CHAPTER 10

HALOALKANES AND HALOARENES

Syllabus

- ➢ *Haloalkanes : Nomenclature, nature of C–X bond, physical and chemical properties, optical rotation mechanism of substitution reactions.*
- ➢ *Haloarenes : Nature of C–X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only).*
  Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Trend Analysis

List of concept names	2018	2019		2020	
	D/OD	D	OD	D	OD
IUPAC name		2Q (1 mark)			
Structure of Haloalkanes and Haloarenes	1Q (3 marks)				
S_N1 Reaction, S_N2 Reaction, Optical Activity and β-elimination Reaction	1Q (1 mark) 1Q (2 marks)	2Q (1 mark) 1Q (3 marks)	2Q (1 mark) 1Q (3 marks)	2Q (1 mark)	3Q (1 mark) 1Q (3 marks)
Structure of Haloalkanes and Haloarenes	1Q (1 mark)	1Q (3 marks)	1Q (3 marks)		1Q (3 marks)
Other Chemical Reactions	1Q (1 mark)	1Q (3 marks)	1Q (3 marks)		1Q (3 marks)

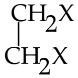
TOPIC-1

Haloalkanes and their Properties

Revision Notes

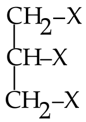
- ➢ Haloalkanes are aliphatic hydrocarbons where a hydrogen atom is replaced by halogen, while haloarenes are aromatic hydrocarbons where hydrogen in the benzene ring is replaced with halogen atom.
- ➢ Halogen atom is attached to sp^3 hybridised carbon atom in haloalkanes while in haloarenes it is attached to sp^2 hybridised carbon atom of the aryl group.
- ➢ **Classification :**
  - **On the basis of the number of halogen atom :** 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,

C_2H_5X
Monohaloalkane



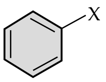
$$\begin{array}{c} CH_2X \\ | \\ CH_2X \end{array}$$

Dihaloalkane

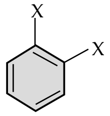


$$\begin{array}{l} CH_2{-}X \\ | \\ CH{-}X \\ | \\ CH_2{-}X \end{array}$$

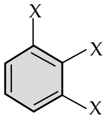
Trihaloalkane



Monohaloarene



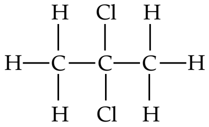
Dihaloarene



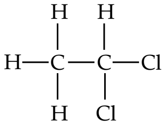
Trihaloarene

Dihalogen compounds may be further classified as :

(i) Geminal dihalides : Two halogen atoms are attached to the same carbon atom. For example,



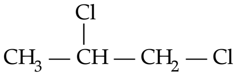
Isopropylidene chloride
(2, 2–Dichloropropane)



Ethylidene chloride
(1, 1–Dichloroethane)

(ii) Vicinal dihalides : Two halogen atoms are attached to adjacent carbon atoms. For example,

$Cl — CH_2 — CH_2 — Cl$
Ethylene dichloride
(1, 2-Dichloroethane)

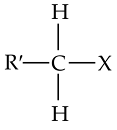


$$CH_3 — \overset{\overset{\large Cl}{|}}{C}H — CH_2 — Cl$$

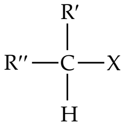
Propylene dichloride
(1, 2-Dichloropropane)

- **On the basis of sp^3 hybridisation :**

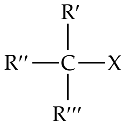
(i) Haloalkanes or alkyl halides (R—X) : General formula is $C_nH_{2n+1}X$. They are further classified as primary, secondary and tertiary haloalkanes.



Primary haloalkane



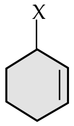
Secondary haloalkane



Tertiary haloalkane

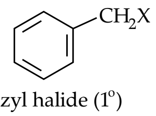
(ii) Allylic halides : Halogen is bonded to allylic carbon.

$CH_2 = CH — CH — X$
Allyl halide
(3-Halo–1–propene)

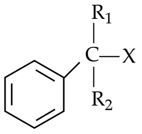


3-Halocylohex–1–ene

(iii) Benzylic halides : Halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring.



Benzyl halide (1°)

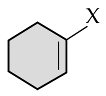


Here, $R_1 = CH_3$, $R_2 = H$ (2°)
or $R_1 = R_2 = CH_3$ (3°)

- **On the basis of sp^2 hybridisation :**

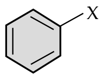
(i) Vinylic halides : Halogen is bonded to one of the carbon atoms of a vinylic carbon.

$CH_2 = CH — X$
Vinyl halide



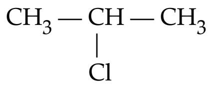
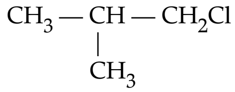
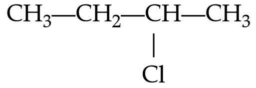
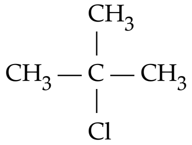
1–Halocylohex–1 –ene

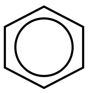
(ii) Aryl halides : Halogen atom is directly bonded to sp^2 hybridised carbon atom of an aromatic ring.



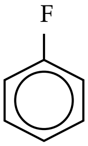
Halobenzene

- **Common and IUPAC name of some halides :**

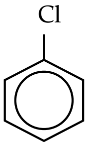
Structure	IUPAC Name	Common names
CH_3Cl	Chloromethane	Methyl chloride
CH_3CH_2Cl	Chloroethane	Ethyl chloride
$CH_3-CH_2-CH_2Cl$	1-Chloropropane	*n*-Propyl chloride
 $CH_3-CH(Cl)-CH_3$	2-Chloropropane	Isopropyl chloride
$CH_3—CH_2—CH_2—CH_2Cl$	1-Chlorobutane	*n*-Butyl chloride
 $CH_3-CH(CH_3)-CH_2Cl$	1-Chloro-2-methyl propane	Isobutyl chloride
 $CH_3—CH_2—CH(Cl)—CH_3$	2-Chlorobutane	Sec. butyl chloride
 $CH_3-C(CH_3)(Cl)-CH_3$	2-Chloro-2-methyl propane	Tertiary butyl chloride
CH_3F	Fluoromethane	Methyl fluoride
CH_3Br	Bromomethane	Methyl bromide
CH_3I	Iodomethane	Methyl iodide
CH_2Cl_2	Dichloromethane	Methylene dichloride
$CHCl_3$	Trichloromethane	Chloroform
CCl_4	Tetrachloromethane	Carbon tetrachloride
$CHBr_3$	Tribromomethane	Bromoform
CHI_3	Triiodomethane	Iodoform
$ClCH_2—CH_2Cl$	1, 2-Dichloroethane	Ethylene dichloride
CH_3CHCl_2	1, 1-Dichloroethane	Ethylidene chloride
$CH_2 = CHCl$	Chloroethene	Vinyl chloride
$CH_2 = CH—CH_2Br$	3-Bromopropene	Allyl bromide
$(CH_3)_3CCH_2Br$	1-Bromo-2, 2-dimethylpropane	neo-pentylbromide
$CF_3CF_2CF_3$	Octafluoropropane	Perfluoropropane
CCl_2F_2	Dichlorodifluoromethane	Freon
$CHCl_2—CHCl_2$	1, 1, 2, 2-Tetrachloroethane	Acetylene tetrachloride
$CHCl = CCl_2$	1, 1, 2-Trichloroethene	Acetylene trichloride



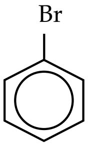
Benzene



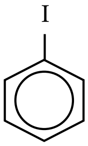
Fluorobenzene



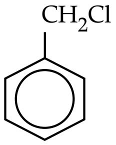
Chlorobenzene



Bromobenzene

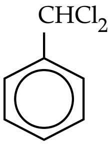


Iodobenzene



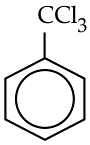
1–Chloro –1–
phenylmethane

(Benzyl chloride)



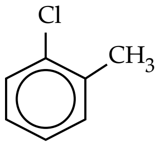
Dichlorophenyl
methane

(Benzylidene chloride)
(Benzal chloride)



Trichlorophenyl
methane

(Benzotrichloride)



1–Chloro–2–methyl
benzene

(2–Chlorotoluene)

- **Methods of preparation of Haloalkanes :**

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

$$R-OH + HX \xrightarrow{ZnCl_2} R-X + H_2O \ (X = Cl, Br, I)$$

$$R-OH + NaBr + H_2SO_4 \longrightarrow R-Br + NaHSO_4 + H_2O$$

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3 \ (X = Cl, Br)$$

$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$

$$R-OH \xrightarrow[X_2=Br_2, I_2]{Red\ P/X_2} R-X$$

$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$$

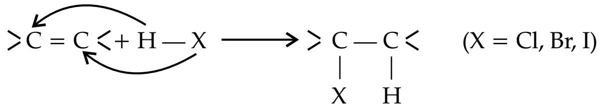
The reactions of primary and secondary alcohols with HX require the presence of the anhydrous $ZnCl_2$.

(b) From hydrocarbons : By free radical halogenation.

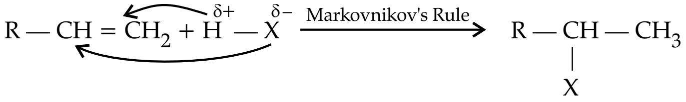
$$\underset{\text{n-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{Or heat}]{Cl_2/\text{UV Light}} \underset{n\text{-Butyl chloride}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{Sec.-Butyl chloride}}{CH_3CH_2CHClCH_3} \ \text{(Major Product)}$$

(c) From alkenes :

(i) Addition of hydrogen halide :



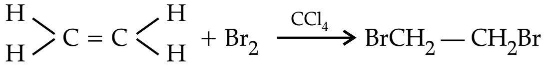
$$>C=C< + H-X \longrightarrow >\underset{X}{C}-\underset{H}{C}< \quad (X = Cl, Br, I)$$



$$R-CH=CH_2 + \overset{\delta+}{H}-\overset{\delta-}{X} \xrightarrow{\text{Markovnikov's Rule}} R-\underset{X}{CH}-CH_3$$

$$R-CH=CH_2 + H-Br \xrightarrow[\text{Anti Markovnikov's addition}]{\text{Benzoyl peroxide}} R-CH_2-CH_2-Br$$

(ii) Addition of Halogens :



$$H_2C=CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2-CH_2Br$$

Vic-Dibromide

(d) Halide Exchange :

(i) By Finkelstein Reaction :

$$R-X + NaI \xrightarrow{\text{Dry acetone}} R-I + NaX \ (X = Cl, Br)$$

(ii) By Swarts Reaction :

$$R-X \xrightarrow{AgF,\ Hg_2F_2,\ CoF_2\ \text{or}\ SbF_3} R-F$$

$$CH_3-Br + AgF \longrightarrow CH_3-F + AgBr$$

- **Nature of C-X bond in haloalkanes :** The carbon-halogen bond is polarised. Carbon atom holds partial positive charge and halogen atom holds partial negative charge. This occurs due to difference in electronegativity. Halogens are more electronegative than carbon. Size of the halogen atoms increases down the group. Fluorine is the smallest and iodine is the largest. Carbon-halogen bond length also increases from C-F to C-I.

- **Physical properties of haloalkanes :** Haloalkanes are colourless when pure but compounds of bromine are coloured.

(i) Melting and boiling points : Haloalkanes, due to polar and strong dipole-interactions between their molecules, have high B.P. and M.P. This increase in B.P. and M.P. depends on increasing size, mass of halogens and magnitude of van der Waals forces of attractions. The increasing order is RF< RCl < RBr < RI. With respect to isomeric alkyl halides, B.P. decreases with increase in branching due to less surface area and weak inter-particle forces.

(ii) Density : It increases with increase in carbon atoms, halogen atoms and atomic mass of the halogen atoms.

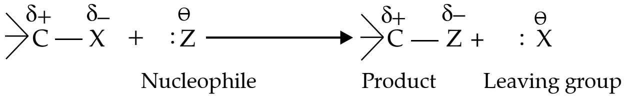
(iii) Solubility : Haloalkanes are insoluble in water but are soluble in organic solvents.

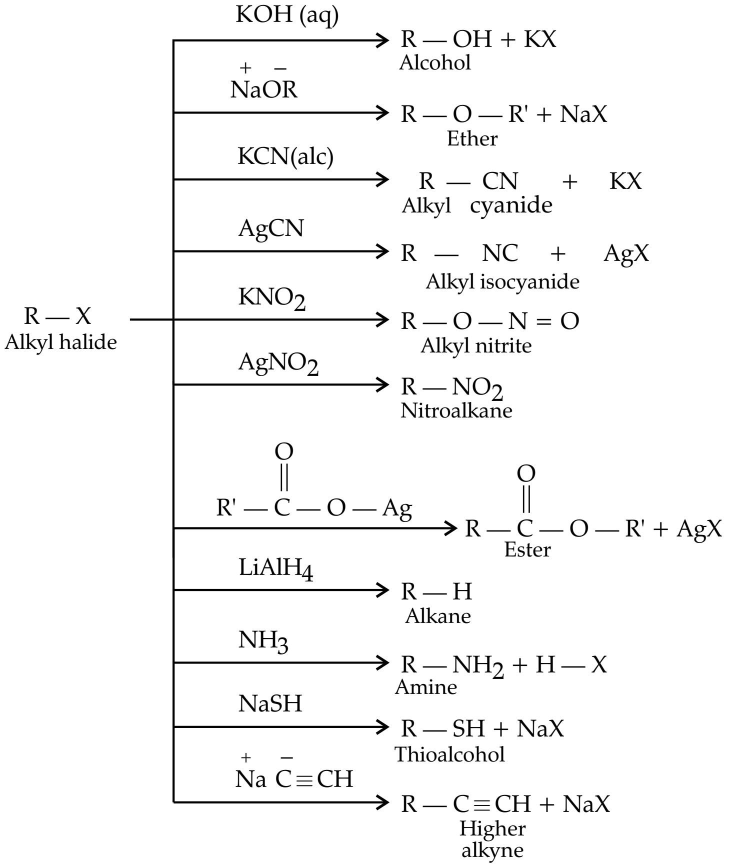
- **Chemical properties of haloalkanes :** Reactivity of haloalkanes depends on the C-X bond cleavage. Higher the bond dissociation energy of C-X bond, lesser will be the reactivity. Dissociation energy of C-X bond decreases with increase in the halogen size, *i.e.,* C–Cl > C–Br > C–I. Reactivity order of haloalkanes would be :

  Chlorides < Bromides < Iodides

There are four types of chemical reactions with haloalkanes :

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

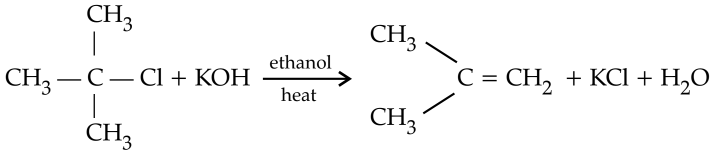




Alkyl halides undergo nucleophilic substitution reactions.

