (x) 2-Methyl-1-propene to 2-chloro-2-methylpropane |
| (xi) Ethyl chloride to propanoic acid | (xii) But-1-ene to <i>n</i> -butyl iodide |

(xiii) 2-Chloropropane to 1-propanol

(xv) Chlorobenzene to *p*-nitrophenol

(xvii) Chloroethane to butane

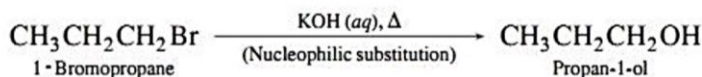
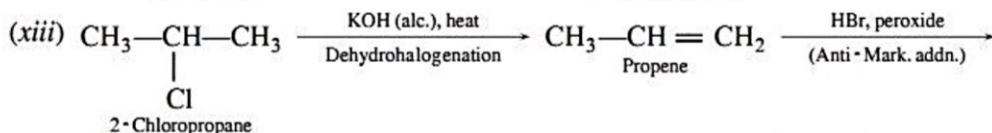
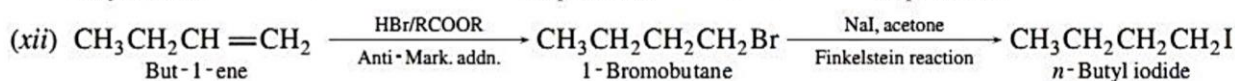
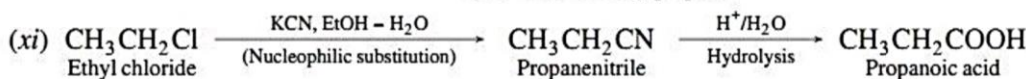
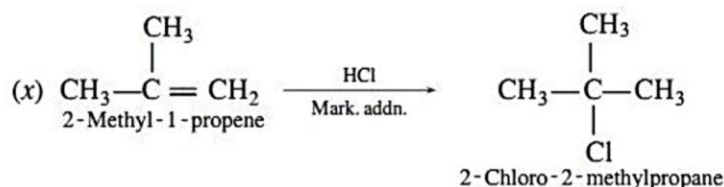
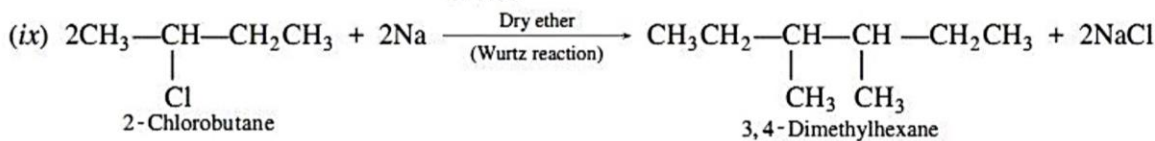
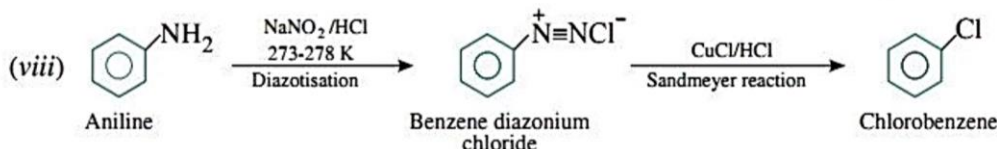
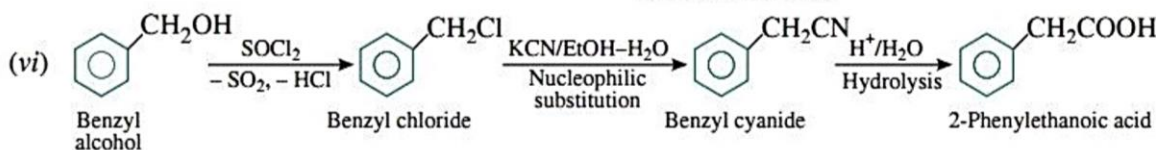
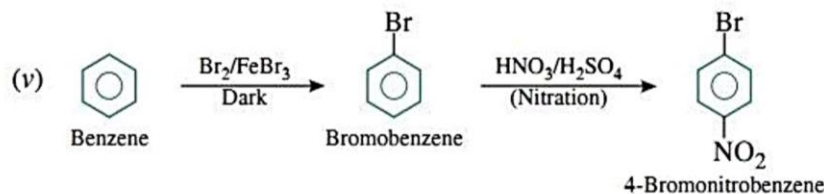
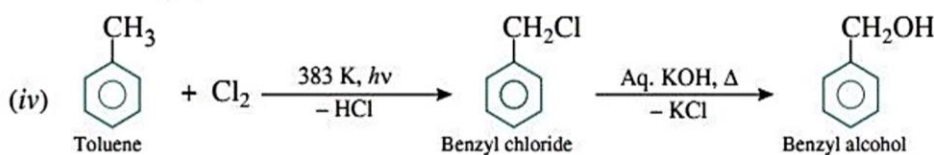
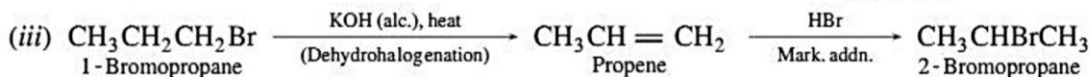
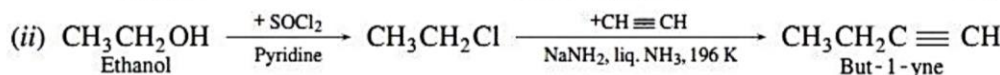
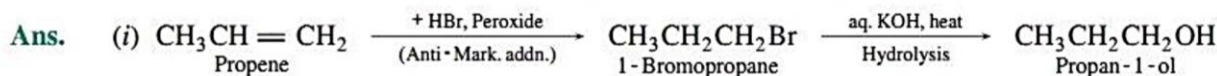
(xix) *tert*-Butyl bromide to isobutyl bromide

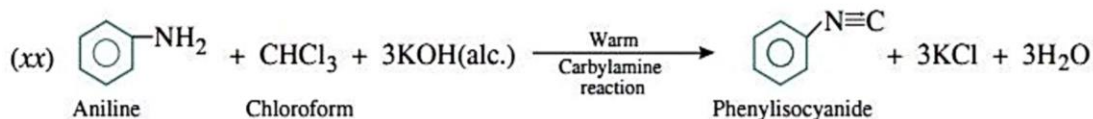
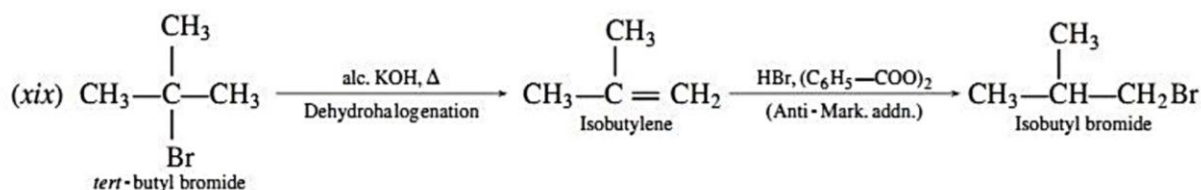
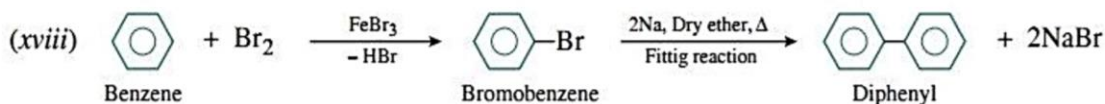
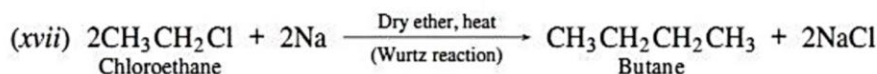
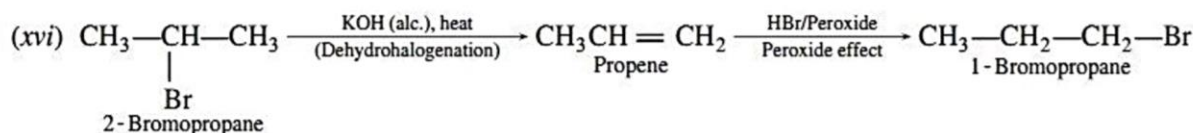
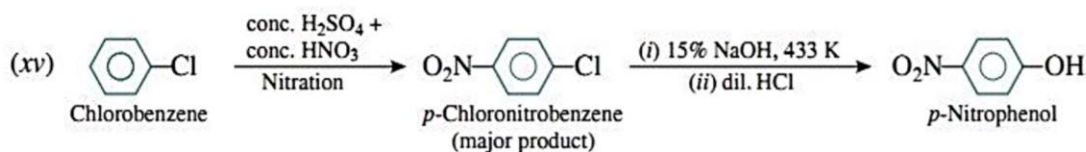
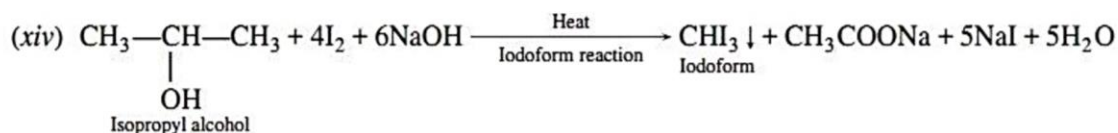
(xiv) Isopropyl alcohol to iodoform

(xvi) 2-Bromopropane to 1-bromopropane

(xviii) Benzene to diphenyl

(xx) Aniline to phenylisocyanide





Q. 20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are major products. Explain. [HOTS]

Ans. In aqueous solution, KOH is almost completely ionised to give OH^- ions which being a strong nucleophile brings about a substitution reaction on alkyl halides to form alcohols. In the aqueous solution, OH^- ions are highly hydrated. This reduces the basic character of OH^- ions which fail to abstract a hydrogen from the β -carbon of the alkyl chloride to form an alkene.