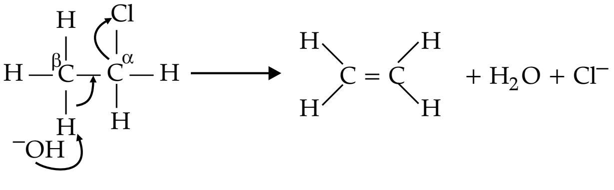
$CH_3CH_2Br + :\ddot{\underset{..}{O}}H^- \longrightarrow CH_3CH_2OH + :\ddot{\underset{..}{Br}}:^-$

(b) Elimination reaction : Alkyl halides undergo β-elimination of hydrogen atom from β-carbon atom and halogen atom to form alkenes on being heated with KOH (alc.) or KNH_2. *e.g.,*



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl + KOH \xrightarrow[\text{heat}]{\text{ethanol}} (CH_3)_2C=CH_2 + KCl + H_2O$$

The reaction is called *dehydrohalogenation.*



The following is order of reactivity :

$RCl < RBr < RI$

$RCH_2X < R_2CHX < R_3CX$

(c) Reaction with metals :

(1) Reaction with magnesium :

$$\underset{\text{Alkyl halide}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Alkyl magnesium halide}\\\text{(Grignard reagent)}}}{RMgX}$$

$$CH_3-CH_2-Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Ethyl magnesium bromide}}{CH_3-CH_2-MgBr}$$

(2) Reaction with sodium (Wurtz reaction) :

$$R-X + 2Na + X-R \xrightarrow{\text{Dry ether}} R-R + 2NaX$$

$$CH_3-CH_2-Cl + 2Na + Cl-CH_2-CH_3 \xrightarrow{\text{Dry ether}} \underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} + 2NaCl$$

(d) Reduction :

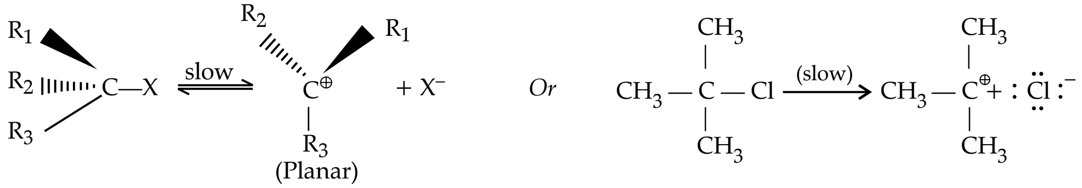
$$R-X + 2(H) \xrightarrow{Zn/HCl(conc.)} R-H + H-X$$

$$CH_3-CH_2-Cl + 2(H) \xrightarrow{Zn/HCl(conc.)} CH_3-CH_3 + HCl$$

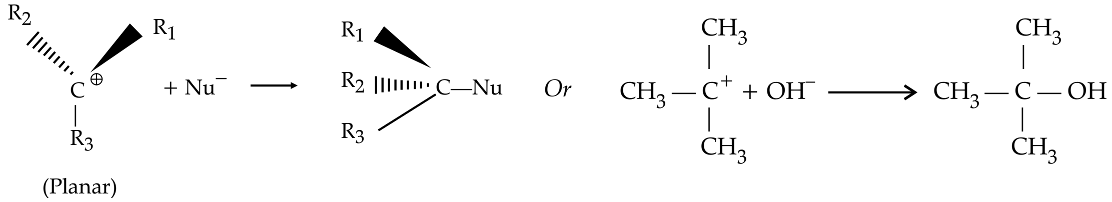
- **Mechanism of Nucleophilic substitution reaction :** Alkyl halides undergo two types of nucleophilic substitution reactions.

(i) Unimolecular nucleophilic substitution reaction (S_N1) : Those substitution reactions in which rate of reaction depends upon the concentration of only one of the reactants, *i.e.*, alkyl halides are called S_N1 reactions, *e.g.*, hydrolysis of tertiary butyl chloride follows S_N1 reaction. This reaction takes place in two steps:

STEP I :

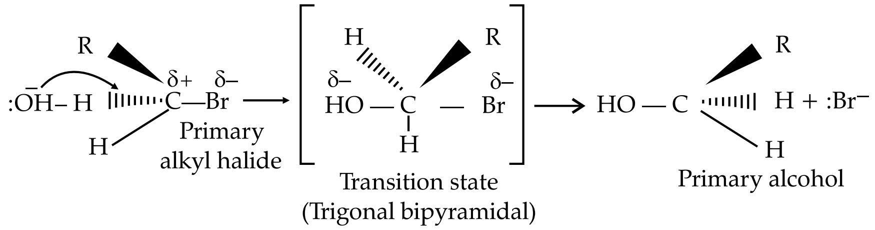


STEP II :



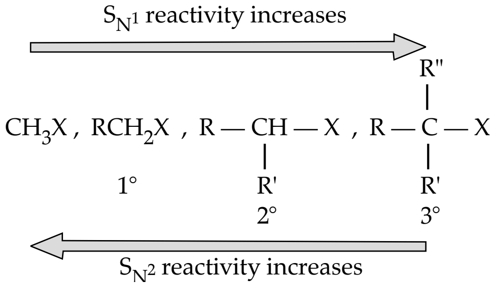
The slowest step is rate determining step which involves one species only. Therefore, rate of reaction depends only on the concentration of tertiary butyl chloride. Polar protic solvents like water, alcohol favour S_N1 because they stabilize carbocation by solvation. Tertiary alkyl halides follow S_N1 mechanism.

(ii) Biomolecular nucleophilic substitution reaction (S_N2) : The reaction whose rate depends on the concentration of two species, alkyl halide and nucleophile. They involve one step mechanism. Back side attack of nucleophile and departing of leaving group take place simultaneously.



Non-polar solvents favour S_N2 mechanism. Primary alkyl halides follow S_N2 mechanism.

- **Reactivity of S_N1 and S_N2 mechanisms :** S = Substitution, N = Nucleophilic, 2 = Bimolecular, 1 = Unimolecular. Nucleophilic substitution seldom occurs exclusively by one mechanism only. With a given halogen, primary, secondary and tertiary halides show opposite order of reactivity in the two mechanisms.

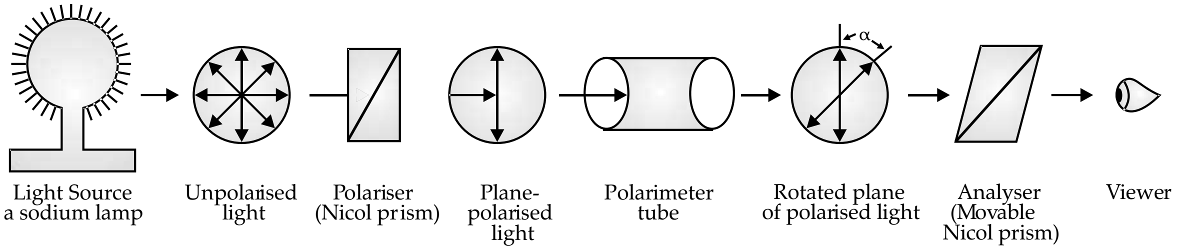


$$CH_3X,\ RCH_2X,\ R-\underset{\underset{R'}{|}}{CH}-X,\ R-\overset{\overset{R''}{|}}{\underset{\underset{R'}{|}}{C}}-X$$

- **Stereoisomerism :** Isomerism exhibited by two or more compounds with the same molecular and structural formula, but different spatial arrangements of atoms or groups in space is called stereoisomerism.
- **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.
- **Nicol prism :** A nicol prism is a special type of prism made from calcite, a special crystalline form of calcium carbonate. It is a device for producing plane polarised light.
- **Optical rotation :** Property of rotating the plane of polarisation either towards left or right.
- **Dextrorotatory :** Those substances which rotate the plane of polarisation of light towards right, *i.e.*, in clockwise direction are called dextrorotatory. It is conventionally given a positive sign. It is denoted by '*d*' and a positive (+) sign is placed before the degree of rotation.
- **Laevorotatory :** Those substances which rotate the plane of polarisation of light towards the left, *i.e.*, in anticlockwise direction are called laevorotatory. It is denoted by '*l*' and a negative (–) sign is placed before the degree of rotation.
- **Specific rotation :** The extent of experimentally observed angle of rotation (optical rotation, represented by α_{obs}) of a substance depends upon the following factors :
  - **(i)** nature of substance,
  - **(ii)** wavelength of the light used,
  - **(iii)** the number of optically active molecules in the path of light beam (which depends upon concentration of sample),
  - **(iv)** length of polarimeter tube,
  - **(v)** solvent used.

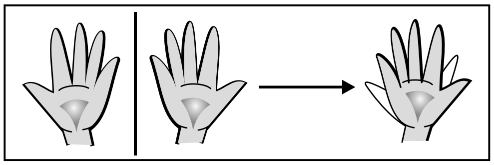
  Specific rotation $[\alpha]_D^{t^\circ C} = \dfrac{\text{observed rotation } (\alpha_{obs})}{\text{length of tube } (d_m) \times \text{concentration of solution (g mol}^{-1})}$

- **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.
- **Polarimeter :** The angle of rotation by which the plane-polarised light is rotated, can be measured by using an instrument called polarimeter. A schematic diagram of a polarimeter is shown in the figure below :



- **Enantiomers :** Those stereoisomers which are mirror images of each other but non-superimposable are called enantiomers, *e.g.*, *d*(+) glucose and *l*(–) glucose are enantiomers.
- **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.

- **Symmetrical objects :** Those objects whose projections are superimposable on their mirror images are symmetrical objects, *e.g.*, a sphere, a cube, a cone, a tetrahedron are all identical to their mirror images and can thus be superimposed.
- **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. A chiral object is also called dissymmetric. e.*g.*,



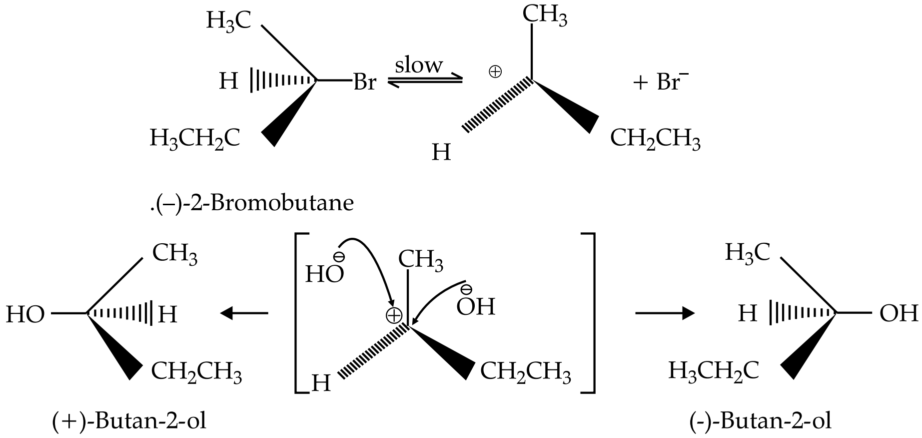
Non-superimposable hands

- **Achiral :** Achiral objects are those objects which are superimposable on their mirror images.
- **Asymmetric carbon (Chiral carbon) :** The carbon atom which is attached with four different groups of atoms is called asymmetric or chiral carbon atom.
- **Racemic mixture :** A mixture containing equal amounts of enantiomers which does not show any optical activity. It is optically inactive due to external compensation.
- **Racemisation :** The process of conversion of an enantiomer into racemic mixture is known as racemisation.
- **Absolute configuration :** The three dimensional structure of a molecule that has one or more centres of chirality is referred to its absolute configuration.
- **Diastereoisomers :** Those pairs of stereoisomers which are not mirror images of each other and are non-superimposable.

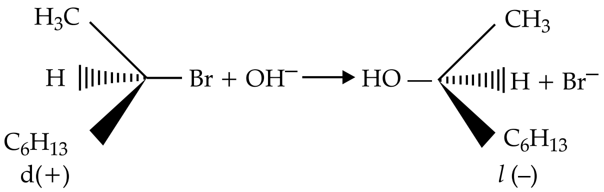
  (i) Diastereoisomers have different physical properties.

  (ii) Diastereoisomers differ in magnitude of specific rotation.

  (iii) A compound with two chiral centres does not always have four stereoisomers.
- **Example of racemisation in S_N1 mechanism :** When optically active alkyl halide undergoes S_N1 mechanism, it is accompanied by racemisation because intermediate carbocation formed is *sp*^{2}-hybridised and polar. Nucleophile (OH^-) has equal probability of attacking it from either side leading to formation of equal amount of dextro and laevo-rotatory alcohols. As the products of S_N1 mechanism has both inversion as well as rotation, the products formed by this reaction would be racemic mixture of alcohols.

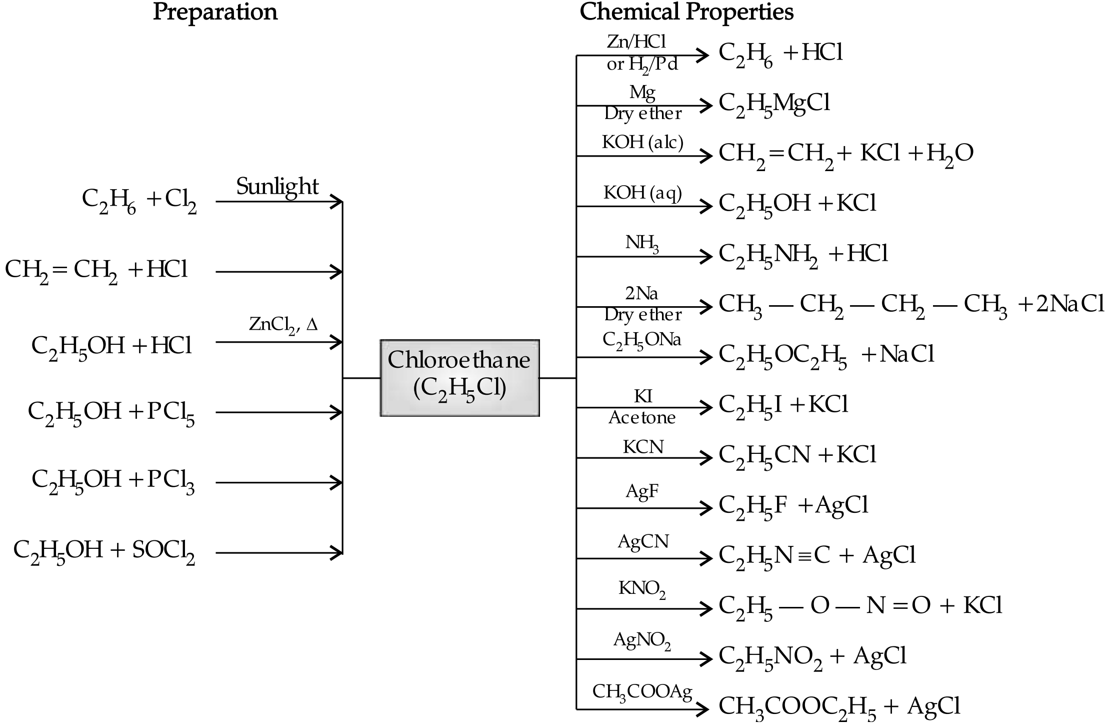


- **Meso compounds :** Those compounds which have two or more (even number) chiral carbon atoms and have an internal plane of symmetry are called meso compounds. They are optically inactive due to internal compensation.
- **Example of inversion in S_N2 mechanism :** When optically active *d* (+) alkyl halide is treated with OH^-, we get optically active *l* (–) alcohol due to back side attack of nucleophile.



When *d*(+)-2-bromooctane is reacted with NaOH, *l*(–)-2-octanol is formed. Thus, S_N2 mechanism leads to inversion of configuration. This inversion is called Walden's inversion.

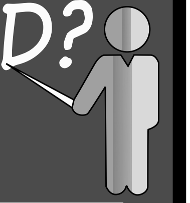
- **Important reactions of chloroethane :**



Know the Terms

- **Synthetic tools :** Alkyl halides are regarded as synthetic tools in the hands of chemistry due to their highly reactive nature.
- **Relative configuration :** Arrangement of atoms in space of a stereo isomer of a compound relative to another compound chosen as arbitrary standard (like glyceraldehyde).

How is it done on the GREENBOARD?



Q.What happens when :

(i) CH_3–Cl is treated with aqueous KOH ?

(ii) CH_3–Cl is treated with KCN ?

(iii) CH_3–Br is treated with Mg in the presence of dry ether ?

Solution

STEP-1: (i) $CH_3-Cl + KOH \rightarrow CH_3OH + KCl$

$(\alpha\theta)$ **Methanol**

STEP-2: (ii) $CH_3-Cl + KCN \rightarrow CH_3CN + KCl$

Methyl cyanide

STEP-3: (iii) $CH_3Br + Mg \xrightarrow{\text{Dry ether}} CH_3MgBr$

Methyl magnesium bromide

Objective Type Questions

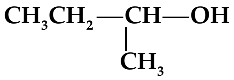
(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q. 1. The order of reactivity of following alcohols with halogen acids is :

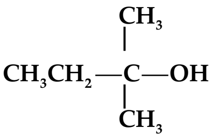
(i) $CH_3CH_2-CH_2-OH$

(ii)



$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$

(iii)



$CH_3CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

(a) (i) > (ii) > (iii) **(b) (iii) > (ii) > (i)**

(c) (ii) > (i) > (iii) **(d) (i) > (iii) > (ii)**

U [NCERT Exemp. Q. 1, Page 133]

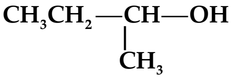
Ans. Correct option : (b)

Explanation : The reactivity order of alcohols towards halogen acids is $3^o > 2^o > 1^o$ as the stability of carbocations is of the order $3^o > 2^o > 1^o$. **[1]**

Q. 2. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

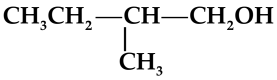
(a) $CH_3CH_2-CH_2-OH$

(b)



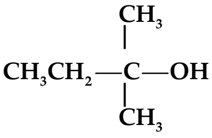
$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$

(c)



$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH$

(d)



$CH_3CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$

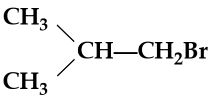
A [NCERT Exemp. Q. 2, Page 133]

Ans. Correct option : (d)

Explanation : As tertiary carbocation is more stable, so tertiary alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature. While primary and secondary alcohols require the presence of a catalyst $ZnCl_2$. **[1]**

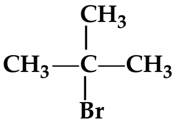
Q. 3. Arrange the following compounds in increasing order of their boiling points:

(i)



(ii) $CH_3CH_2CH_2CH_2Br$

(iii)



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_3$

(a) (ii) < (i) < (iii) **(b) (i) < (ii) < (iii)**

(c) (iii) < (i) < (ii) **(d) (iii) < (ii) < (i)**

U [NCERT Exemp. Q. 8, Page 135]

Ans. Correct option : (c)

Explanation : Boiling points of isomeric haloalkanes decrease with increase in branching as with increase in branching surface area decreases which leads to decrease in intermolecular forces. **[1]**

Q. 4. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as

(a) a dehydrohalogenation reaction

(b) a substitution reaction

(c) an addition reaction

(d) a dehydration reaction

R [CBSE Delhi Set 1 2020]

Ans. Correct option : (b)

Explanation : $R - X + NaOH \rightarrow R - OH + NaX$

[1]

[B] ASSERTION & REASON TYPE QUESTIONS :

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

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

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

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

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

Q. 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.

R [CBSE SQP 2020]

Ans. Correct option: (d)

Explanation: Aryl halides are less reactive towards nucleophilic substitution reactions because of the carbon halogen bond in aryl halides has partial double bond character. **[1]**

Q. 2. Assertion (A): Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

Reason (R): This reaction proceeds through the formation of a carbocation. U [NCERT Exemplar]

Ans. Correct option: (d)

Explanation: Hydrolysis of (–)-2-bromooctane proceeds through the formation of a carbocation following S_N1 reaction. **[1]**

Q. 3. Assertion (A): tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane

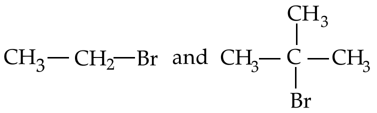
Reason (R): In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide. U **[NCERT Exemplar]**

Ans. Correct option: (a)

Explanation: 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 so tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane. **[1]**

[C] VERY SHORT ANSWER TYPE QUESTIONS :

Q. 1. Which would undergo S_N2 reaction faster in the following pair and Why?



$CH_3—CH_2—Br$ and $CH_3—C(CH_3)(Br)—CH_3$

A&E **[CBSE Delhi Set-1, 2, 3 2015]**

Ans. $CH_3 — CH_2 — Br$ would undergo S_N^2 reaction faster it has less steric hindrance than tert - butyl bromide. **1**

$CH_3 — CH_2 — Br$

Because it is a primary halide / (1*) halide ½ + ½

[CBSE Marking Scheme, 2015]

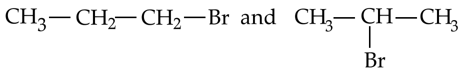
Commonly Made Error

- Sometimes, students can not identify correct alkyl halide for given reaction.

Answering Tip

- Clearly understand the concept of S_N^2 reaction.

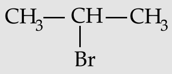
Q. 2. Which would undergo S_N1 reactions faster in the following pair :



$CH_3—CH_2—CH_2—Br$ and $CH_3—CH(Br)—CH_3$

U **[CBSE OD 2015]**

Ans.



$CH_3—CH(Br)—CH_3$ **1**

Commonly Made Error

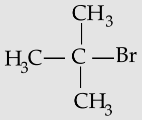
- Students often confuse in reactivity of alkyl halides-primary, secondary, teritary towards S_N1 and S_N2 reactions.

Answering Tip

- Clearly understand the concept of S_N1 reaction.

Q. 3. Write the structure of an isomer of compound C_4H_9Br which is most reactive towards S_N1 reaction. A **[CBSE OD 2016]**

Ans.



$H_3C—C(CH_3)_2—Br$ 2-Bromo-2 methylpropane **1**

[CBSE Marking Scheme, 2016]

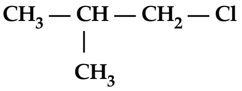
Commonly Made Error

- Students often get confused between S_N1 and S_N2 reaction.

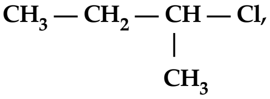
Answering Tip

- Assign proper numbering to carbon atom before drawing the branch chains.

Q. 4. Out of

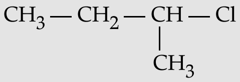


$CH_3 — CH(CH_3) — CH_2 — Cl$ and



$CH_3 — CH_2 — CH(CH_3) — Cl$, which is more reactive towards S_N1 reaction and why? U

Ans.



$CH_3 — CH_2 — CH(CH_3) — Cl$

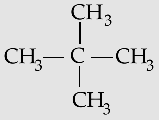
is more reactive as being secondary halide it forms more stable carbocation intermediate than primary halides. **1**

[CBSE Marking Scheme, 2016]

Q. 5. Amongst the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields a single monochloride.

U **[CBSE SQP 2016]**

Ans. Neopentane or 2, 2-Dimethylpropane.



$CH_3—C(CH_3)_2—CH_3$ **1**

AI **Q. 6. Write the structure of 1-Bromo-4-chlorobut-2-ene.** A **[CBSE Delhi Set-1 2017]**

Ans. $BrCH_2CH = CHCH_2Cl$ **1**

[CBSE Marking Scheme, 2017]

Q. 7. Write the structure of 3-Bromo-2-methylprop-1-ene. A **[CBSE Delhi Set-3 2017]**

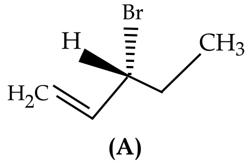
Ans. $BrCH_2(CH_3)C = CH_2$ **1**

[CBSE Marking Scheme, 2017]

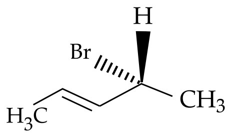
Q. 8. Among the isomers of pentane (C_5H_{12}), write the one which on photochemical chlorination yields a single monochloride. A **[CBSE Foreign Set-1 2017]**

Ans. Neopentane / $C(CH_3)_4$ 1
[CBSE Marking Scheme, 2017]

Q. 9. Identify the compound that on hydrogenation produces an optically active compound from the following compounds:



(A)



(B)

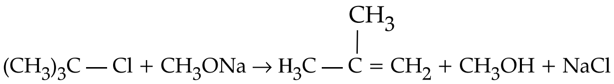
[CBSE SQP 2018-19]

Ans. B. 1
[CBSE Marking Scheme, 2018]

Q. 10. Predict the major product formed when sodium ethoxide reacts with tert. Butyl chloride.
A **[CBSE Comptt. Delhi/O.D. 2018]**

Ans. 2-Methylprop-1-ene/isobutene/ structure 1
[CBSE Marking Scheme, 2018]

Detailed Answer:

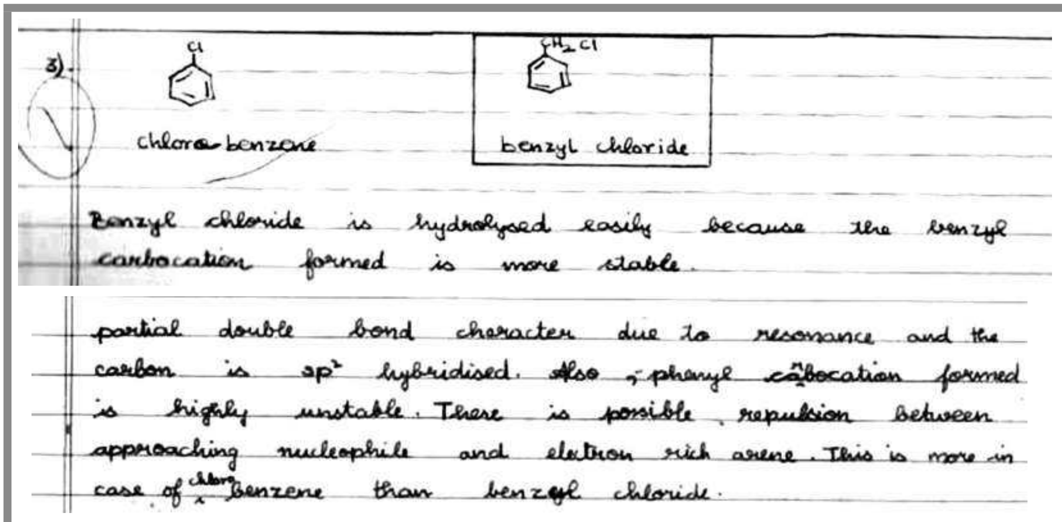


$$(CH_3)_3C-Cl + CH_3ONa \rightarrow H_3C-\overset{\overset{CH_3}{|}}{C}=CH_2 + CH_3OH + NaCl$$

2-Methylprop-1-ene (Isobutene)

Q. 11. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why? A&E **[CBSE Delhi/OD 2018]**

Ans. Benzyl chloride; ½
Due to resonance, stable benzyl carbocation is formed. ½
[CBSE Marking Scheme, 2018]



3).

chloro-benzene

benzyl chloride

Benzyl chloride is hydrolysed easily because the benzyl carbocation formed is more stable.

partial double bond character due to resonance and the carbon is sp² 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]

Detailed Answer:

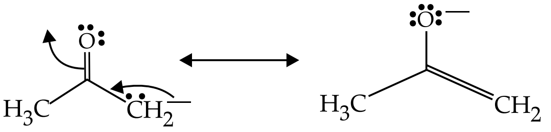
Benzyl chloride gets easily hydrolysed by aqueous NaOH as chlorobenzene possesses partial double bond character in the C−Cl bond. The lone pairs delocalized in the ring strethens C−Cl bond reducing its reactivity. Whereas benzyl chloride undergoes S_N1 reaction to form stable benzyl carbocation.

Q. 12. Define ambident nucleophile with an example.
R **[CBSE Delhi Set-1 2019]**

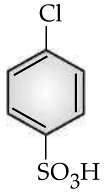
Ans. Nucleophiles having two nucleophilic centres. $CN^-/SCN^-/NO_2^-$(any one) [½ + ½]
[CBSE Marking Scheme, 2019]

Detailed Answer:

An ambident nucleophile is an anionic nucleophile in which the negative charge is delocalized by resonance over two unlike atoms.



Q. 13. Write the IUPAC name of the given compound :



A **[CBSE Delhi Set-2 2019]**

Ans. 4-chlorobenzensulphonic acid 1
[CBSE Marking Scheme, 2019]

Q. 14. Write on the sterochemical difference between S_N1 and S_N2 reactions.
R **[CBSE Delhi Set-3 2019]**

Ans.

S_N1	S_N2
Produces racemic mixture	Proceed with inversion

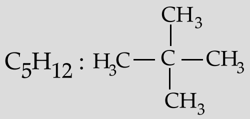
1
[CBSE Marking Scheme, 2019]

Detailed Answer:

An S_N1 reaction proceeds with racemisation and an S_N2 reaction proceeds with complete stereochemical inversion.

Q. 15. A hydrocarbon C_5H_{12} gives only one monochloride on photochemical chlorination. Identify the compound. R **[CBSE Delhi Set 3 2020]**

Ans.



$C_5H_{12} : H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

(All the hydrogen atoms are equivalent and replacement of anyone hydrogen given monohalo derivative.)

Q. 16. Out of $CH_3CH_2CH_2Cl$ and $CH_2 = CH - CH_2 - Cl$, which one is more reactive towards S_N1 reaction? R **[CBSE OD Set 3 2020]**

Ans. $CH_2 = CH - CH_2Cl$ 1

Short Answer Type Questions-I (2 marks each)

Q. 1. 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) CH_3I as I^- ion is better leaving group than Br^- ion. 1

(ii) CH_3Cl as 1° alkyl halides are more reactive than tert-alkyl halides in S_N2 reaction with OH^-. 1

Q. 2. Write the equations for the preparation of 1-bromobutane from :

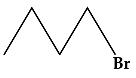
(i) 1-butanol

(ii) but-1-ene A **[CBSE Comptt. Delhi 2016]**

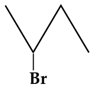
Ans. (i) $CH_3CH_2CH_2CH_2-OH \xrightarrow{HBr} CH_3CH_2CH_2CH_2Br$ 1

(ii) $CH_3CH_2CH = CH_2 \xrightarrow{HBr/Peroxide} CH_3CH_2CH_2CH_2Br$ 1

AI **Q. 3. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction ?**



(a)



(b)

A **[CBSE Comptt. Delhi Set-I, 2 2017]**

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

(a) Inversion of configuration

(b) Racemisation A **[CBSE Delhi 2014]**

Ans. (i) (b) is chiral ½

(a) undergoes faster S_N^2 ½

(ii) (a) S_N2 ½

(b) S_N1 ½

[CBSE Marking Scheme 2014]

Q. 4. (i) Allyl chloride can be distinguished from vinyl chloride by NaOH and silver nitrate test. Comment.

(ii) Alkyl halide reacts with lithium aluminium hydride to give alkane. Name the attacking reagent which will bring out this change.

A&E + R **[CBSE SQP 2017]**

Ans. (i) Vinyl chloride does not respond to NaOH and silver nitrate test because of partial double bond character due to resonance. 1

(ii) Hydride ion / H^- 1

[CBSE Marking Scheme 2017]

Q. 5. Which alkyl halide from the following pair is (i) Chiral and (ii) undergoes S_N1 reaction faster?

(a) $(CH_3)_3CBr$

(b) $CH_3CH_2CHBrCH_3$

A **[CBSE Comptt. Set-2 2017]**

Ans. (i) (b) is chiral. 1

(ii) (a) **[CBSE Marking Scheme 2017]** 1

Q. 6. Which one of the following compounds is more reactive towards S_N2 reaction and why?

$CH_3CH(Cl)CH_2CH_3$ or $CH_3CH_2CH_2Cl$

A&E **[CBSE Comptt. Delhi/OD 2018]**

Ans. $CH_3CH_2CH_2Cl$, due to primary halide which has less steric hindrance. 1+1

[CBSE Marking Scheme 2018]

Detailed Answer:

In S_N2 reaction, attack of nucleophile takes place from backward direction. Primary alkyl halide is the least sterically hindered among primary, secondary and tertiary alkyl halides. While in secondary halides presence of bulky $-CH_3$ group cause steric hindrance for nucleophilic attack. Therefore, primary alkyl halides are more reactive towards S_N2 reaction.

Q. 7. The following haloalkanes are hydrolysed in presence of aq KOH.

(i) 1-Chlorobutane

(ii) 2-chloro-2-methylpropane

Which of the above is most likely to give racemic mixture? Justify your answer.

A&E **[CBSE SQP 2021]**

Ans. Racemic mixture will be given by 2-chloro-2-methylpropane as it is an optically active compound. **[1]**

When 2-chloro-2-methylpropane undergoes S_N1 reaction, both front and rear attack are possible, resulting in a racemic mixture. **[1]**

Short Answer Type Questions-II

(3 marks each)

Q. 1. Give reasons :

(i) C – Cl bond length in chlorobenzene is shorter than C – Cl bond length in $CH_3 – Cl$.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) S_N1 reactions are accompanied by racemization in optically active alkyl halides.