On the other hand, an alcoholic solution of KOH contains alkoxide (OR^-) ions which being a much stronger base than OH^- ions preferentially eliminates a molecule of HCl from an alkyl chloride to form alkenes.

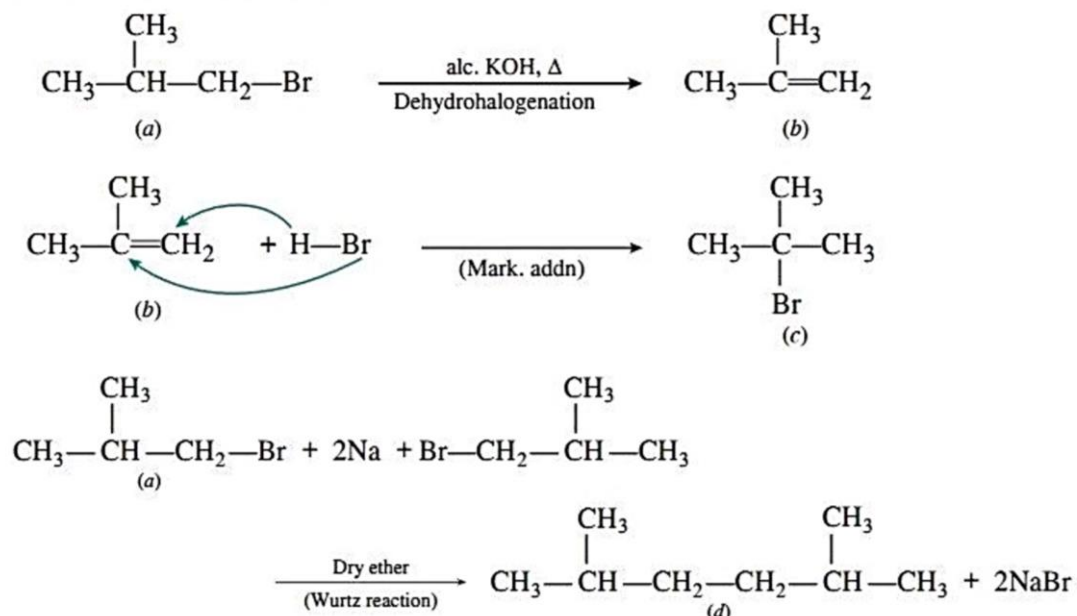
Q. 21. Primary alkyl halide $\text{C}_4\text{H}_9\text{Br}$ (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal, it gives compound (d), C_8H_{18} which is different from the compound formed when *n*-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions. [HOTS]

Ans.

Compound	Structural Formula	Name
(a)	$\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{Br}$	1-Bromo-2-methylpropane
(b)	$\text{CH}_3-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2$	2-Methylprop-1-ene

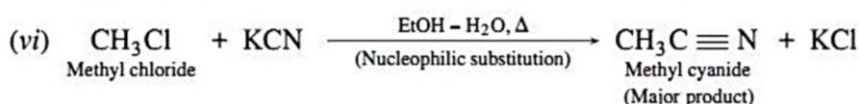
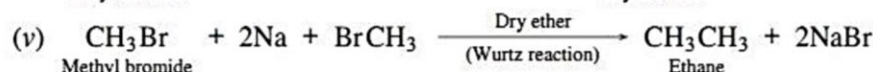
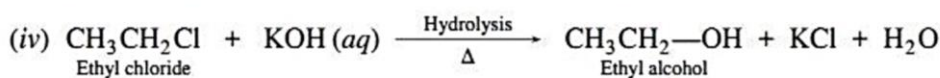
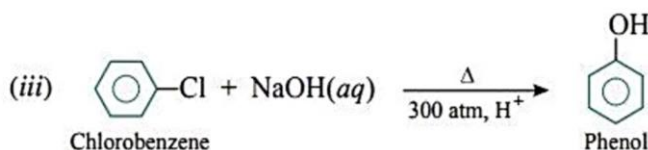
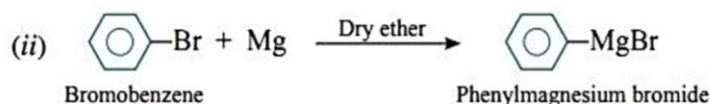
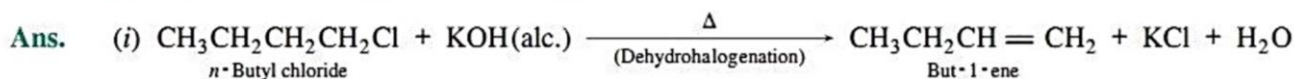
(c)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{Br} \end{array}$	2-Bromo-2-methylpropane
(d)	$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\ \qquad \qquad \quad \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_3 \end{array}$	2, 5-Dimethylhexane

Equations of the Reactions:



Q. 22. What happens when

- n*-butyl chloride is treated with alcoholic KOH,
- bromobenzene is treated with Mg in the presence of dry ether,
- chlorobenzene is subjected to hydrolysis,
- ethyl chloride is treated with aqueous KOH,
- methyl bromide is treated with sodium in the presence of dry ether,
- methyl chloride is treated with KCN?

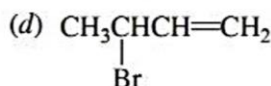
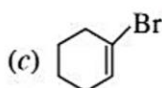
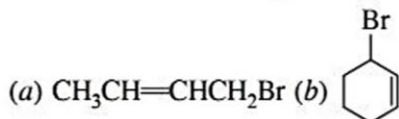




Multiple Choice Questions

Choose and write the correct option(s) in the following questions.

1. Which of the following is vinylic halide?



2. The position of Br in the compound in $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$ can be classified as _____.

[NCERT Exemplar]

- (a) Allyl (b) Aryl (c) Vinyl (d) Secondary

3. Which of the following is an example of vic-dihalide?

[NCERT Exemplar]

- (a) Dichloromethane (b) 1,2-dichloroethane
(c) Ethylidene chloride (d) Allyl chloride

4. Ethylidene chloride is a/an _____.

[NCERT Exemplar]

- (a) vic-dihalide (b) gem-dihalide
(c) allylic halide (d) vinylic halide

5. Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group. Identify haloalkane from the following compounds.

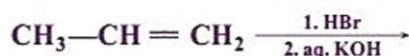
- (a) 2-Bromopentane (b) Vinyl chloride (chloroethene)
(c) 2-Chloroacetophenone (d) Chlorobenzene

6. Which is the correct IUPAC name for $\text{CH}_3-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_2-\text{Br}$?

[NCERT Exemplar]

- (a) 1-Bromo-2-ethylpropane (b) 1-Bromo-2-ethyl-2-methylethane
(c) 1-Bromo-2-methylbutane (d) 2-Methyl-1-bromobutane

7. Consider the following reaction:



The major end product is

[CBSE 2022 (56/3/4)]

- (a) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$ (b) $\text{CH}_3-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$
(c) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$ (d) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Br}$

8. The synthesis of alkyl fluoride is best obtained from :

[CBSE 2023 (56/1/1)]

- (a) Free radicals (b) Swarts reaction
(c) Sandmeyer reaction (d) Finkelstein reaction

9. Ethylene chloride and ethylidene chloride are isomers. Identify the correct statements.

- (i) Both the compounds form same product on treatment with alcoholic KOH.
(ii) Both the compounds form same product on treatment with aq. NaOH.
(iii) Both the compounds form same product on reduction.
(iv) Both the compounds are optically active.