A&E **[CBSE Delhi 2016]**

Ans. (i) In chlorobenzene, each carbon atom is sp^2 hybridised and due to resonance there is a partial double bond character, so bond length is short. **1**

(ii) In chlorobenzene, carbon to which chlorine is attached to sp^2 hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3 hybridised. So the dipole moment is lower in chlorobenzene. In chlorobenzene, –I and +R effect oppose each other while in the other only –I effect is the only contributing factor resulting in lower dipole moment of cyclohexyl chloride. **1**

(iii) In S_N1 reaction, carbocation intermediate formed is a planar molecule which will lead to form *d*- and *l*- products. Hence, racemization occurs. **1**

[CBSE Marking Scheme 2016]

AI **Q. 2. Following compounds are given to you :**

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

(i) Write the compound which is most reactive towards S_N2 reaction.

(ii) Write the compound which is optically active.

(iii) Write the compound which is most reactive towards β-elimination reaction.

U **[CBSE Delhi/OD, Set-1, 2, 3 2017]**

Ans. (i)	1-Bromopentane	1
(ii)	2-Bromopentane	1
(iii)	2-Bromo-2-methylbutane	1

[CBSE Marking Scheme 2017]

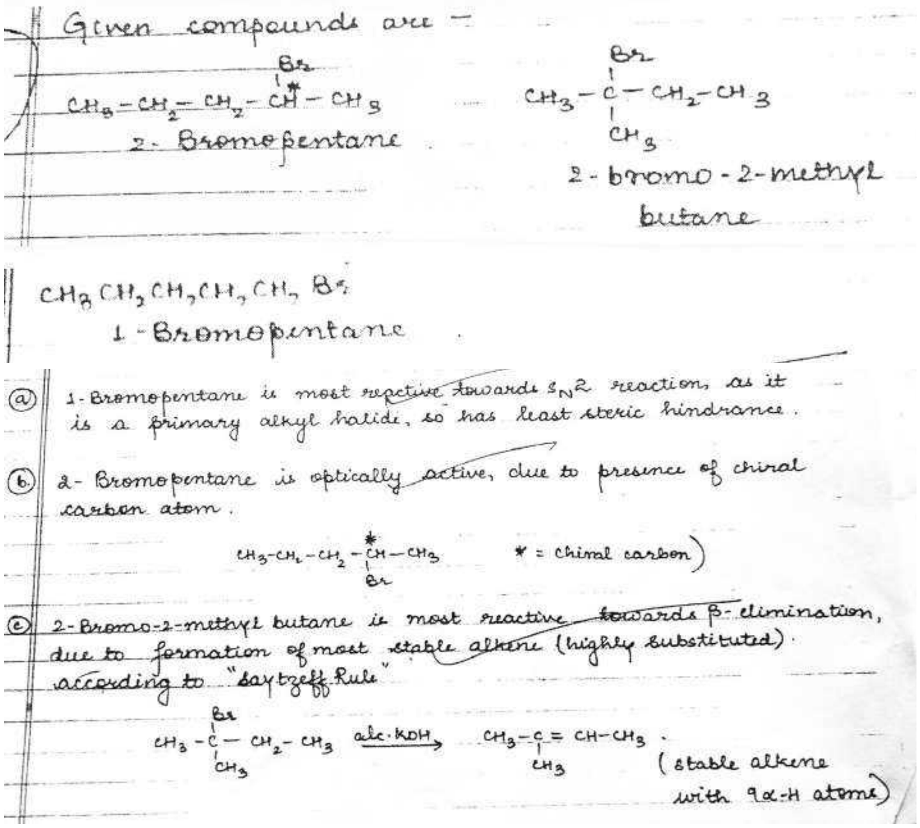
Commonly Made Error

- There is confusion in the order of reactivity of 1°, 2° and 3° towards S_N1, optical activity and elimination reaction.

Answering Tip

- Understand the variation in reactivity of 1°, 2° and 3° haloalkanes.

OR



Given compounds are –

$CH_3-CH_2-CH_2-\overset{Br}{\overset{|}{\overset{*}{C}H}}-CH_3$

2- Bromopentane

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_2-CH_3$

2-bromo-2-methyl butane

$CH_3CH_2CH_2CH_2CH_2Br$

1-Bromopentane

ⓐ 1-Bromopentane is most reactive towards S_N2 reaction, as it is a primary alkyl halide, so has least steric hindrance.

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

$CH_3-CH_2-CH_2-\underset{\underset{Br}{|}}{\overset{*}{C}H}-CH_3$ ($*$ = Chiral carbon)

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

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_2-CH_3 \xrightarrow{alc.KOH} CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$. (stable alkene with 9α-H atoms)

3

[Topper's Answer 2017]

Detailed Answer:

(i) 1-Bromopentane as primary alkyl halides are most reactive towards S_N^2 reaction.

(ii) 2-Bromopentane as it contains asymmetric carbon atom.

(iii) 2-Bromo-2-methylbutane as tertiary alkyl halide is most reactive towards β-elimination reaction.

AI Q. 3. Give the IUPAC name of the product formed when :

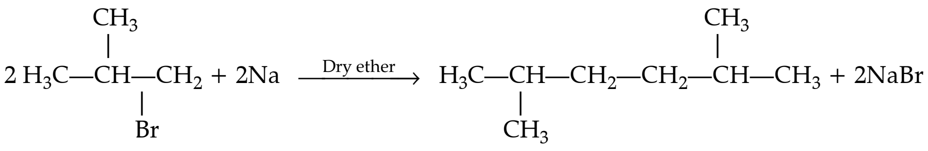
(i) 2-Methyl-1-bromopropane is treated with sodium is the presence of dry ether.
(ii) 1-Methyl cyclohexene is treated with HI.
(iii) Chloroethane is treated with silver nitrite. A **[CBSE SQP 2017]**

Ans. (i) 2,5-Dimethyl hexane.
(ii) 1-Methyl-1-iodocyclohexane
(iii) Nitroethane **1+1+1**

[CBSE Marking Scheme 2017]

Detailed Answer:

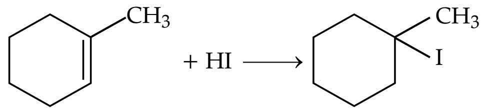
(i)



$$2\,H_3C-\overset{\displaystyle CH_3}{\overset{|}{C}H}-\underset{\underset{\displaystyle Br}{|}}{CH_2}+2Na\xrightarrow{\text{Dry ether}}H_3C-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3+2NaBr$$

2-Methyl-1-bromopropane 2,5-Dimethyl hexane

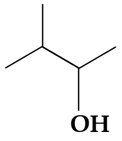
(ii)



1-Methyl cyclohexene 1-Methyl-1-iodocyclohexane

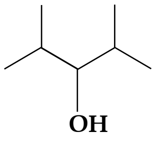
(iii) $C_2H_5Cl + AgNO_2 \longrightarrow C_2H_5NO_2 + AgCl$

Q. 4. (a) Identify the chiral molecule in the following pair :



(i)

&

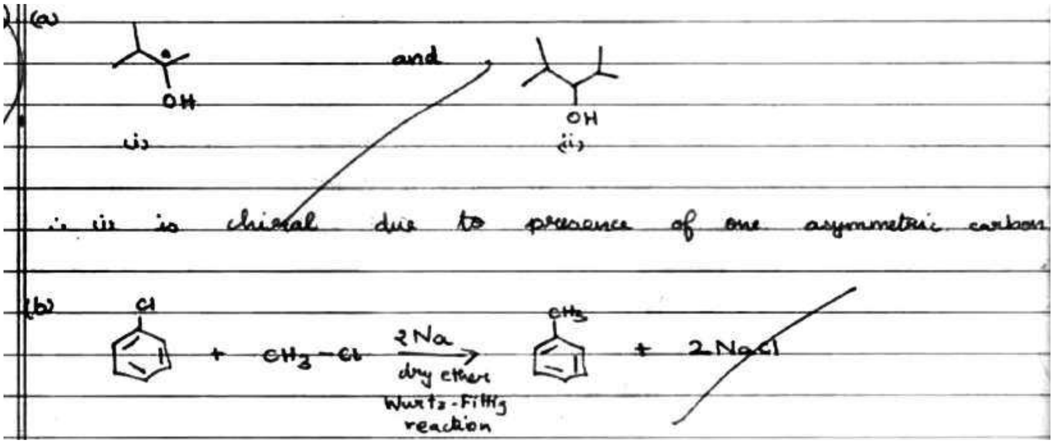


(ii)

(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH. A **[CBSE D/OD 2018]**

Ans.



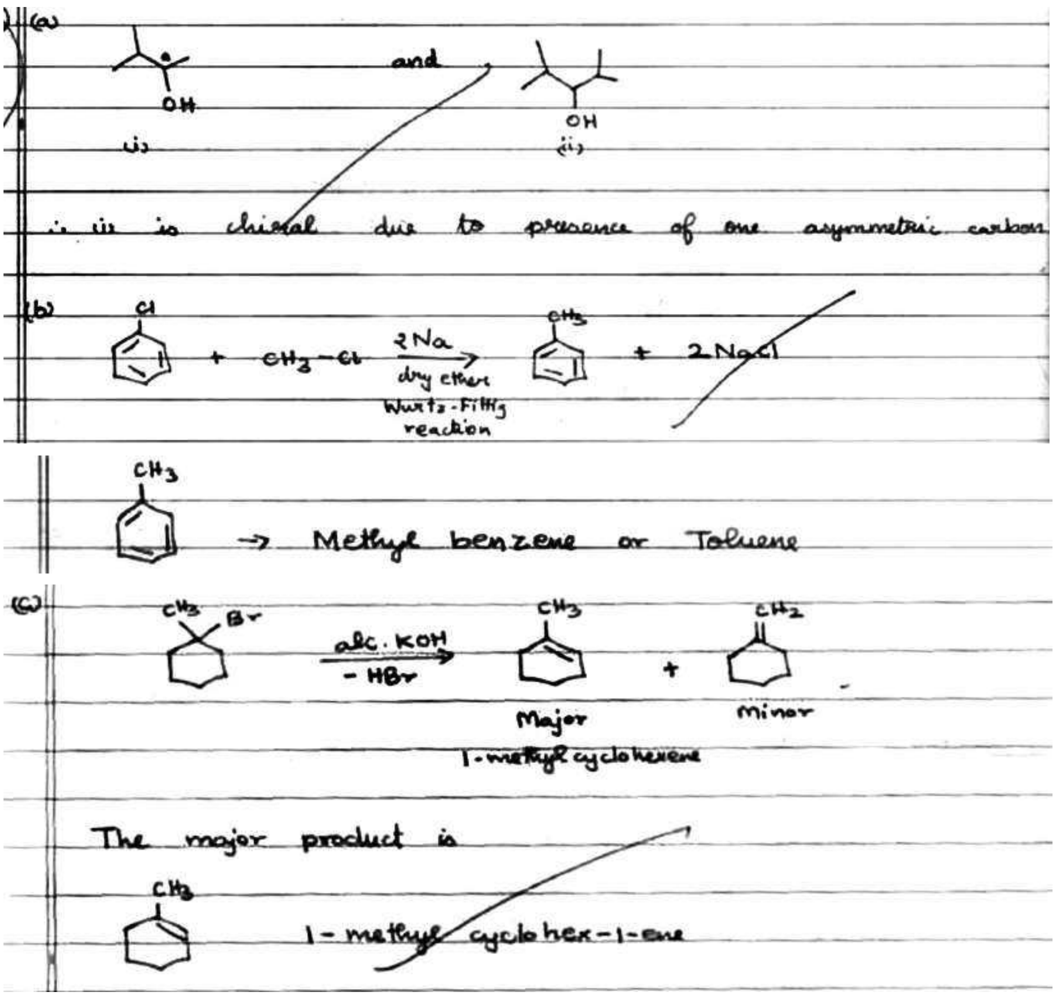
(a) OH (i) and OH (ii)

∴ (ii) is chiral due to presence of one asymmetric carbon

(b) Cl + CH₃—Cl $\xrightarrow[\text{dry ether}]{2Na}$ CH₃ + 2NaCl

Wurtz-Fittig reaction

Ans.



(a) and

OH

i)

OH

ii)

∴ i) is chiral due to presence of one asymmetric carbon

(b) Cl + CH₃–Cl $\xrightarrow[\text{dry ether}]{2Na}$ CH₃ + 2NaCl

Wurtz-Fittig reaction

CH₃ → Methyl benzene or Toluene

(c) CH₃ Br $\xrightarrow[-HBr]{alc. KOH}$ CH₃ + CH₂

Major

1-methyl cyclohexene

Minor

The major product is

CH₃ 1-methyl cyclohex-1-ene

[Topper's Answer 2018]

AI Q. 5. Among all the isomers of molecular formula C_4H_9Br, identify

(a) the one isomer which is optically active.
(b) the one isomer which is highly reactive towards S_N2.
(c) the two isomers which give same product on dehydrohalogenation with alcoholic KOH.

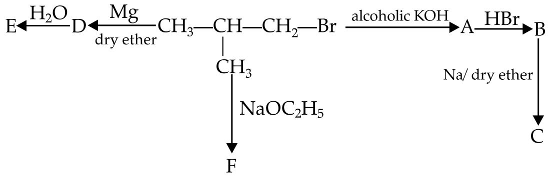
A&E [CBSE OD Set-2 2019]

Ans. (i)	$CH_3CH_2CH(Br)CH_3$	1
(ii)	$CH_3CH_2CH_2CH_2Br$	1
(iii)	$(CH_3)_3CBr$ and $(CH_3)_2CHCH_2Br$	
	[CBSE Marking Scheme, 2019]	½ + ½

IUPAC-Name:

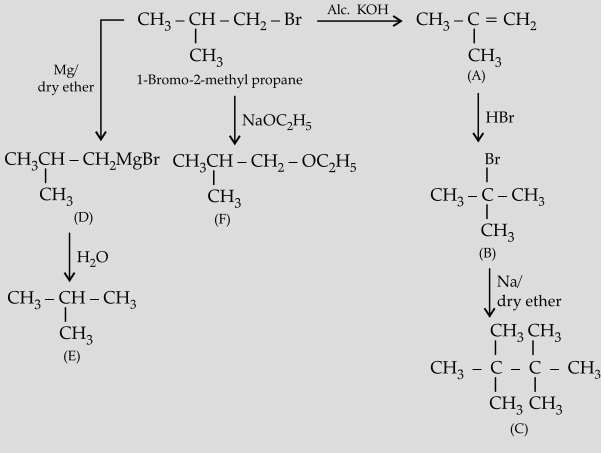
- **(i)** 2–Bromobutane
- **(ii)** 1– Bromobutane
- **(iii)** 2–Bromo–2–methylpropane and 1–Bromo–2–methylpropane.

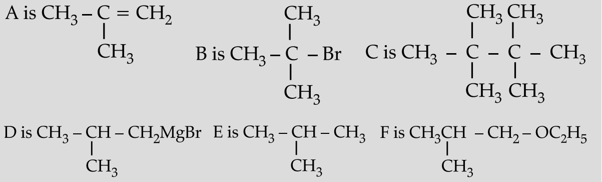
AI Q. 6. Identify A, B, C, D, E and F in the following :



A&E [CBSE Delhi Set 1 2020]

Ans.





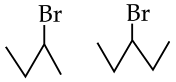
A is $CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$ B is $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$ C is $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

D is $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2MgBr$ E is $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$ F is $CH_3\underset{\underset{CH_3}{|}}{CH}-CH_2-OC_2H_5$

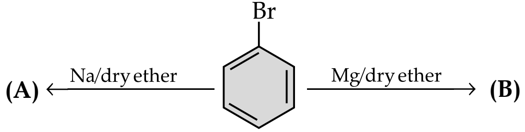
[½ × 6 =3]

Q. 7. **(i) Write the structure of major alkene formed by β-elimination of 2, 2, 3-trimethyl-3-bromopentane with sodium ethoxide in ethanol.**

(ii) Which one of the compounds in the following pairs in chiral?

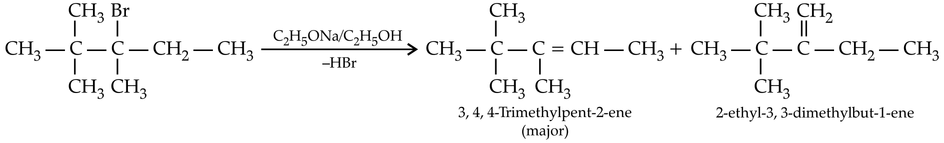


(iii) Identify (A) and (B) in the following:



A&E **[CBSE OD Set 1 2020]**

Ans. (i)

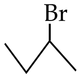


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3 \xrightarrow[-HBr]{C_2H_5ONa/C_2H_5OH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{C}=CH-CH_3 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{CH_2}{\overset{\|}{C}}-CH_2-CH_3$$

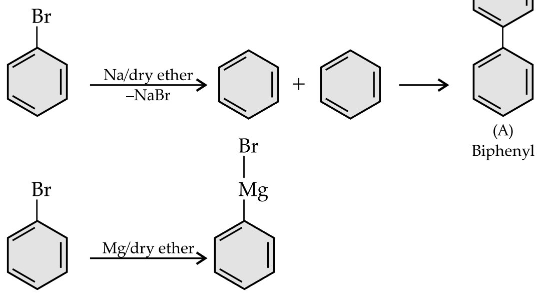
3, 4, 4-Trimethylpent-2-ene (major)

2-ethyl-3, 3-dimethylbut-1-ene

(ii)



(iii)



(A)
Biphenyl

(B)
Phenyl magnesium bromide

[1 +1 +1 = 3]

Q. 8. **How can you convert the following?**

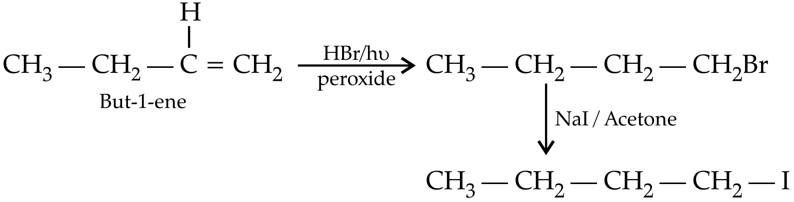
(i) But-1-ene to 1-iodobutane

(ii) Benzene to acetophenone

(iii) Ethanol to propanenitrile

A&E **[CBSE OD Set 1 2020]**

Ans. (i)



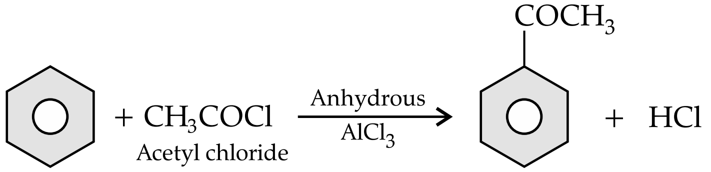
$$\underset{\text{But-1-ene}}{CH_3-CH_2-\overset{H}{\overset{|}{C}}=CH_2} \xrightarrow[peroxide]{HBr/h\upsilon} CH_3-CH_2-CH_2-CH_2Br$$

$$\downarrow \text{NaI / Acetone}$$

$$CH_3-CH_2-CH_2-CH_2-I$$

1-iodobutane

(ii)



Acetyl chloride

Acetophenone

(iii) $C_2H_5OH \xrightarrow{RedP/Br_2} CH_3-CH_2-Br \xrightarrow[\text{Aq. ethanol}]{KCN} \underset{\text{Propanenitrile}}{CH_3CH_2CN}$

[1 +1 +1 = 3]

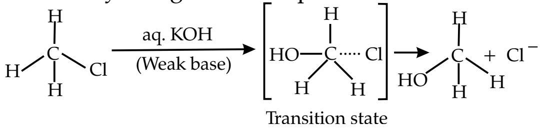
Long Answer Type Questions

(5 marks each)

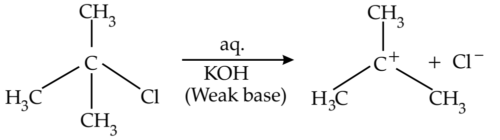
Q. 1. **Some alkyl halides undergo substitution reactions whereas some undergo elimination reactions on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.**

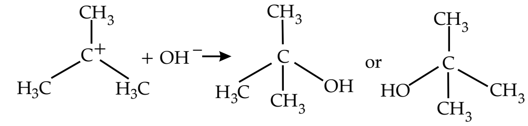
C **[NCERT Exemp. Q. 95, Page 149]**

Ans. Primary alkyl halides prefer to undergo substitution reactions by S_N2 mechanism. A transition state is formed in which carbon is bonded to nucleophile and finally halogen atom is pushed out.

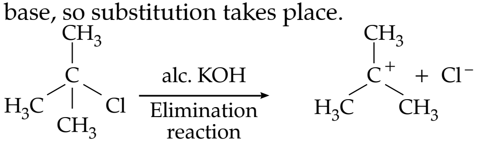


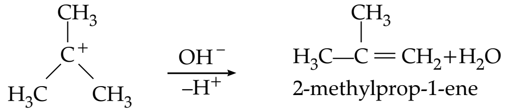
tert-n-butyl halides prefer to undergo elimination reactions due to the formation of stable carbocations. 3^o alkyl halides follow S_N1 mechanism by forming tertiary carbocations. Now, if the reagent used is a weak base then substitution occurs while if it is a strong base then instead of substitution, elimination occurs.





Here the reagent used *i.e.*, aq. KOH It is a weak base, so substitution takes place.





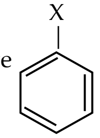
Here the reagent used *i.e.*, alc. KOH is a strong base, so elimination competes over substitution and alkene is formed.

Secondary alkyl halide can undergo substitution or elimination depending on type of solvent and temperature conditions. 5

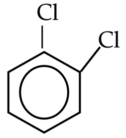
TOPIC-2

Haloarenes and Polyhalogen Compounds

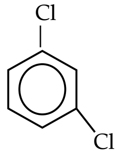
Revision Notes

- **Haloarenes :** Haloarenes are the compounds formed by replacing one or more hydrogen atoms in an aromatic ring with halogen atoms. For example, monohalogen derivative  (X = F, Cl, Br, or I).

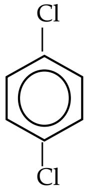
- When two halogens are at 1, 2- positions of benzene ring, it is called ortho substituted derivative. *e.g.*,



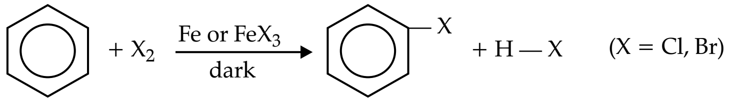
- When two halogens are at 1, 3- positions of benzene ring, it is called meta substituted derivative. *e.g.*,

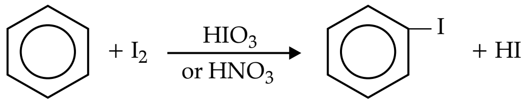


- When two halogens are at 1, 4- positions of benzene ring, it is called para substituted derivative. *e.g.*,



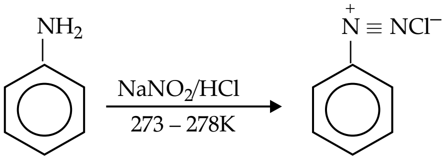
- **Methods of preparation of Haloarenes : (i) Reacting benzene directly with halogen :**



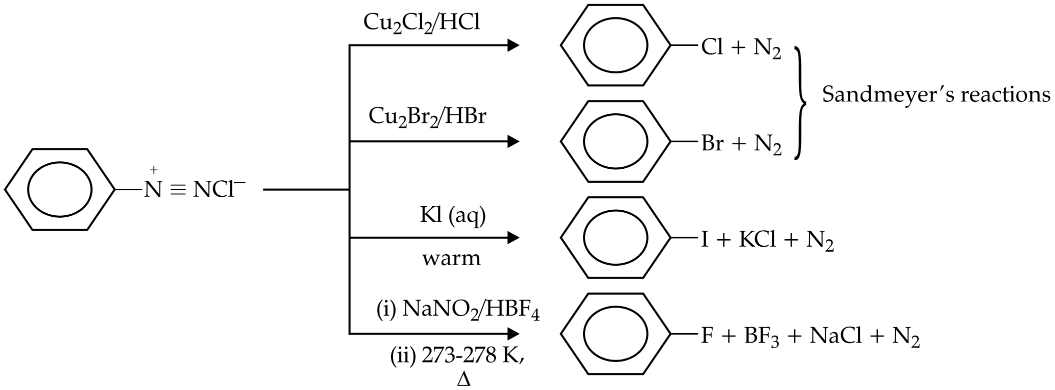


Iodobenzene

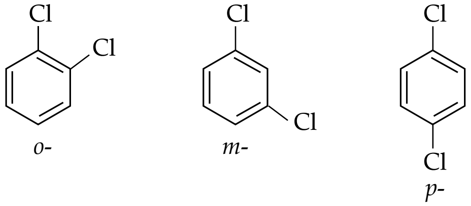
(ii) Starting with diazonium salts :



Benzene diazonium chloride



- **Physical properties of Haloarenes :** Isomeric haloarenes have similar boiling points. But *para* isomer has higher melting point than other two *i.e.*, ortho and meta because of the symmetry in *para* isomer which occupies the crystal lattice better than *ortho* and *meta* isomers.

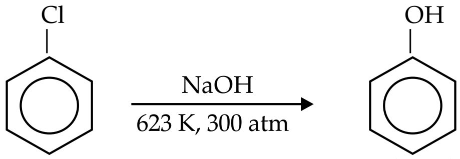


	o-	*m-*	*p-*
b.p. (K)	453	446	448
m.p. (K)	256	249	323

- **Chemical properties of Haloarenes :**

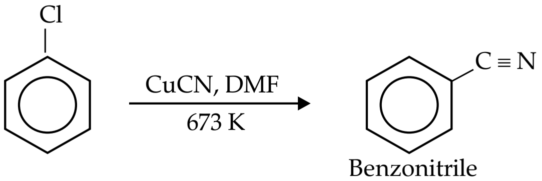
  (a) Nucleophilic substitution reactions are very less possible with haloarenes as C—X bond attains partial double bond character because of resonance effect, difference in hybridization, instability of the formed phenyl cation. Due to these repulsions, it makes difficult for electron rich nucleophile to attack electron rich haloarenes. Under higher temperatures, some of the below mentioned nucleophilic reactions are possible.

  (i) Substitution by —OH group (Dow's process) :

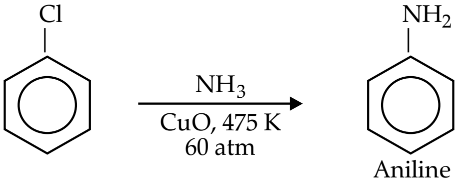


Chlorobenzene   Phenol

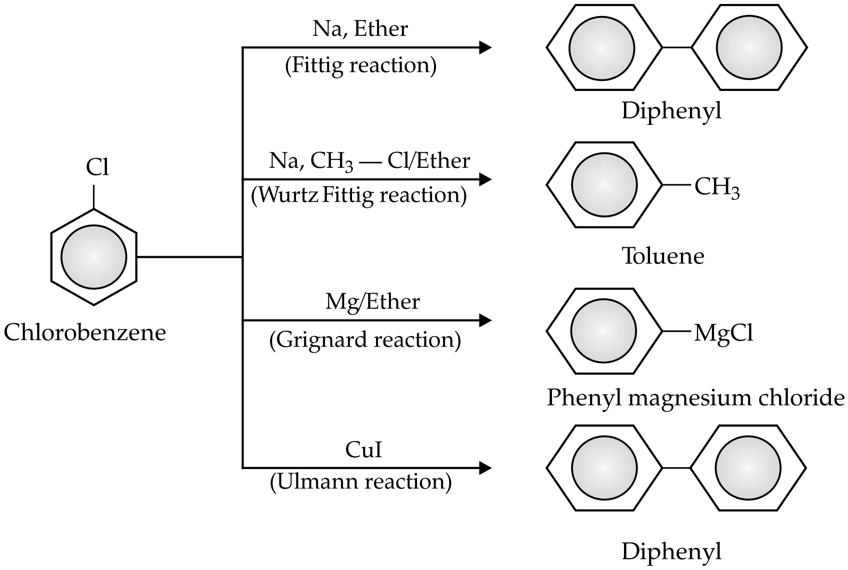
(ii) Substitution by —CN group :



(iii) Substitution by —NH_2 group :

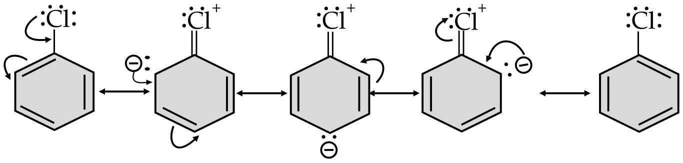


(iv) Reaction with metals :



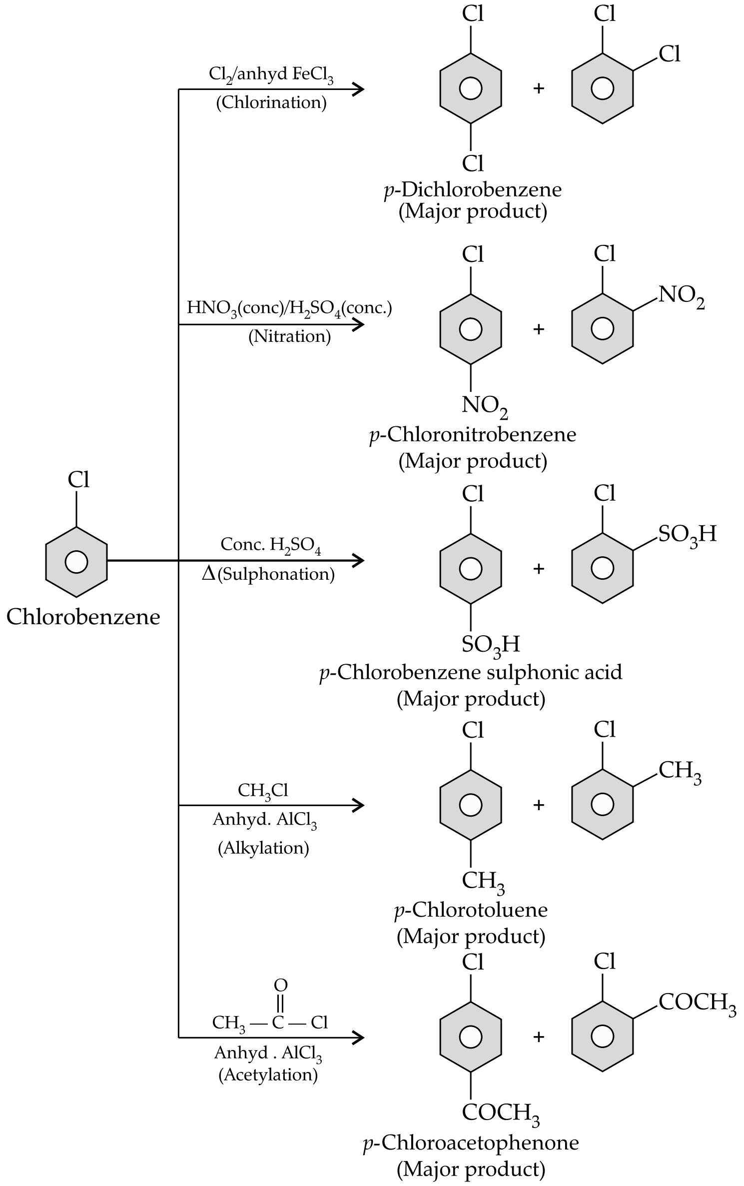
- **Nature of C—X bond in haloarene** : The C—X bond of aryl halide is less reactive than that of haloalkanes. One reason is that in aryl halide, halogen atom is attached to sp^2-hybrid carbon atom whereas in alkyl halides, it is attached to sp^3-hybrid carbon atom. Due to more electronegativity of sp^2-hybrid carbon in comparison to sp^3-carbon atom, there is less charge in separation of C—X bond in haloarene.

  Secondly in aryl halides like chlorobenzene, the lone pair of electrons present on chlorine atom migrate towards the aromatic ring by +R effect due to conjugation of lone pair of electrons with π-electrons of the aromatic ring. As a result of which, the halogen atom is attached with the aromatic ring by partial double bond. The phenyl cation formed is highly unstable. The replacement of such a halogen atom by other nucleophiles becomes difficult.



(v) Electrophilic substitution reactions of haloarenes :

It takes place at ortho and para positions :



- **Polyhalogen compounds :** Carbon compounds containing more than one halogen atoms are usually referred to as polyhalogen compounds. Many of those compounds are useful in industry and agriculture.

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

$$CH_4 + 2Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + 2HCl$$

The mixture so obtained is separated by fractional distillation.