[NCERT Exemplar]

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

10. Arrange the following compounds in the increasing order of their densities. [NCERT Exemplar]



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

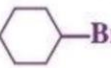
11. Arrange the following compounds in increasing order of their boiling points. [NCERT Exemplar]

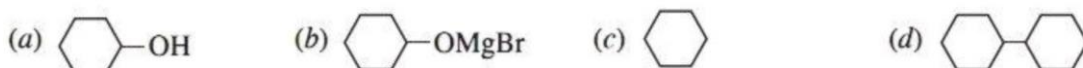


- (a) (ii) < (i) < (iii) (b) (i) < (ii) < (iii) (c) (iii) < (i) < (ii) (d) (iii) < (ii) < (i)

12. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of AlCl_3 . Which of the following species attacks the benzene ring in this reaction? [NCERT Exemplar]

- (a) Cl^- (b) Cl^+ (c) AlCl_3 (d) $[\text{AlCl}_4]^-$

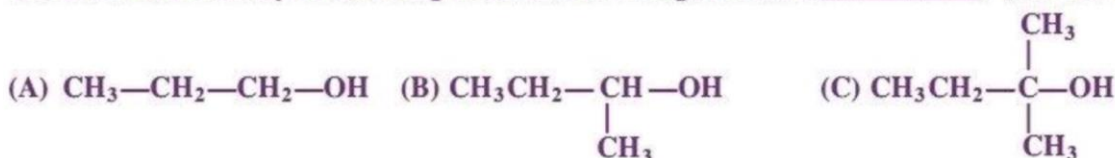
13. In the reaction  $\xrightarrow[\text{dry ether}]{\text{Mg}}$ 'X' $\xrightarrow[\text{dry ether}]{\text{H}_2\text{O}}$ 'Y', compound 'Y' is [CBSE 2022 (56/3/4)]



14. Racemisation occurs in [CBSE 2023 (56/2/1)]

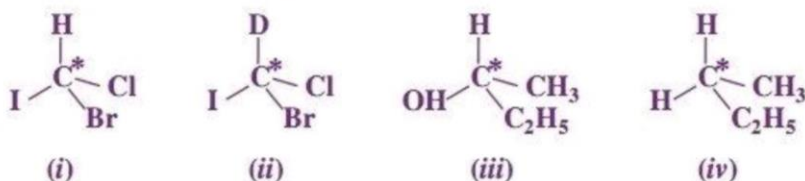
- (a) $\text{S}_{\text{N}}1$ reaction (b) $\text{S}_{\text{N}}2$ reaction
(c) Neither $\text{S}_{\text{N}}1$ nor $\text{S}_{\text{N}}2$ reaction (d) $\text{S}_{\text{N}}2$ reaction as well as $\text{S}_{\text{N}}1$ reaction

15. The order of reactivity of following alcohols with halogen acids is _____. [NCERT Exemplar]



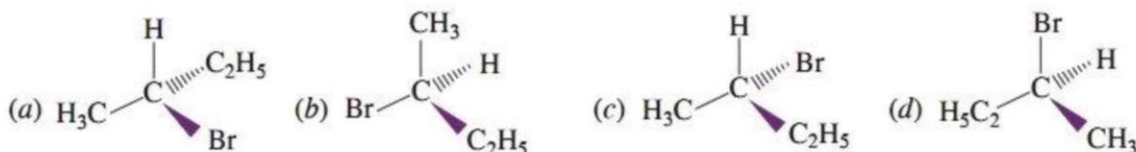
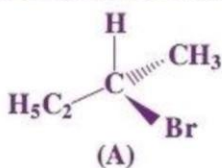
- (a) (A) > (B) > (C) (b) (C) > (B) > (A) (c) (B) > (A) > (C) (d) (A) > (C) > (B)

16. In which of the following molecules carbon atom marked with asterisk (*) is asymmetric? [NCERT Exemplar]



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

17. Which of the following structures is enantiomeric with the molecule (A) given below: [NCERT Exemplar]





Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

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- Assertion (A) : Thionyl chloride are preferred over Phosphorus chlorides (tri and penta) for the preparation of alkyl chlorides from alcohols.
Reason (R) : Thionyl chloride give pure alkyl halides.
- Assertion (A) : Alkyl halides are insoluble in water.
Reason (R) : Alkyl halides have halogen attached to sp^3 hybrid carbon. [CBSE Sample Paper 2022]
- Assertion (A) : KCN reacts with methyl chloride to give methyl isocyanide.
Reason (R) : CN^- is an ambident nucleophile.
- Assertion (A) : *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.
Reason (R) : In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.
- Assertion (A) : Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.
Reason (R) : This reaction proceeds through the formation of a carbocation.
- Assertion (A) : Nucleophilic substitution of iodoethane is easier than chloroethane.
Reason (R) : Bond enthalpy of C–I bond is less than that of C–Cl bond. [CBSE 2023 (56/2/1)]
- Assertion (A) : Aryl halides undergo nucleophilic substitution reactions with ease.
Reason (R) : The carbon halogen bond in aryl halides has partial double bond character. [CBSE Sample Paper 2020]
- Assertion (A) : Chlorobenzene is less reactive towards nucleophilic substitution reaction.
Reason (R) : Nitro group in chlorobenzene increases its reactivity towards nucleophilic substitution reaction. [CBSE Sample Paper 2021 (56/3/4)]
- Assertion (A) : Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene.
Reason (R) : $-NO_2$ group is a *m*-directing group.
- Assertion (A) : It is difficult to replace chlorine by $-OH$ in chlorobenzene in comparison to that in chloroethane.
Reason (R) : Chlorine-carbon (C–Cl) bond in chlorobenzene has a partial double bond character due to resonance.
- Assertion (A) : In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.
Reason (R) : Halogen atom is a ring deactivator.
- Assertion (A) : Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.
Reason (R) : Oxidising agent oxidises I_2 into HI.

Answers

1. (a) 2. (b) 3. (d) 4. (a) 5. (c) 6. (a) 7. (d) 8. (c) 9. (d) 10. (a)
 11. (b) 12. (c)

18. Two possible stereo-structure of $\text{CH}_3\text{—CH(OH)COOH}$ which are optically active are called
 (a) mesomers (b) enantiomers
 (c) diastereomers (d) atropisomers
19. Which of the following reactions are feasible? [CBSE 2023 (56/2/1)]
 (a) $\text{CH}_3\text{CH}_2\text{Br} + \text{Na}^+ \text{O}^-\text{C}(\text{CH}_3)_3 \longrightarrow \text{CH}_3\text{CH}_2\text{—O—C}(\text{CH}_3)_3$
 (b) $(\text{CH}_3)_3\text{C—Cl} + \text{Na}^+ \text{O}^-\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_2\text{—O—C}(\text{CH}_3)_3$
 (c) Both (a) and (b)
 (d) Neither (a) nor (b)
20. Major product obtained on reaction of 3-Phenyl propene with HBr in presence of organic peroxide [CBSE Sample Paper 2022]
 (a) 3-Phenyl-1-bromopropane (b) 1-Phenyl-3-bromopropane
 (c) 1-Phenyl-2-bromopropane (d) 3-Phenyl-2-bromopropane
21. For the following (i) I^\ominus , (ii) Cl^\ominus , (iii) Br^\ominus , the increasing order of nucleophilicity would be:
 (a) $\text{I}^\ominus < \text{Br}^\ominus < \text{Cl}^\ominus$ (b) $\text{Br}^\ominus < \text{Cl}^\ominus < \text{I}^\ominus$
 (c) $\text{Cl}^\ominus < \text{Br}^\ominus < \text{I}^\ominus$ (d) $\text{I}^\ominus < \text{Cl}^\ominus < \text{Br}^\ominus$
22. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is _____. [NCERT Exemplar]
 (a) Electrophilic elimination reaction (b) Electrophilic substitution reaction
 (c) Free radical addition reaction (d) Nucleophilic substitution reaction
23. Complete the following analogy:
 $\text{S}_\text{N}2$: Inversion of configuration :: $\text{S}_\text{N}1$: _____
 (a) Racemisation (b) Retention
 (c) Optical rotation (d) Chiral
24. Match the following:

Column-I	Column-II
(i) $\text{S}_\text{N}1$ reaction	A. vic-dibromides
(ii) Chemical in fire extinguisher	B. gem-dihalides
(iii) Bromination of alkenes	C. Racemisation
(iv) Alkylidene halides	D. Saytzeff rule
(v) Elimination of HX from alkylhalide	E. Chlorobromocarbons

- (a) (i) — C, (ii) — E, (iii) — A, (iv) — B, (v) — D
 (b) (i) — A, (ii) — B, (iii) — C, (iv) — D, (v) — E
 (c) (i) — B, (ii) — C, (iii) — E, (iv) — D, (v) — A
 (d) (i) — A, (ii) — C, (iii) — E, (iv) — D, (v) — B

Answers

1. (c) 2. (a) 3. (b) 4. (b) 5. (a) 6. (c) 7. (a) 8. (b) 9. (a) 10. (a)
 11. (c) 12. (b) 13. (c) 14. (a) 15. (b) 16. (b) 17. (a) 18. (b) 19. (a) 20. (b)
 21. (c) 22. (b) 23. (a) 24. (a)



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Reason (R) : Oxidising agent oxidises I_2 into HI.

Answers

1. (a) 2. (b) 3. (d) 4. (a) 5. (c) 6. (a) 7. (d) 8. (c) 9. (d) 10. (a)
 11. (b) 12. (c)



Passage-based/Case-based/ Source-based Questions

Read the given passages and answer the questions that follow.

PASSAGE-1

Nucleophilic Substitution

Nucleophilic Substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. S_N1 is a two step reaction while S_N2 is a single step reaction. For any haloalkane which mechanism is followed depends on factors such as structure of haloalkane which mechanism is followed depends on factors such as structure of haloalkane, properties of leaving group, nucleophilic reagent and solvent.

Influences of solvent polarity: In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction. In S_N2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane at 25 °C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence the level of solvent polarity has influence on both S_N1 and S_N2 reaction, but with different results. Generally speaking weak polar solvent is favourable for S_N2 reaction, while strong polar solvent is favourable for S_N1 . Generally speaking the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example ethanol containing water). [CBSE 2023 (56/5/2)]

Answer the following questions:

1. Why racemisation occurs in S_N1 ?
2. Why is ethanol less polar than water?
3. Which one of the following in each pair is more reactive towards S_N2 reaction?