(ii) Chloroform : It is manufactured by chlorination of methane followed by separation by fractional distillation.

$$CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{h\nu} CHCl_3 + 3HCl.$$

(iii) Iodoform (Triiodomethane) : It is prepared by heating ethanol or acetone with sodium hydroxide and iodine or Na_2CO_3 and I_2 in water. It is insoluble in water, yellow precipitate of CHI_3 is formed. This reaction is called iodoform reaction.

$$CH_3CH_2OH + 6NaOH + 4I_2 \xrightarrow{\text{heat}} CHI_3 + 5NaI + HCOONa + 5H_2O$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{\text{heat}} CHI_3 + 3NaI + CH_3COONa + 3H_2O$$

(iv) Carbon tetrachloride (Tetrachloromethane) : It is prepared by chlorination of methane or by action of chlorine on CS_2 in the presence of $AlCl_3$ as catalyst.

$$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + SCl_2$$

(Sulphur dichloride)

$$CH_4 + 4Cl_2 \xrightarrow{h\nu} CCl_4 + 4HCl$$

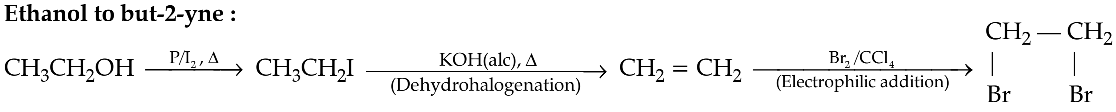
- **Some Important Conversions :**

(i) Propene to propan-1-ol :

$$CH_3CH = CH_2 \xrightarrow[\text{(Anti-Markvonikov, addtion)}]{\text{HBr/peroxide}} CH_3CH_2CH_2Br \xrightarrow[\text{(Hydrolysis)}]{\text{aq. KOH, }\Delta} CH_3CH_2CH_2OH$$

Propene 1-Bromopropane Propan-1-ol

(ii) Ethanol to but-2-yne :



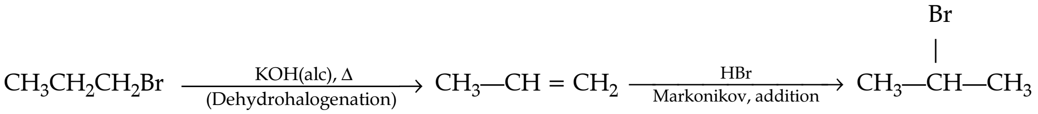
$$CH_3CH_2OH \xrightarrow{P/I_2,\,\Delta} CH_3CH_2I \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}, \Delta} CH_2 = CH_2 \xrightarrow[\text{(Electrophilic addition)}]{Br_2/CCl_4} \underset{Br}{\underset{|}{CH_2}} — \underset{Br}{\underset{|}{CH_2}}$$

Ethanol Iodoethane Ethene

$$\xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}, \Delta} HC{\equiv}CH \xrightarrow[196K]{NaNH_2,\text{liq.}NH_3} Na—C{\equiv}C—Na \xrightarrow[\text{(Nucleophilic substitution)}]{CH_3I\text{(excess)}} CH_3—C{\equiv}C—CH_3$$

But-2-yne

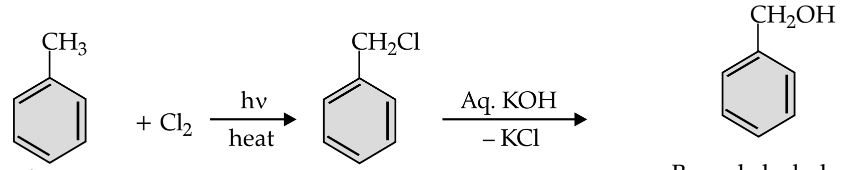
(iii) 1-Bromopropane to 2-bromopropane :



$$CH_3CH_2CH_2Br \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}, \Delta} CH_3—CH = CH_2 \xrightarrow[\text{Markonikov, addition}]{HBr} CH_3—\overset{Br}{\overset{|}{CH}}—CH_3$$

1–Bromopropane 1-Propene 2–Bromopropane

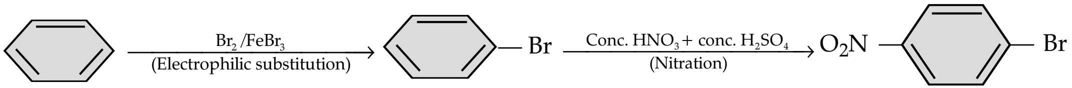
(iv) Toluene to benzyl alcohol :



Toluene

Benzyl alcohol

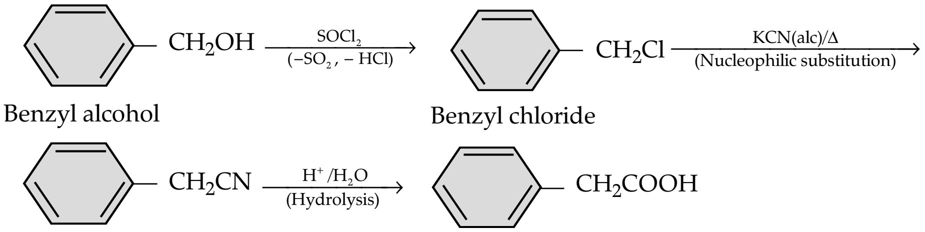
(v) Benzene to 4-bromonitrobenzene :



Benzene

4-Bromonitrobenzene

(vi) Benzyl alcohol to 2-phenylethanoic acid :



Benzyl alcohol

Benzyl chloride

Benzyl cyanide

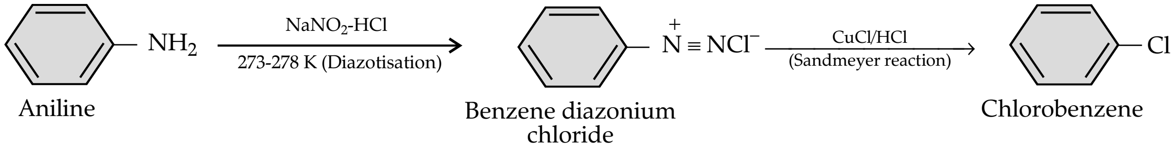
2-Phenylethanoic acid

(vii) Ethanol to propanenitrile :

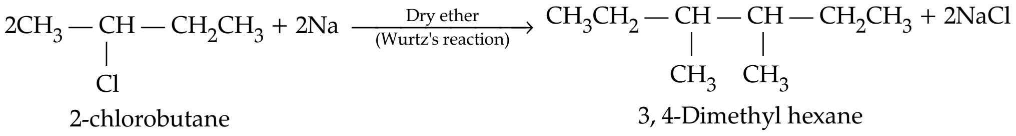
$$CH_3CH_2OH \xrightarrow{P/I_2,\,\Delta} CH_3CH_2I \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KCN (alc)}/\Delta} CH_3CH_2CN$$

Ethanol 1-Iodoethane Propanenitrile

(viii) Aniline to chlorobenzene :



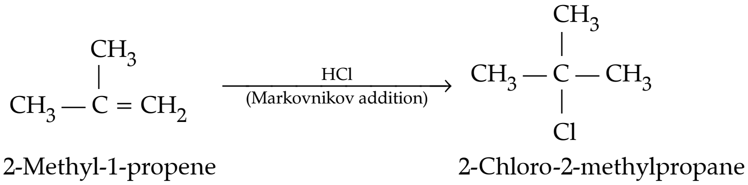
(ix) 2-Chlorobutane to 3, 4-dimethyl hexane :



$$2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2CH_3 + 2Na \xrightarrow[\text{(Wurtz's reaction)}]{\text{Dry ether}} CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3 + 2NaCl$$

2-chlorobutane — 3, 4-Dimethyl hexane

(x) 2-Methyl-1-propene to 2-chloro-2-methyl propane :



$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{(Markovnikov addition)}]{\text{HCl}} CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2-Methyl-1-propene — 2-Chloro-2-methylpropane

(xi) Ethyl chloride to propanoic acid :

$$CH_3CH_2Cl \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KCN (alc)}/\Delta} CH_3CH_2CN \xrightarrow[\text{(Hydrolysis)}]{H^+/H_2O} CH_3CH_2COOH$$

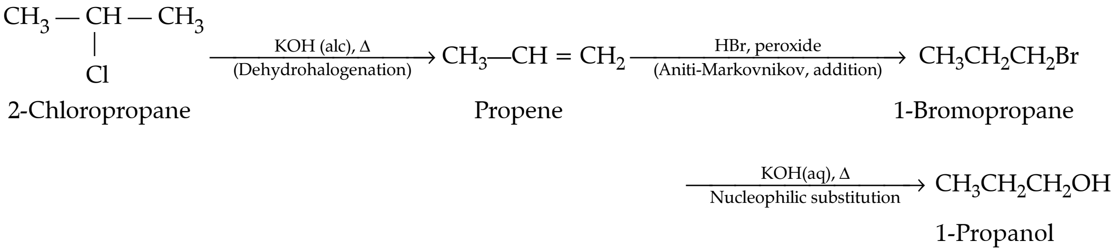
Ethyl chloride — Ethyl cyanide — Propanoic acid

(xii) But-1-ene to *n*-butyl iodide :

$$CH_3CH_2CH=CH_2 \xrightarrow[\text{(Anti-Markovnikov addition)}]{\text{HBr/peroxide}} CH_3CH_2CH_2CH_2Br \xrightarrow[\text{(Finkelstein reaction)}]{\text{NaI, acetone}} CH_3CH_2CH_2CH_2I$$

But-1-ene — 1-Bromobutane — *n*-Butyl iodide

(xiii) 2-Chloropropane to 1-propanol :



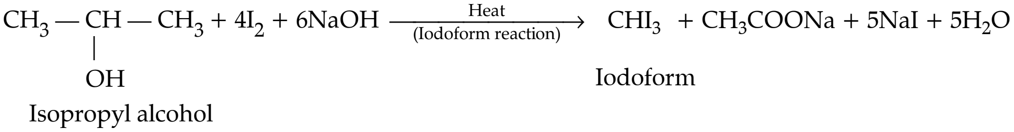
$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc)}, \Delta} CH_3-CH=CH_2 \xrightarrow[\text{(Aniti-Markovnikov, addition)}]{\text{HBr, peroxide}} CH_3CH_2CH_2Br$$

2-Chloropropane — Propene — 1-Bromopropane

$$\xrightarrow[\text{Nucleophilic substitution}]{\text{KOH(aq)}, \Delta} CH_3CH_2CH_2OH$$

1-Propanol

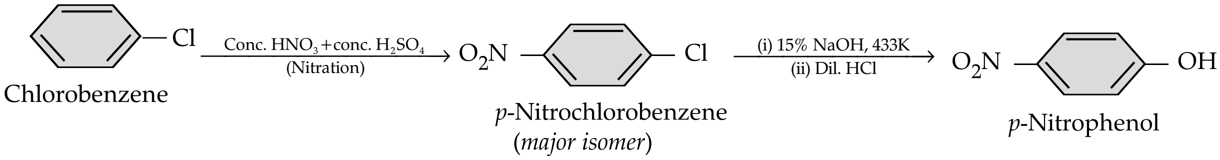
(xiv) Isopropyl alcohol to iodoform :



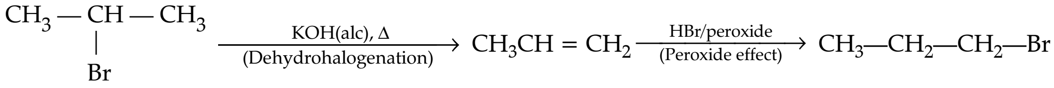
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + 4I_2 + 6NaOH \xrightarrow[\text{(Iodoform reaction)}]{\text{Heat}} CHI_3 + CH_3COONa + 5NaI + 5H_2O$$

Isopropyl alcohol — Iodoform

(xv) Chlorobenzene to *p*-nitrophenol :



(xvi) 2-Bromopropane to 1-bromopropane :



$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}, \Delta} CH_3CH=CH_2 \xrightarrow[\text{(Peroxide effect)}]{\text{HBr/peroxide}} CH_3-CH_2-CH_2-Br$$

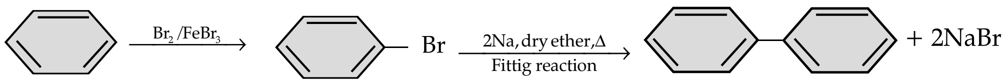
2-Bromopropane Propene 1-Bromopropane

(xvii) Chloroethane to butane :

$$2CH_3CH_2-Cl + 2Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}, \Delta} CH_3CH_2-CH_2CH_3 + 2NaCl$$

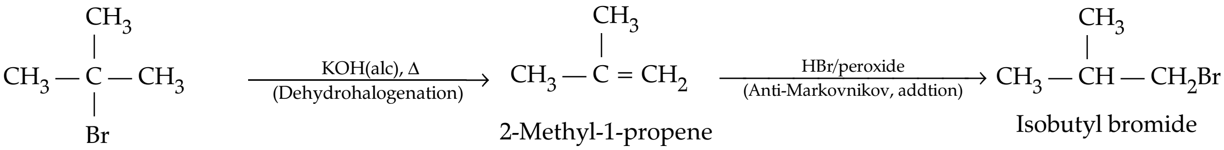
Chloroethane Butane

(xviii) Benzene to diphenyl :



Benzene Bromobenzene Diphenyl

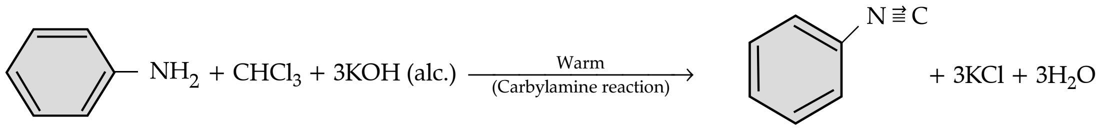
(xix) *tert*-Butyl bromide to iso-butyl bromide :



$$CH_3-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}, \Delta} CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[\text{(Anti-Markovnikov, addtion)}]{\text{HBr/peroxide}} CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2Br$$

tert-Butyl bromide 2-Methyl-1-propene Isobutyl bromide

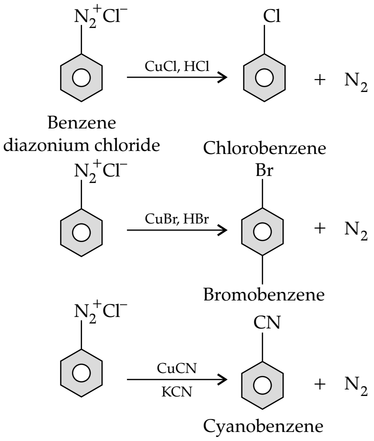
(xx) Aniline to phenyl isocyanide :



Aniline Phenyl isocyanide

- **Important Name Reactions :**

(i) Sandmeyer's Reaction :



(ii) Finkelstein Reaction :

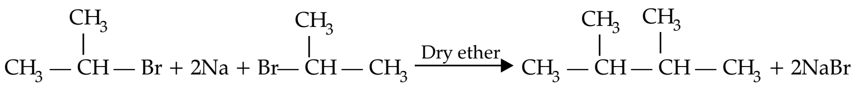
$$CH_3CH_2Cl + NaI \xrightarrow{\text{Dry acetone}} CH_3CH_2I + NaCl$$

Ethyl iodide

(iii) Wurtz Reaction :

$$CH_3Br + 2Na + BrCH_3 \xrightarrow{\text{Dry ether}} CH_3CH_3 + 2NaBr$$

Ethane

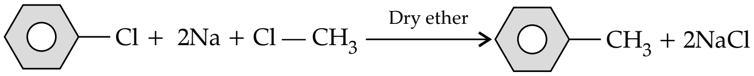


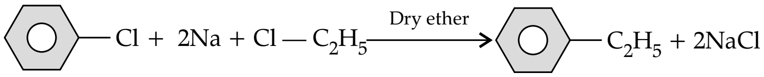
$$CH_3-\overset{\overset{CH_3}{|}}{C}H-Br + 2Na + Br-\overset{\overset{CH_3}{|}}{C}H-CH_3 \xrightarrow{\text{Dry ether}} CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CH_3 + 2NaBr$$

Isopropyl bromide

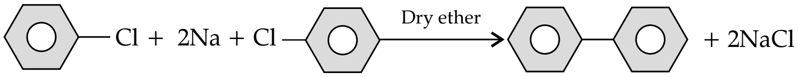
2, 3-Dimethyl butane

(iv) Wurtz-Fittig Reaction :

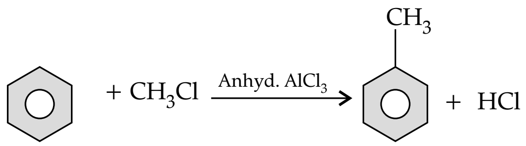




(v) Fittig's Reaction :

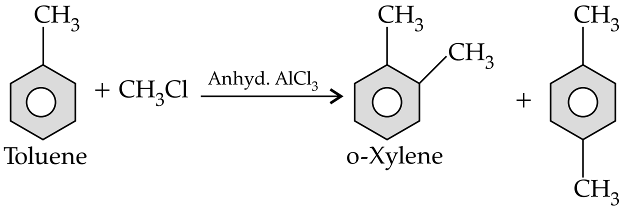


(vi) Friedel-Crafts Alkylation :



Benzene

Toluene

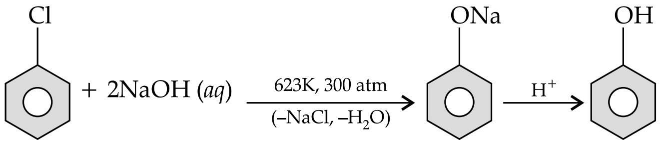


Toluene

o-Xylene

p-Xylene

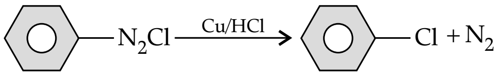
(vii) Dow's Process :



(viii) Hunsdiecker's Reaction :

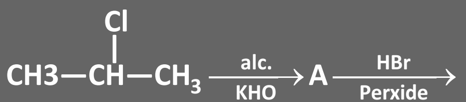
$$R-COOAg + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} R-Br + AgBr + CO_2$$

(ix) Gattermann's Reaction :



How is it done on the GREENBOARD?

Q. (i) Write the structural formula of A, B, C and D in the following sequence of reaction :



$$CH3-\underset{}{\overset{Cl}{CH}}-CH_3 \xrightarrow[KHO]{alc.} A \xrightarrow[Perxide]{HBr}$$

$$B \xrightarrow[\text{dry ether}]{NaI} C \xrightarrow[\text{dry ether}]{Mg} D$$

(ii) Illustrate Sandmeyer's reaction with the help of a suitable example.

Solution

STEP-1: (i) A: $CH_3-CH=CH_2$

STEP-2: B: $CH_3-CH_2-CH_2Br$

STEP-3: C: $CH_3-CH_2-CH_2I$

STEP-4: D: $CH_3-CH_2-CH_2MgI$

(ii)

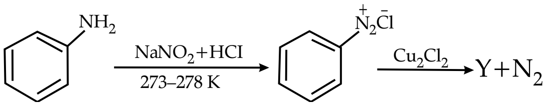
Aryl halide
X = Cl, Br, CN

Objective Type Questions

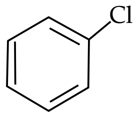
(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

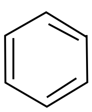
Q. 1. Identify the compound Y in the following reaction.



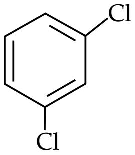
(a)



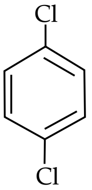
(b)



(c)



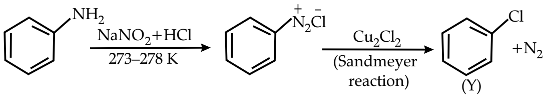
(d)



R **[NCERT Exemp. Q. 3, Page 134]**

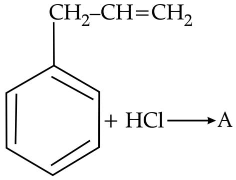
Ans. Correct option : (a)

Explanation : When a primary aromatic amine is dissolved or suspended in cold aqueous mineral acid and treated with sodium nitrite, a diazonium salt is formed. When this freshly prepared diazonium salt is mixed with cuprous chloride, diazonium group is replaced by Cl. Then, chlorobenzene is formed which is Y in this reaction.

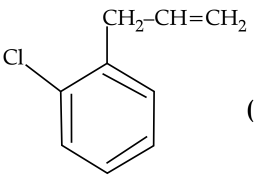


[1]

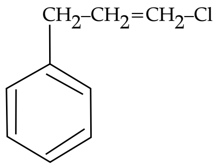
Q. 2. What is 'A' in the following reaction?



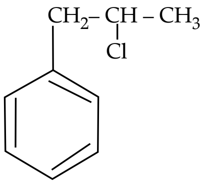
(a)



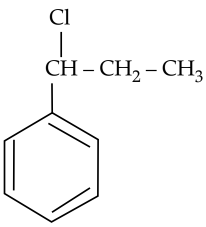
(b)



(c)



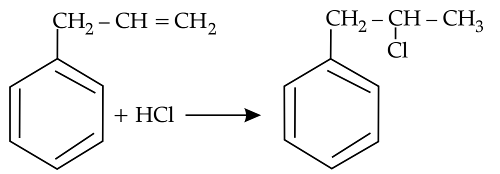
(d)



R **[NCERT Exemp. Q. 15, Page 136]**

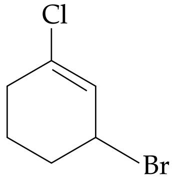
Ans. Correct option : (c)

Explanation : In this reaction, addition of HCl takes place on doubly bonded carbons in accordance with Markovnikov's rule, that is, addition of negative addendum will take place on that carbon which has lesser number of hydrogen.



[1]

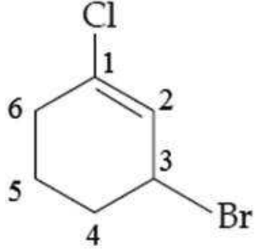
Q. 3. The IUPAC name of the compound shown below is:



(a) 2-bromo-6-chlorocyclohex-1-ene
(b) 6-bromo-2-chlorocyclohexene
(c) 3-bromo-1-chlorocyclohexene
(d) 1-bromo-3-chlorocyclohexene [CBSE SQP 2020]

Ans. Correct option : (c)

Explanation :



IUPAC name: 3-bromo-1-chlorocyclohexene

[B] ASSERTION & REASONS:

In the following questions a statement of assertion followed by a statement of reasin is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion
(c) Assertion is correct statement but reason is wrong statement
(d) Assertion is wrong statement but reason is correct statement

Q. 1. Assertion (A): Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.

Reason (R) : Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring. R **[NCERT Exemplar]**

Ans. Correct option: (a)

Explanation: Nitro group being an electron withdrawing group, decreases the electron density of benzene ring thus increasing the reactivity of haloarenes towards nucleophilic substitution. **[1]**

Q. 2. Assertion (A) : In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.

Reason (R) : Halogen atom is a ring deactivator.

R **[NCERT Exemplar]**

Ans. Correct option: (b)

Explanation : Halogens are ortho-para directing due to (+M) or (+R) effect. Moreover, they are deactivating due to high electronegativity. **[1]**

Q. 3. Assertion (A) : It is difficult to replace chlorine by –OH in chlorobenzene in comparison to that in chloroethane.

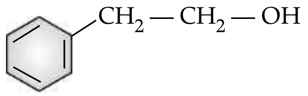
Reason (R) : Carbon-chlorine (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance. U **[NCERT Exemplar]**

Ans. Correct option: (a)

Explanation : Chlorobenzene is very less reactive to nucleophilic substitution reaction by –OH group as Carbon-chlorine (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance. **[1]**

[C] VERY SHORT ANSWER TYPE QUESTIONS :

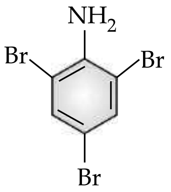
AI Q. 1. Write the IUPAC name of the given compound.



A **[CBSE OD 2016]**

Ans. 2–phenylethanol. **1**
[CBSE Marking Scheme 2016]

Q. 2. Write the IUPAC name of the given compound.



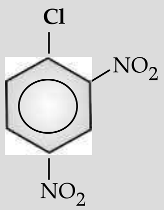
A **[CBSE Delhi 2016]**

Ans. 2, 4, 6-Tribromoaniline/2,4,6-Tribromobenzenenamine. **1**
[CBSE Marking Scheme 2016]

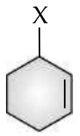
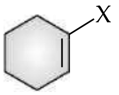
Q. 3. Write the structure of 2,4-dinitrochlorobenzene.

U **[CBSE Delhi Set-2 2017]**

Ans.



1
[CBSE Marking Scheme 2017]

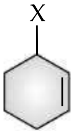
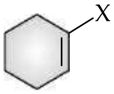
Q. 4. Out of  and  **which is an example of allylic halide?**

U **[CBSE OD Set-1 2017]**

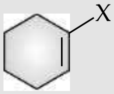
Ans. 

1

[CBSE Marking Scheme 2017]

Q. 5. Out of  **and**  **which is an example of vinylic halide?**

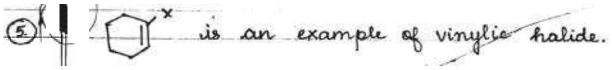
U **[CBSE OD Set-2 2017]**

Ans. 

1

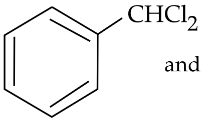
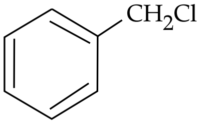
[CBSE Marking Scheme 2017]

OR



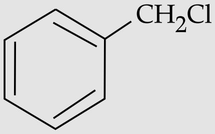
⑤ is an example of vinylic halide.

[Topper's Answer 2017]

Q. 6. Out of  and 

which is an example of benzylic halide?

A **[CBSE OD Set-3 2017]**

Ans. 

1

[CBSE Marking Scheme 2017]

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

R **[CBSE OD Set-1 2019]**

Ans. Cyclohexyl chloride; Because of partial double bond character od C−Cl bond in Chlorobenzene /Resonance effect / sp^3 hybridized carbon in cyclohexyl chloride whereas sp^2 carbon in chlorobenzene. 1

[CBSE Marking Scheme 2019]

Detailed Answer:

Cyclohexyl chloride is more reactive towards nucleophilic substitution reaction because in cyclohexyl chloride chlorine atom is attached to sp^3 hybridized while in chlorobenze it is sp^2 hybridized. Thus it has higher tendency to release electrons. In chlorobenzene, due to resonance, cleavage of C-Cl bond is difficult than cyclohexyl chloride which makes it less reactive towards nucleophilic substitution.

Q. 8. Out of Chlorobenzene and p-nitrochlorobenzene, which one is more reactive towards nucleophilic substitution reaction and why?

R **[CBSE OD Set-2 2019]**

Ans. *p*-Nitrochlorobenzene; Due to electron withdrawing nature of $-NO_2$ group. ½ + ½

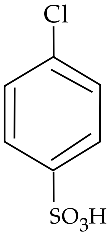
[CBSE Marking Scheme 2019]

Detailed Answer:

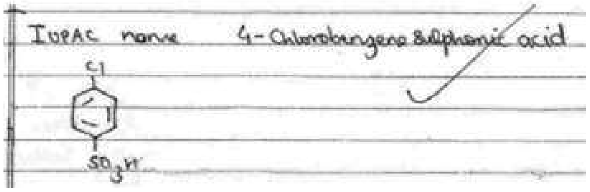
The relative p-nitrochlorobenzene is more reactive towards nucleophilic substation reaction due to its electron –withdrawing inductive and resonance effects which resultd in the stabilized carbanion formed by the $-NH_2$ group.

Q. 9. Write the IUPAC name of the given compound :

A **[CBSE Delhi Set 1 2019]**

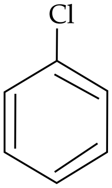
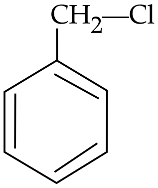


Ans.



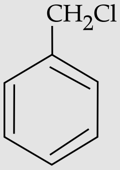
IUPAC name 4-Chlorobenzene sulphonic acid

[Topper's Answer 2019]

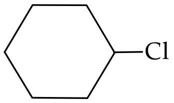
Q. 10. Out of  **and**  **which will undergo S_N1 reaction faster with OH^-?**

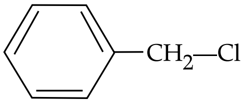
A&E **[CBSE Delhi Set 2 2020]**

Ans.



because conjunction between positive charge and double bond, resonance is possible.

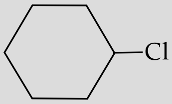
Q. 11. Out of 

and 

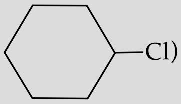
which one is more reactive towards S_N1 reaction?

A&E **[CBSE OD Set 1 2020]**

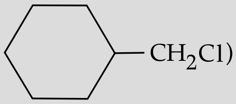
Ans.



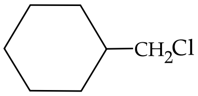
because cyclohexyl chloride

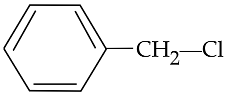
(

) is a secondary halide and it is more reactive towards S_Nl, reaction than primary halide

(

)

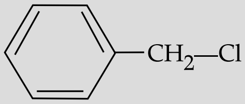
Q. 12. Out of 

and 

which will react faster in S_N1 reaction with OH^-?

A&E **[CBSE OD Set 2 2020]**

Ans.



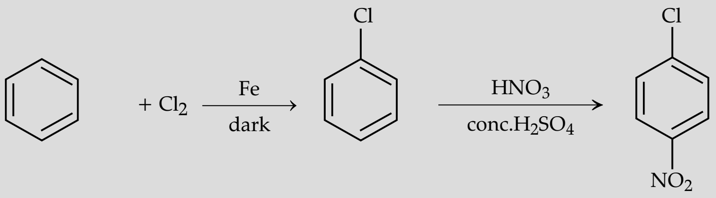
Short Answer Type Questions-I

(2 marks each)

Q. 1. How will you carry out the following conversion :
(i) 2-Bromopropane to 1-bromopropane
(ii) Benzene to p-chloronitrobenzene

U **[CBSE Comptt. OD Set-1, 2, 3 2017]**

Ans. (i) $CH_3-CH(Br)-CH_3 \xrightarrow{\text{alc KOH}} CH_3-CH{=}CH_2 \xrightarrow{\text{HBr, Peroxide}} CH_3-CH_2-CH_2-Br$

(ii) 

1+1
[CBSE Marking Scheme 2017]

Commonly Made Error

- A number of students cannot represent proper reagents used for a particular reaction.

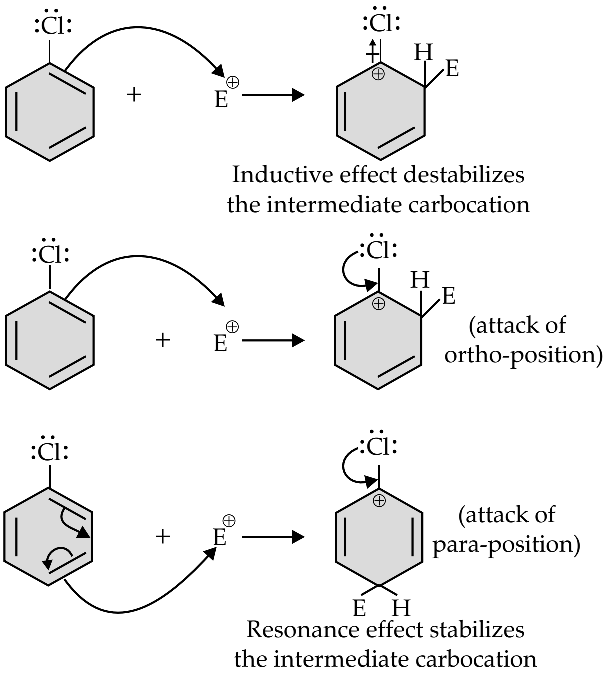
Answering Tip

- Practice the organic reactions with reference to reagents used.

AI **Q. 2. Explain why in spite of being an electron withdrawing group, chlorine is ortho- and para- directing in electrophilic aromatic substitution reactions.** A&E

Ans. Although chlorine is an electron withdrawing group, yet it is *ortho-para* directing in nature in electrophilic aromatic substitution because when chlorine is present in benzene ring, it releases electron by resonance whereas it acts as withdrawing group only through inductive effect.