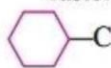



OR

Arrange the following in the increasing order of their reactivity towards S_N1 reactions:

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

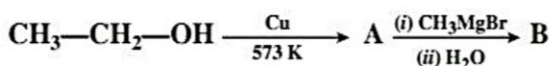
Answers

1. This is because the carbocation formed in the slow step being sp^2 hybridised is planar therefore, the attack of nucleophile on it can occur from both the faces with equal chance giving a mixture containing two enantiomers in equal amount i.e., racemic mixture.
 2. The electron releasing alkyl group to which —OH is attached increased electron density on oxygen tending to decrease the polarity of O—H bond in alcohols.
 3. (i) As I^- ion is better leaving group than Cl^- ion due to its larger size. Therefore $\text{CH}_3\text{—CH}_2\text{—I}$ reacts faster than $\text{CH}_3\text{—CH}_2\text{—Cl}$ in S_N2 reactions.
(ii)  being a primary halide undergoes S_N2 reaction faster than .
- OR
- (i) 1-Bromopentane < 2-Bromopentane < 2-Bromo-2-methylbutane
(1°) (2°) (3°)
 - (ii) 1-Bromo-3-methylbutane < 2-Bromo-3-methylbutane < 2-Bromo-2-methylbutane
(1°) (2°) (3°)

PASSAGE-2

Grignard reagents are alkyl magnesium halides. Due to large electronegativity difference between carbon and magnesium, the carbon-magnesium bond has significant ionic character. The hydrocarbon part of the Grignard reagents acts as a source of carbanions. Therefore, Grignard reagents readily undergo nucleophilic addition reactions to aldehydes and ketones forming the addition products which upon hydrolysis yield alcohols.

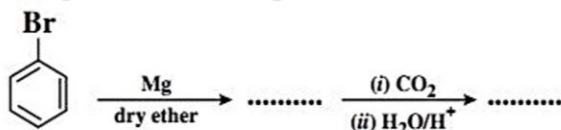
1. What will be the product formed when chlorobenzene reacts with magnesium in presence of dry ether?
2. Write the structure of B in the following reactions.



3. Give the mechanism of addition of Grignard reagent to carbonyl compound forming an alcohol.

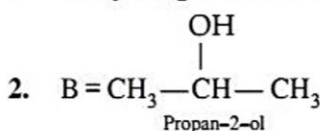
OR

Complete the following:

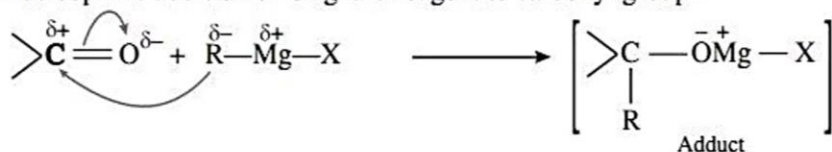


Answers

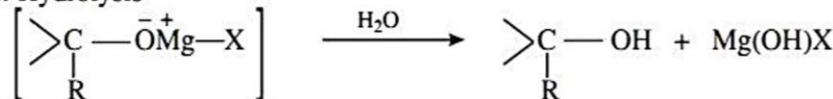
1. Phenyl magnesium chloride (Grignard reagent)



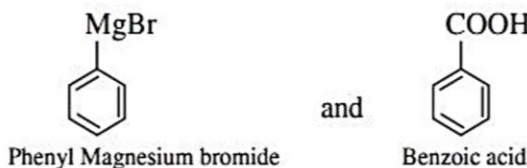
3. **Step I:** Nucleophilic addition of Grignard reagent to carbonyl group.



Step II: Hydrolysis



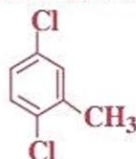
OR



CONCEPTUAL QUESTIONS

- Q. 1. Write the IUPAC name of the following compound:

[CBSE (AI) 2013]



Ans. 2, 5-Dichlorotoluene/1,4-Dichloro-2-methylbenzene

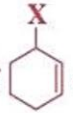

- Q. 2. Write the structure of the compound, 1-bromo-4-chlorobut-2-ene.

[CBSE (Delhi) 2017]


Ans. $\text{Cl—CH}_2\text{—CH=CH—CH}_2\text{—Br}$

1

[CBSE Marking Scheme Delhi 2017]

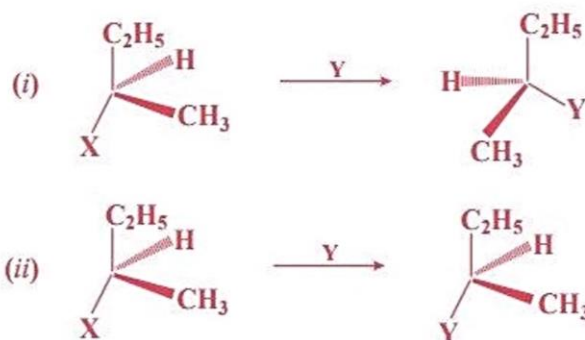
Q. 3. Out of  and , which is an example of allylic halide?

[CBSE (AI) 2017]

Ans. 

Q. 4. Which of the following two reactions is S_N2 and why?

[CBSE North 2016]



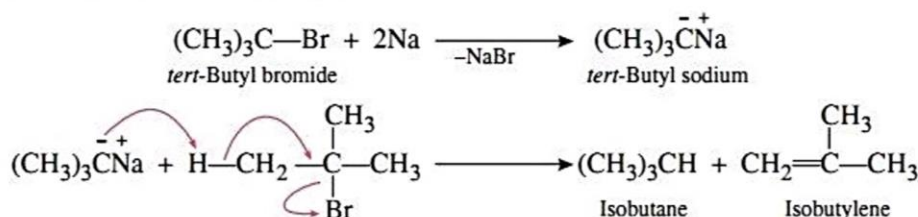
Ans.

5. The reaction (i) is S_N2 reaction. This is because it leads to inversion of configuration. In the reaction (ii) the configuration of a chiral carbon has been inverted. Inversion of configuration is a character of S_N2 reaction. [Topper's North 2016]

Q. 5. Wurtz reaction fails in case of *tert*-alkyl halides. Why?

[HOTS]

Ans. This is because *tert*-alkyl halides prefer to undergo dehydrohalogenation in the presence of sodium metal instead of undergoing Wurtz reaction.



Q. 6. Identify the chiral molecule in the following pair:

[CBSE (AI) 2014]



Ans. 

Q. 7. Out of chlorobenzene and cyclohexyl chloride, which one is more reactive towards nucleophilic substitution reaction and why?

[CBSE 2019 (56/2/1)]

Ans. Cyclohexyl chloride is more reactive than chlorobenzene towards nucleophilic substitution reactions. Due to resonance the C-Cl bond in chlorobenzene acquires partial double bond character which makes the substitution of chlorine more difficult in chlorobenzene than in cyclohexyl chloride where the C-Cl bond has pure single bond character.

Q. 8. Why is *t*-butyl bromide more reactive towards S_N1 reaction as compared to *n*-butyl bromide?

[CBSE 2019 (56/4/1)]



Ans. Due to higher stability of tertiary carbocation than primary carbocation.

Q. 9. Give one chemical test to distinguish between C_2H_5Br and C_6H_5Br .

Ans. Hydrolysis of C_2H_5Br with aqueous KOH followed by acidification with dil. HNO_3 and subsequent treatment with $AgNO_3$ gives light yellow ppt. of $AgBr$ whereas C_6H_5Br does not give this test.

Q. 10. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why? [CBSE 2018]

Ans.

 chlorobenzene	 benzyl chloride
--	--

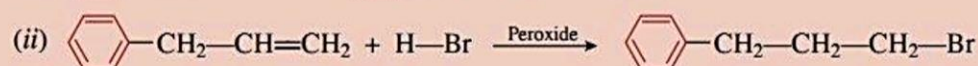
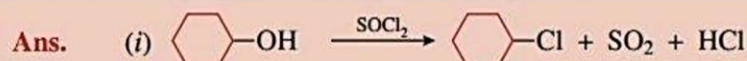
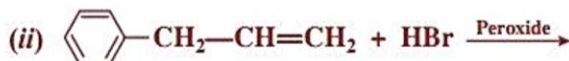
Benzyl chloride is hydrolysed easily because the benzyl carbocation formed is more stable. On the other hand, C-Cl bond in chlorobenzene acquires partial double bond character due to resonance and the carbon is sp^2 hybridised. Also, phenyl carbocation formed is highly unstable. There is possible repulsion between approaching nucleophile and electron rich arene. This is more in case of chlorobenzene than benzyl chloride. [Topper's Answer 2018]



Short Answer Questions-I

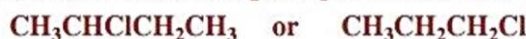
Each of the following questions are of 2 marks.

Q. 1. Draw the structure of major monohalo product in each of the following reactions: [CBSE Delhi 2014]



[CBSE Marking Scheme Delhi 2014]

Q. 2. Which one of the following compounds is more easily hydrolysed by KOH and why?

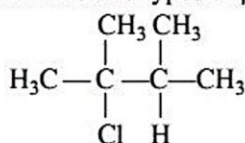


[CBSE (AI) 2012]

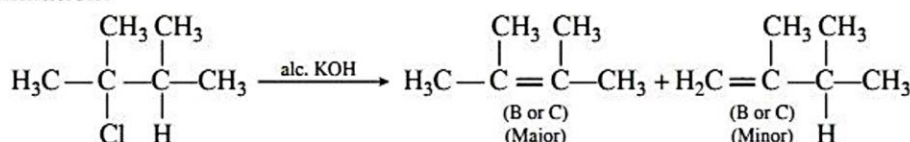
Ans. Due to +I effect of alkyl groups, the 2° carbonium ion $CH_3-\overset{+}{CH}-CH_2-CH_3$ derived from sec. butyl chloride is more stable than the 1° carbonium ion $CH_3-CH_2-\overset{+}{CH}_2$ derived from *n*-propyl chloride. Therefore sec. butyl chloride gets hydrolysed more easily than *n*-propyl chloride under S_N1 conditions.

- Q. 3.** An alkyl halide (A) of molecular formula $C_6H_{13}Cl$ on treatment with alcoholic KOH gives two isomeric alkenes (B) and (C) of molecular formula C_6H_{12} . Both alkenes on hydrogenation give 2, 3-dimethylbutane. Write the structures of (A), (B) and (C). [CBSE 2023 (56/4/2)]

Ans. Alkyl halide reacts with alcoholic KOH to give β -elimination reaction. Since there are two isomers formed the compound (A) should have two types of β -carbon from which hydrogen is eliminated (A) is



Elimination:



- Q. 4.** Give reasons for the following:

[CBSE 2019 (56/4/1)] [CBSE (AI) 2017]

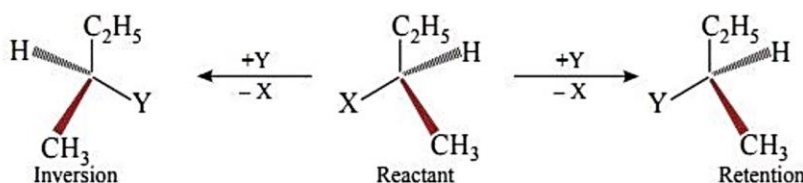
- Chloroethane is insoluble in water.
- Thionyl chloride method is preferred for preparing alkyl chlorides from alcohols.

- Ans.** (i) Chloroethane is unable to form hydrogen bonds with water. Hence, it is insoluble in water. 1
(ii) The byproducts of the reaction, i.e., SO_2 and HCl being gases escape into the atmosphere leaving behind alkyl chlorides in almost pure state. 1

[CBSE Marking Scheme Delhi 2019 (56/4/1)]

- Q. 5.** Differentiate between retention and inversion.

Ans. If the relative configuration of the atoms/groups around a chiral centre in an optically active molecule remains the same before and after the reaction, the reaction is said to proceed with retention of configuration. On the other hand, if the relative configuration of the atoms/groups around a stereocentre in the product is opposite to that in the reactant, the reaction is said to proceed with inversion of configuration. For example,

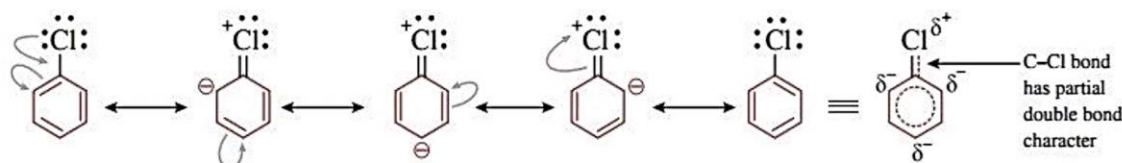


- Q. 6.** Give reasons:

[CBSE Delhi 2016]

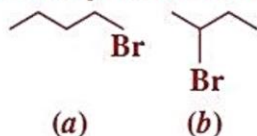
- $\text{C}-\text{Cl}$ bond length in chlorobenzene is shorter than $\text{C}-\text{Cl}$ bond length in CH_3-Cl .
- $\text{S}_{\text{N}}1$ reactions are accompanied by racemisation in optically active alkyl halides.

Ans. (i) In chlorobenzene, $\text{C}-\text{Cl}$ bond acquires partial double bond character while in methyl chloride, $\text{C}-\text{Cl}$ bond has pure single bond character. As a result $\text{C}-\text{Cl}$ bond in chlorobenzene is shorter than methyl chloride.



- Carbocations are intermediate in $\text{S}_{\text{N}}1$ reactions. Carbocations being sp^2 hybridised are planar species, therefore, attack of nucleophile on it can occur from both front and rear with almost equal ease giving a racemic mixture.

Q. 7. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?



(ii) Out of S_N1 and S_N2 , which reaction occurs with

(a) Inversion of configuration (b) Racemisation

[CBSE Delhi 2014]

Ans. (i) , 2-bromobutane is a chiral molecule.



, primary halides undergo faster S_N2 reactions than secondary halides due to less steric hinderance.

(ii) (a) S_N2 reaction occurs with inversion of configuration.

(b) S_N1 reaction occurs with racemisation.

Q. 8. Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:

$C_6H_5CH_2Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$

Ans. $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$ (S_N1).

$C_6H_5C(CH_3)(C_6H_5)Br < C_6H_5CH(C_6H_5)Br < C_6H_5CH(CH_3)Br < C_6H_5CH_2Br$ (S_N2).

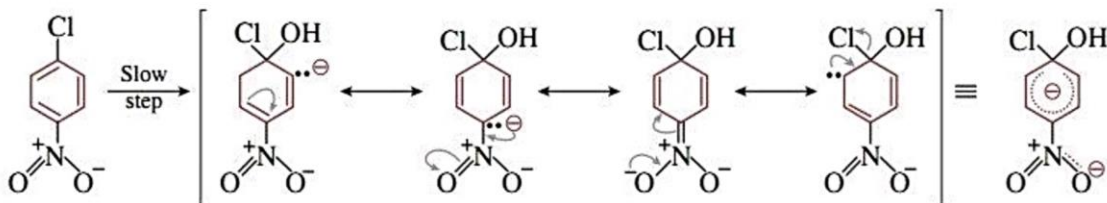
Of the two secondary bromides, the carbocation intermediate obtained from $C_6H_5CH(C_6H_5)Br$ is more stable than that obtained from $C_6H_5CH(CH_3)Br$ because it is stabilised by two phenyl groups due to resonance. Hence, the former bromide is more reactive than the latter in S_N1 reaction. Phenyl group is bulkier than a methyl group. Thus, $C_6H_5CH(C_6H_5)Br$ is less reactive than $C_6H_5CH(CH_3)Br$ in S_N2 reactions.

Q. 9. Give reasons for the following:

(i) *p*-nitrochlorobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structures as well.

(ii) Iodoform is obtained by reaction of acetone with hypiodite ion but not iodide ion.

Ans. (i) In *p*-nitrochlorobenzene a carbanion intermediate is formed. This is stabilised by resonance as shown below.



The $-I$ effect of nitro group further stabilises the intermediate. Hence, *p*-nitrochlorobenzene reacts faster than chlorobenzene.

(ii) Hypiodite ion can act as an oxidising agent while iodide ion does not.

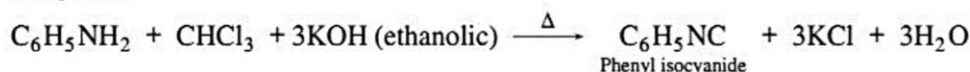
Q. 10. How will you distinguish between the following pairs of compounds:

(i) Chloroform and carbon tetrachloride.

(ii) Benzyl chloride and chlorobenzene.

[CBSE Sample Paper 2014]

Ans. (i) On heating chloroform and carbon tetrachloride with aniline and ethanolic potassium hydroxide separately chloroform forms pungent smelling isocyanide but carbon tetrachloride does not form this compound.



(ii) On adding sodium hydroxide and silver nitrate to both the compounds benzyl chloride forms white precipitate but chlorobenzene does not form white precipitate.



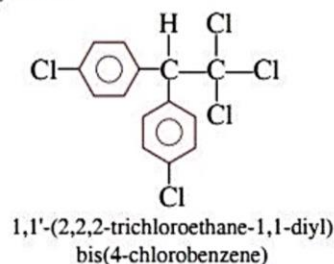
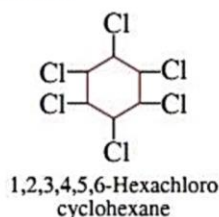
Q. 11. Give the structural formula and IUPAC name of the following compounds:

(i) BHC

(ii) DDT

Ans. (i) BHC

(ii) DDT

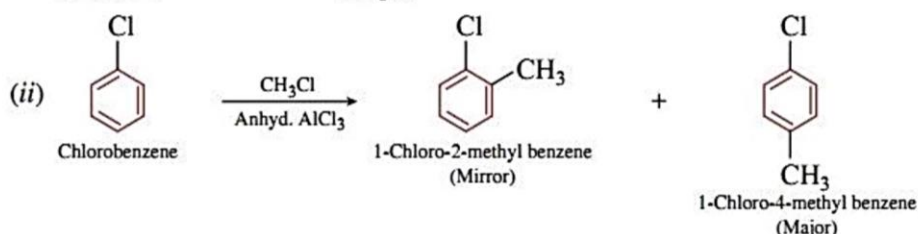
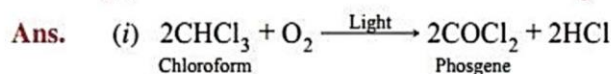


Q. 12. Write equations for the following:

[CBSE 2023 (56/5/2)]

(i) Oxidation of chloroform by air and light

(ii) Reaction of chlorobenzene with CH_3Cl /anhyd. AlCl_3

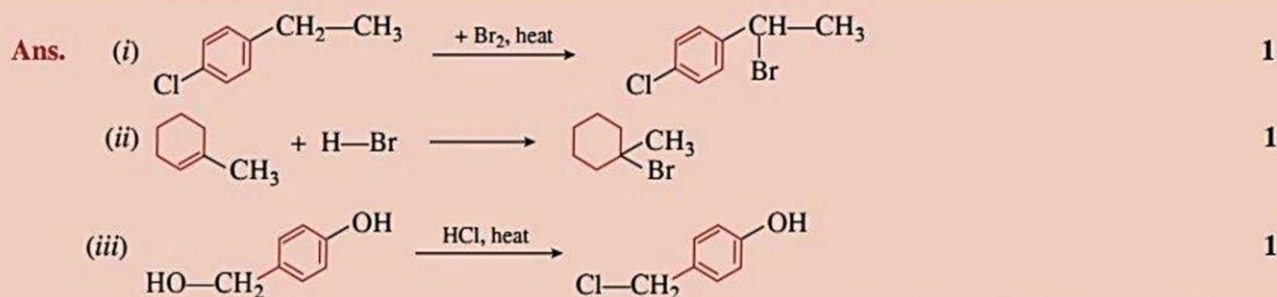
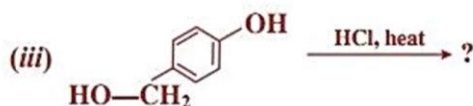
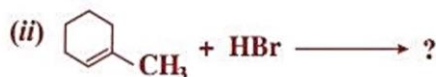
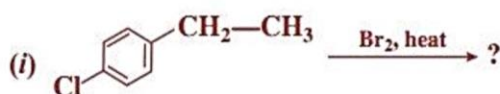


Short Answer Questions-II

Each of the following questions are of 3 marks.

Q. 1. Draw the structures of the major monohalo product for each of the following reactions:

[CBSE (F) 2017]

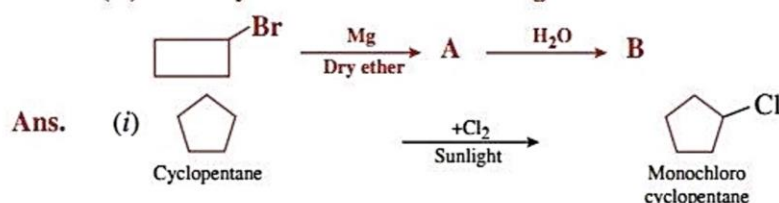


[CBSE Marking Scheme (F) 2017]

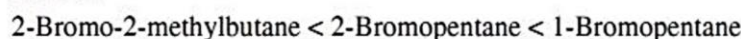
Q. 2. Answer any 3 of the following:

[CBSE 2023 (56/2/1)]

- Which isomer of C_5H_{10} gives a single monochloro compound C_5H_9Cl in bright sunlight?
- Arrange the following compounds in increasing order of reactivity towards S_N2 reaction :
2-Bromopentane, 1-Bromopentane, 2-Bromo-2-methylbutane
- Why *p*-dichlorobenzene has higher melting point than those of ortho- and meta-isomers?
- Identify A and B in the following :



- Due to steric reasons the order of reactivity in S_N2 reactions follows the order $3^\circ < 2^\circ < 1^\circ$. i.e., greater the steric hindrance slower is the reaction. Therefore, order of reactivity of given alkyl halide is as follows:



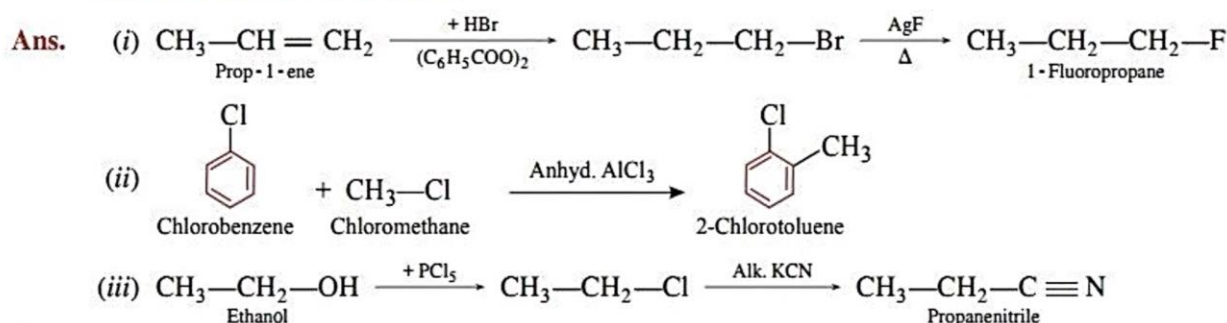
- It is due to the greater symmetry of para-isomer that fits in the crystal better as compared to ortho and meta-isomers.



Q. 3. How do you convert the following:

[CBSE Panchkula 2015]

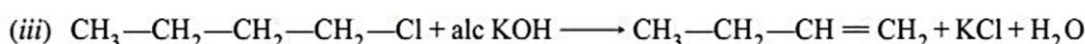
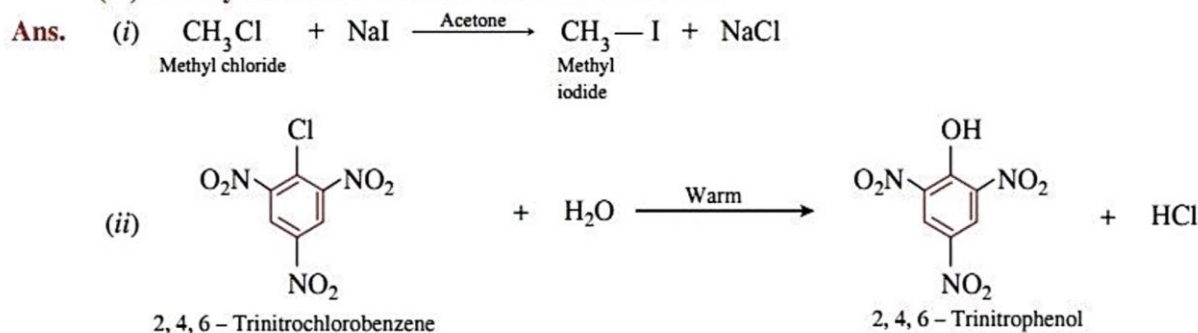
- Prop-1-ene to 1-fluoropropane
- Chlorobenzene to 2-chlorotoluene
- Ethanol to propanenitrile



Q. 4. Write main product formed when :

[CBSE 2023 (56/1/1)]

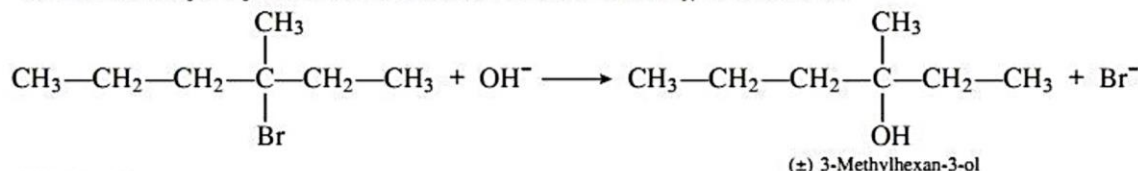
- Methyl chloride is treated with NaI/Acetone.
- 2,4,6-trinitrochlorobenzene is subjected to hydrolysis.
- n*-Butyl chloride is treated with alcoholic KOH.



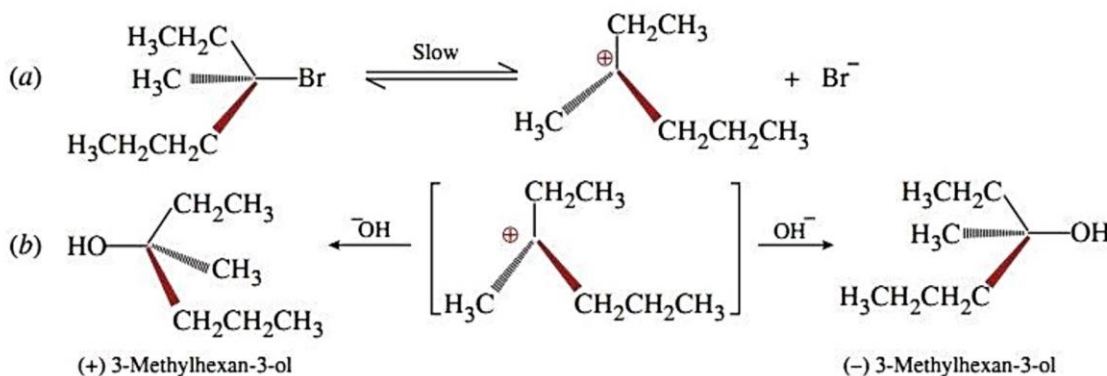
- Q. 5. (i) Explain why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
(ii) An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give a racemic mixture of products. Write the mechanism involved in this reaction.

[CBSE Sample Paper 2016]

- Ans. (i) Refer to Q. 12 (i), NCERT Exercises.
(ii) Since the optically active compound, $C_7H_{15}Br$ reacts with KOH forms a racemic mixture, therefore it must be tertiary alkyl halide and the reaction will follow S_N1 mechanism.

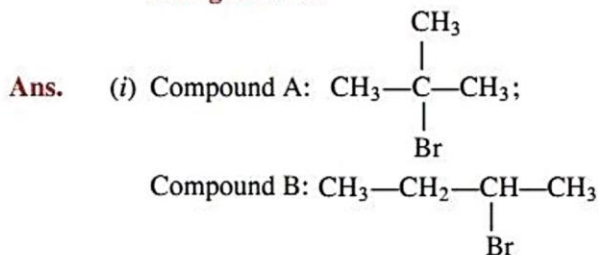


Mechanism:



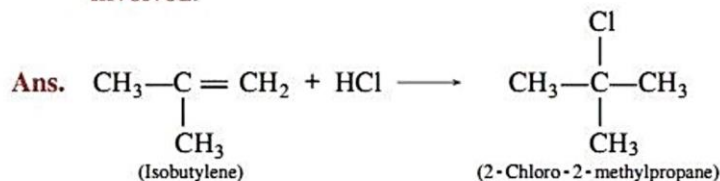
- Q. 6. Compound 'A' with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.

- (i) Write down the structural formula of both compounds 'A' and 'B'.
(ii) Out of these two compounds, which one will be converted to the product with inverted configuration? [NCERT Exemplar] [HOTS]

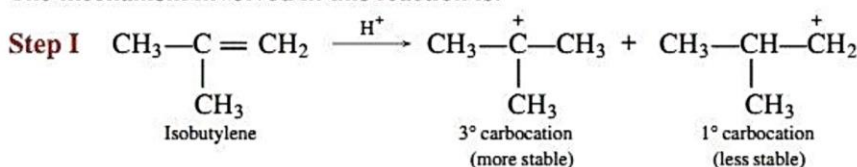


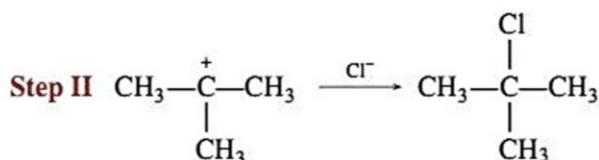
(ii) Compound 'B'

- Q. 7. Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved. [NCERT Exemplar]

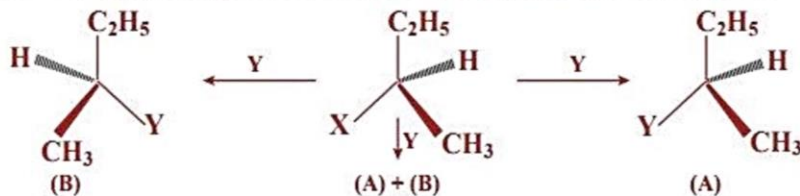


The mechanism involved in this reaction is:





Q. 8. Consider the three types of replacement of group X by group Y as shown here.



This can result in giving compound (A) or (B) or both. What is the process called if

- (A) is the only compound obtained?
- (B) is the only compound obtained?
- (A) and (B) are formed in equal proportions?

[CBSE (F) 2013]

Ans. (i) Retention (ii) Inversion
(iii) Racemisation

Q. 9. Following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

- Write the compound which is most reactive towards $\text{S}_\text{N}2$ reaction.
- Write the compound which is optically active.
- Write the compound which is most reactive towards β -elimination reaction. [CBSE Delhi 2017]

Ans.

Ans. (a) Given compounds are -

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{Br}}{\underset{*}{\text{C}}}-\text{CH}_3$
2-Bromopentane

$\text{CH}_3-\overset{\text{Br}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_3$
2-bromo-2-methylbutane

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
1-Bromopentane

(a) 1-Bromopentane is most reactive towards $\text{S}_\text{N}2$ reactions as it is a primary alkyl halide, so has least steric hindrance.

(b) 2-Bromopentane is optically active, due to presence of chiral carbon atom.

$\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{Br}}{\underset{*}{\text{C}}}-\text{CH}_3$ (* = chiral carbon)

(c) 2-Bromo-2-methylbutane is most reactive towards β -elimination, due to formation of most stable alkene (highly substituted) according to "Saytzeff Rule".

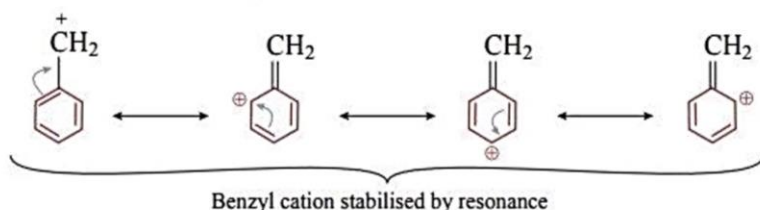
$\text{CH}_3-\overset{\text{Br}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{alc. KOH}} \text{CH}_3-\overset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_3$
(stable alkene with 9 α -H atoms)

[Topper's Answer 2017]

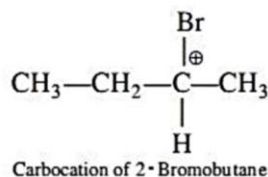
Q. 10. Give reasons for the following:

- Benzyl chloride is highly reactive towards the S_N1 reaction.
- 2-bromobutane is optically active but 1-bromobutane is optically inactive.
- Electrophilic reactions in haloarenes occur slowly. [CBSE Bhubaneswar 2015] [HOTS]

Ans. (i) Benzyl chloride is highly reactive towards the S_N1 reaction because the intermediate benzyl carbocation formed in slowest step is stabilised through resonance.



- 2-bromobutane is a chiral molecule as it contains an asymmetric carbon atom therefore, it is optically active whereas 1-bromobutane is an achiral molecule as it does not contain asymmetric carbon atom therefore it is optically inactive.
- Halogen in haloarenes withdraws electrons through $-I$ effect and release electrons through $+R$ effect. The inductive effect is stronger than resonance effect and causes net electron withdrawal. As a result, the electrophilic substitution reactions in haloarenes occur slowly.



Q. 11. Give reasons for the following observations:

- p*-dichlorobenzene has higher melting point than those of *o*- and *m*- isomers.
- Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.
- The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product. [CBSE 2019 (56/4/1)]

Ans. (i) It is due to the greater symmetry of para-isomer that fits in the crystal better as compared to ortho and meta-isomers.

(ii) As C-X bond in aryl halide acquires a partial double bond character due to resonance while the C-X bond in alkyl halide is a pure single bond.

(iii) Alkoxide ion present in alcoholic KOH, is not only a strong nucleophile but also a strong base so preferentially eliminate a molecule of HCl from alkyl halide to form alkenes.

Q. 12. (i) Why are alkyl halides insoluble in water?

- Why is butan-1-ol optically inactive but butan-2-ol is optically active?
- Although chlorine is an electron withdrawing group, yet it is *ortho*, *para* directing in electrophilic aromatic substitution reactions. Why? [CBSE (F) 2015]

Ans. (i) This is due to the inability of alkyl halide molecule to form intermolecular hydrogen bonds with water molecules.

- (ii) $\text{CH}_3-\text{CH}_2-\text{C}^*(\text{OH})(\text{H})-\text{CH}_3$, due to presence of a chiral carbon butan-2-ol is an optically active compound.

- As the weaker resonance ($+R$) effect of Cl which stabilise the carbocation formed tends to oppose the stronger inductive ($-I$) effect of Cl which destabilise the carbocation at ortho and para positions and makes deactivation less for ortho and para position.

Q. 13. Give reasons:

- n*-Butyl bromide has higher boiling point than *t*-butyl bromide.
- Racemic mixture is optically inactive.
- The presence of nitro group ($-\text{NO}_2$) at *o/p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. [CBSE Delhi 2015; 2019 (56/4/1)]

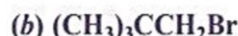
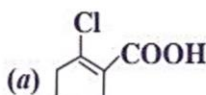
- Ans.
- n*-Butyl bromide being a straight chain alkyl halide has larger surface area than *tert*.butyl bromide. Larger the surface area, larger the magnitude of the van der Waal's forces and hence higher is the boiling point.
 - A racemic mixture contains the two enantiomers *d* and *l* in equal proportions. As the rotation due to one enantiomer is cancelled by equal and opposite rotation of another enantiomer, therefore, it is optically inactive.
 - The presence of NO_2 group at *o/p* position in haloarenes helps in the stabilisation of resulting carbanion by $-R$ and $-I$ effects and hence increases the reactivity of haloarenes towards nucleophilic substitution reactions.



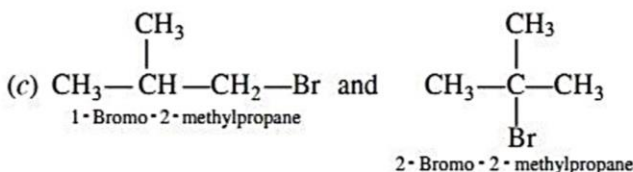
Long Answer Questions

Each of the following questions are of 5 marks.

- Q. 1. (i) Among all the isomers of molecular formula $\text{C}_4\text{H}_9\text{Br}$, identify [CBSE 2019 (56/2/1)]
- the one isomer which is optically active.
 - the one isomer which is highly reactive towards $\text{S}_\text{N}2$.
 - the two isomers which give same product on dehydrohalogenation with alcoholic KOH.
- (ii) Give IUPAC name of the following organic compounds:

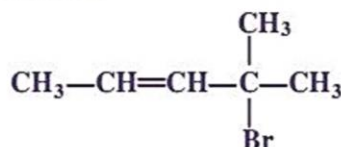


- Ans. (i) (a) $\text{CH}_3-\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$ (b) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br}$
2-Bromobutane 1-Bromobutane



- (ii) (a) 2-chloro cyclopent-1-ene-1-carboxylic acid
(b) 1-bromo-2, 2-dimethyl propane

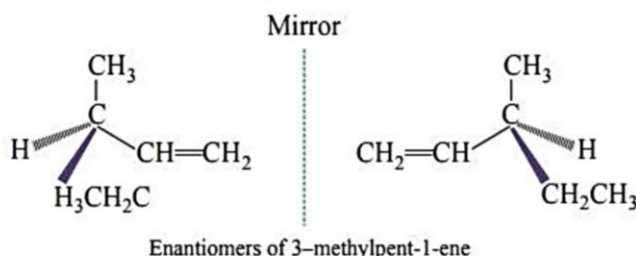
- Q. 2. (i) (a) Write equation for preparation of 1-iodobutane from 1-chlorobutane.
(b) Out of 2-bromopentane, 2-bromo-2-methylbutane and 1-bromopentane, which compound is most reactive towards elimination reaction and why?
(c) Give IUPAC name of



[CBSE 2019 (56/4/1)]

(ii) What are enantiomers? Draw the structures of the possible enantiomers of 3-methylpent-1-ene.

- Ans. (i) (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{NaI} \xrightarrow{\text{Dry acetone}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I} + \text{NaCl}$
 (b) 2-Bromo-2-methylbutane is more reactive as it gives more substituted alkene on elimination.
 (c) 4-Bromo-4-methylpent-2-ene
 (ii) Stereoisomers which are non-superimposable mirror images of each other are called enantiomers.



Questions for Practice

Choose and write the correct answer for each of the following.

- The IUPAC name of the compound is:
 - 4-fluoro-1-methyl-3-nitrobenzene
 - 1-fluoro-4-methyl-2-nitrobenzene
 - 2-fluoro-5-methyl-1-nitrobenzene
 - 4-methyl-1-fluoro-2-nitrobenzene
- Molecules whose mirror image is non superimposable over them are known as chiral. Which of the following molecules is chiral in nature?
 - 2-Bromobutane
 - 1-Bromobutane
 - 2-Bromopropane
 - 2-Bromopropan-2-ol
- Which of the following alkyl halides will undergo $\text{S}_{\text{N}}1$ reaction most readily? [NCERT Exemplar]
 - $(\text{CH}_3)_3\text{C}-\text{F}$
 - $(\text{CH}_3)_3\text{C}-\text{Cl}$
 - $(\text{CH}_3)_3\text{C}-\text{Br}$
 - $(\text{CH}_3)_3\text{C}-\text{I}$
- The reagents for the following conversion is/are
 $\text{Br}-\text{CH}_2-\text{CH}_2-\text{Br} \xrightarrow{?} \text{H}-\text{C}\equiv\text{C}-\text{H}$
 - $\text{Zn}/\text{CH}_3\text{OH}$
 - alcoholic KOH followed by NaNH_2
 - aqueous KOH followed by NaNH_2
 - alcoholic KOH
- Consider the following compounds:

I

II

III

the correct order of reactivity towards $\text{S}_{\text{N}}2$ reaction is [CBSE 2022 (56/3/4)]

 - $\text{I} > \text{III} > \text{II}$
 - $\text{II} > \text{III} > \text{I}$
 - $\text{II} > \text{I} > \text{III}$
 - $\text{III} > \text{I} > \text{II}$

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
 (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
 (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
 (d) Assertion (A) is incorrect, but Reason (R) is correct statement.

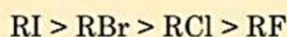
6. Assertion (A) : Hydroxyketones are not directly used in Grignard reaction.

Reason (R) : Grignard reagents reacts with hydroxyl group.

7. Assertion (A) : Chlorination of ethylbenzene with Cl_2 in presence of heat and light mainly yields 1-chloro-2-phenylethane.

Reason (R) : The reaction occurs through intermediate formation of the radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_3$.

8. Assertion (A) : The boiling points of alkyl halides decrease in the order:



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

9. Assertion (A) : 3° alkyl halides are most reactive towards $\text{S}_{\text{N}}1$ reaction.

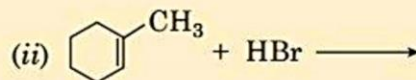
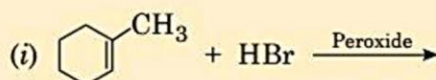
Reason (R) : In $\text{S}_{\text{N}}1$ reaction, the rate of the reaction depends only on the concentration of alkyl halide.

10. Assertion (A) : Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene.

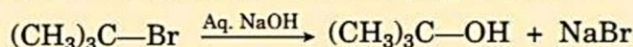
Reason (R) : $-\text{NO}_2$ group is a *m*-directing group.

Answer the following questions:

11. Complete the following reaction equations:



12. Write the mechanism of the following $\text{S}_{\text{N}}1$ reaction:



[CBSE 2020 (56/4/2)]

13. (i) Which is a better nucleophile, a bromide ion or an iodide ion?

(ii) Which will have a higher boiling point?

1-Chloropentane or 2-methyl-2-chlorobutane

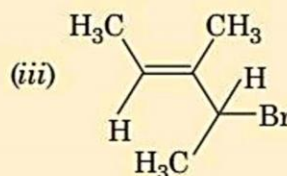
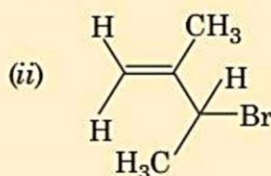
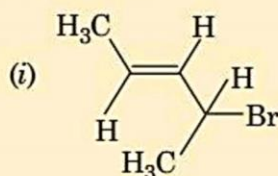
14. How the following conversion can be carried out?

Ethanol to But-2-yne

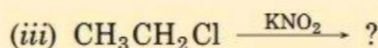
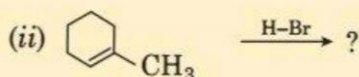
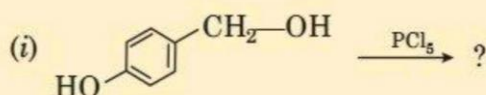
[HOTS]

15. Write IUPAC names of the following:

[CBSE (AI) 2011]



16. Write the major product(s) in the following reactions:



[CBSE (F) 2016]

17. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photochlorination. Give the structure of the hydrocarbon.

18. Account for the following:

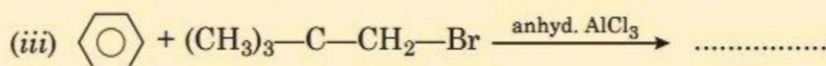
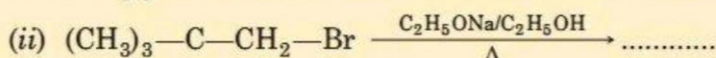
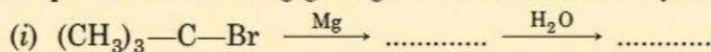
[CBSE 2023 (56/4/2)]

- Benzyl chloride is highly reactive towards $\text{S}_{\text{N}}1$ reaction.
- (\pm)-Butan-2-ol is optically inactive, though it contains a chiral carbon atom.
- Chloroform is stored in closed dark coloured bottles.

19. How will you bring about following conversions?

- Chlorobenzene to phenol
- Isopropyl bromide to *n*-propyl bromide
- Aniline to iodobenzene

20. Complete the following giving the structures of major organic products.



21. A compound 'A' having molecular formula $\text{C}_4\text{H}_9\text{Br}$ on reaction with alcoholic KOH gives a compound 'B'. Bromination of 'B' gives compound 'C'. Compound 'C' on treatment with soda amide gives a gaseous compound 'D'. The gas 'D' when passed through ammonical silver nitrate solution forms white precipitate.

Identify compounds A, B, C and D and write down the reactions involved.

Answers

1. (a) 2. (a) 3. (d) 4. (b) 5. (c) 6. (a) 7. (d) 8. (b) 9. (b) 10. (d)