By inductive effect, chlorine atom destabilizes the intermediate carbocation formation but by resonance, chlorine atom stabilises the intermediate carbocation and effect is more at *o*-and *p*-positions. Resonance effect opposes inductive effect. Inductive effect is stronger than resonance effect due to which reactivity is controlled by inductive effect and orientation by resonance.



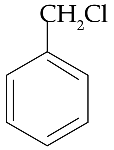
Commonly Made Error

- Students write lengthy answers. Give point wise explanation, highlight the key points.

Answering Tip

- Give resonance structures in support of answer.

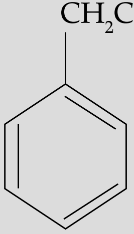
Q. 3. Which one of the following compounds will undergo hydrolysis at a faster rate by S_N1 mechanism? Justify.



or $CH_3CH_2CH_2Cl$

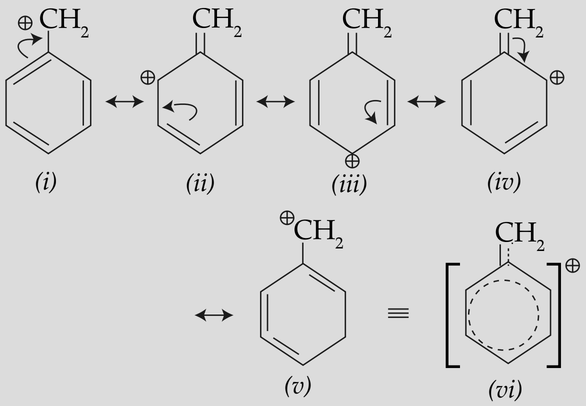
U **[CBSE SQP 2020]**

Ans. The following compound will undergo S_N1 faster:



½

Greater the stability of the carbocation, greater will be its ease of formation from the corresponding halide and faster will be the rate of reaction. The benzylic carbocation formed gets stabilised through resonance. ½



½

$CH_3CH_2CH_2Cl$ forms a 1^0 carbocation, which is less stable than benzylic carbocation. ½

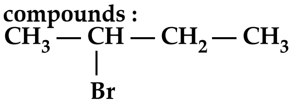
[CBSE SQP Marking Scheme 2020]

Short Answer Type Questions-II

(3 marks each)

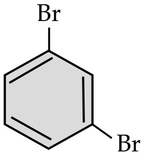
Q. 1. Give the IUPAC names of the following compounds :

(i)



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

(ii)



(iii) $CH_2 = CH - CH_2 - Cl$

A **[CBSE Comptt. OD 2015]**

Ans. (i) 2-bromobutane	1
(ii) 1, 3-dibromobenzene	1
(iii) 3-chloropropene	1

[CBSE Marking Scheme 2015]

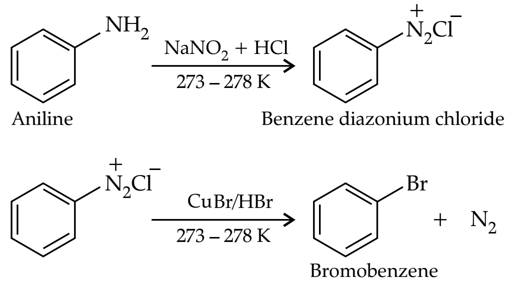
AI Q. 3. How can the following conversion be carried out :

(i) Aniline to bromobenzene

(ii) Chlorobenzene to 2-chloroacetophenone

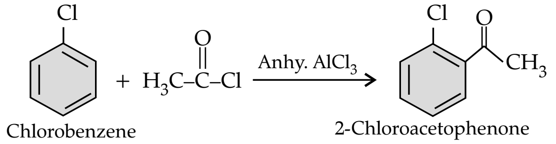
(iii) Chloroethane to butane

Ans. (i)



1

(ii)



1

(iii) $2CH_3CH_2Cl \xrightarrow[\text{dry ether}]{\text{Na}} CH_3CH_2CH_2CH_3$ 1

Chloroethane Butane

Q. 4. What happens when

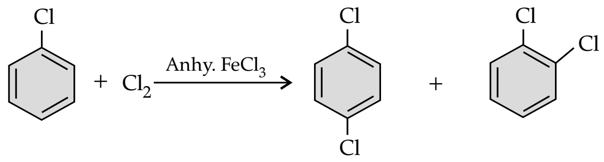
(i) Chlorobenzene is treated with $Cl_2/FeCl_3$,

(ii) Ethyl chloride is treated with $AgNO_2$,

(iii) 2-bromopentane is treated with alcoholic KOH ?

Write the chemical equations in support of your answer. **A [CBSE OD 2015]**

Ans. (i)



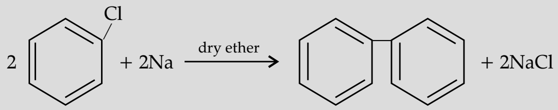
1

(ii) $CH_3CH_2Cl + AgNO_2 \rightarrow CH_3CH_2NO_2 + AgCl$ 1

(iii) $CH_3CH_2CH_2CH(Br)CH_3 + KOH\ (alc.) \rightarrow CH_3CH_2CH{=}CH\ CH_3$ 1

AI Q. 5. How do you convert : (i) Chlorobenzene to biphenyl, (ii) Propene to 1-iodopropane, (iii) 2-bromobutane to but-2-ene.

Ans. (i) Chlorobenzene to biphenyl : When two molecules of chlorobenzene combine with sodium metal in the presence of dry ether,it forms biphenyl.

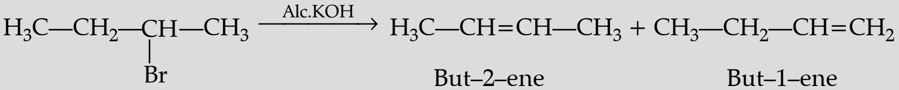


Chlorobenzene Biphenyl 1

(ii) Propene to 1–iodopropane :

$CH_3CH = CH_2 \xrightarrow{\text{HBr/Peroxide}} CH_3CH_2CH_2Br \xrightarrow{\text{NaI/acetone}} CH_3CH_2CH_2I$ 1

(iii) 2–bromobutane to but–2–ene

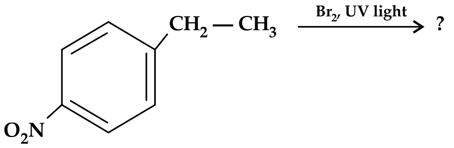


$$H_3C—CH_2—\underset{\substack{|\\ Br}}{CH}—CH_3 \xrightarrow{\text{Alc.KOH}} H_3C—CH{=}CH—CH_3 + CH_3—CH_2—CH{=}CH_2$$

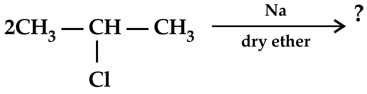
2–Bromobutane But–2–ene (80%) But–1–ene (20%) 1

Q. 6. Write the major product (s) in the following :

(i)



(ii)

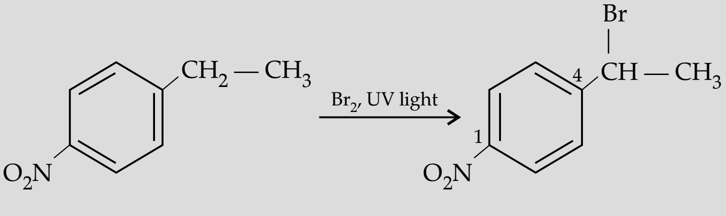


$$2CH_3 — \underset{\substack{|\\ Cl}}{CH} — CH_3 \xrightarrow[\text{dry ether}]{\text{Na}} ?$$

(iii) $CH_3 — CH_2 — Br \xrightarrow{\text{AgCN}} ?$ **A [CBSE OD 2016]**

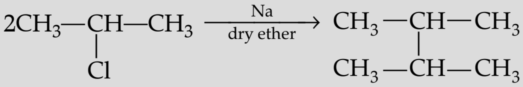
OR

(i)



4 – Ethylnitrobenzene 4 – (1 – Bromoethyl) nitrobenzene 1

(ii)



$$2CH_3—\underset{\substack{|\\ Cl}}{CH}—CH_3 \xrightarrow[\text{dry ether}]{\text{Na}} \begin{array}{c} CH_3—CH—CH_3 \\ | \\ CH_3—CH—CH_3 \end{array}$$

2,3-dimethyl butane 1

(iii) $CH_3CH_2Br \xrightarrow{\text{AgCN}} C_2H_5NC$ 1

Carbylaminoethane (Ethyl isocyanide) **[CBSE Marking Scheme 2016]**

Commonly Made Error

- Students sometimes do not draw the structure or not mention the name of the reagent or product.

Answering Tip

- Write all the steps and reagents involved in the conversion.

Q. 7. Give reasons :

(i) n-Butyl bromide has higher boiling point than t-butyl bromide.

(ii) Racemic mixture is optically active.

(iii) The presence of nitro group (–NO_2)at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

A&E **[CBSE Delhi 2015]**

Ans.(i) Larger the surface area, higher the van der Waals' forces, higher the boiling point. **1**

(ii) Rotation due to one enantiomer is cancelled by another enantiomer. **1**

(iii) –NO_2 acts as Electron withdrawing group or –I effect. **1**

[CBSE Marking Scheme 2015]

Commonly Made Error

- Students often do not answer in detail and the answer does not convey complete understanding of the concept.

Answering Tip

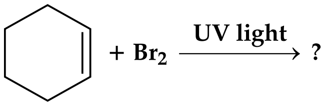
- While attempting reason based question, write cause and consequence of the condition.

Detailed Answer:

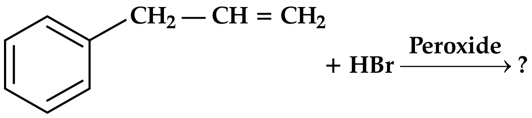
(i) *n*-Butyl bromide is a straight chain molecule with strong intermolecular forces whereas *t*-butyl bromide is a branched chain molecule with weak intermolecular forces due to smaller surface area. Hence, *n*-Butyl bromide has higher boiling point than *t*-butyl bromide.

Q. 8. Write the major monohalo product(s) in each of the following reactions :

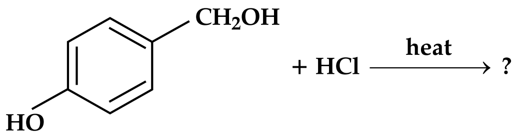
(i)



(ii)

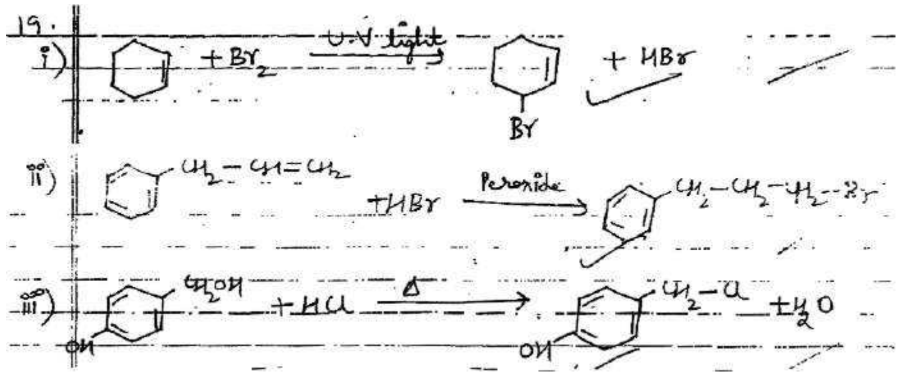


(iii)



A **[CBSE OD Set-2 2016]**

Ans.

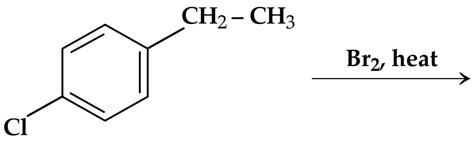


3

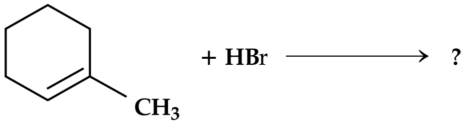
[Topper's Answer 2016]

Q. 9. Draw the structures of the major monohalo product for each of the following reactions :

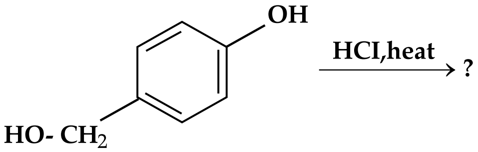
(i)



(ii)

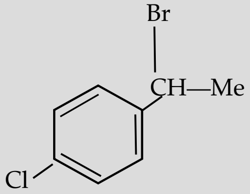


(iii)

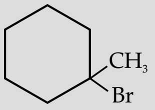


A **[CBSE Foreign Set-1, 2, 3 2017]**

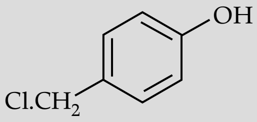
Ans. (i)



(ii)



(iii)



1+1+1

[CBSE Marking Scheme 2017]

Q. 10. (i) Account for the following :

(a) Electrophilic substitution reactions in haloarenes occur slowly.

(b) Haloalkanes, though polar, are insoluble in water.

(ii) Arrange the following compounds in increasing order of reactivity towards S_N2 displacement :

2–Bromo–2–Methylbutane, 1-Bromopentane, 2–Bromopentane

A&E + U **[CBSE Comptt. OD Set-1, 2, 3 2017]**

Ans. (i) (a) Due to-I effect of X, the ring set partially deactivated.

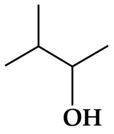
(b) They fail to form Hydrogen bonds with water / more energy is required to break hydrogen **1**

(ii) 2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane **[CBSE Marking Scheme 2017]1**

Detailed Answer :

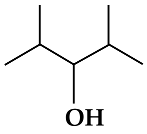
(i) (a) It is due to the fact that non bonding pair of electrons on the halogen are in conjugation with the ring causing resonance stabilization of halo arenes by delocalisation of electrons.

Q. 11. (a) Identify the chiral molecule in the following pair :



(i)

&



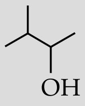
(ii)

(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

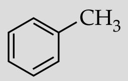
(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH.

A **[CBSE Delhi/OD 2018]**

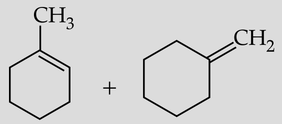
Ans. (a) (i)



(b)



(c)



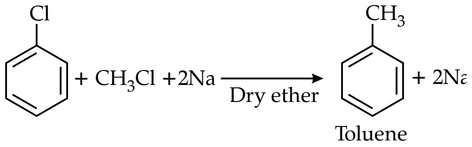
[Major] [Minor] **1+1+1**

[CBSE Marking Scheme 2018]

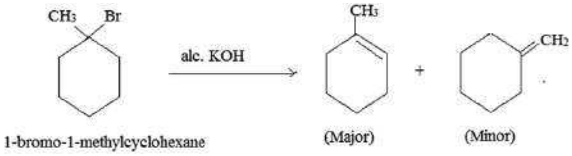
Detailed Answer:

(a) Structure (i) contains chiral carbon and it is optically active so it is a chiral molecule.

(b) Wurtz-Fittig reaction

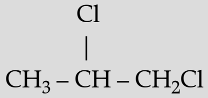


(c)



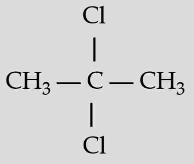
Q. 12. A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. Write the structures of the possible isomers. Give the IUPAC name of the isomer which can exhibit enantiomerism. A **[CBSE SQP 2018, 2019]**

Ans.



$CH_3-\underset{}{\overset{Cl}{\overset{|}{CH}}}-CH_2Cl$ ½

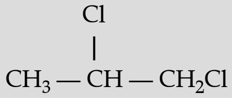
$CH_3-CH_2-CHCl_2$ ½



$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3$ ½

$ClCH_2-CH_2-CH_2Cl$ ½

The following isomer will exhibit enantiomerism:



$CH_3-\overset{\overset{Cl}{|}}{CH}-CH_2Cl$ ½

IUPAC name: 1, 2-Dichloropropane. ½

[CBSE Marking Scheme 2018]

AI **Q. 13. Write the product(s) formed when**

(i) 2-Bromopropane undergoes dehydrohalogenation reaction.

(ii) Chlorobenzene undergoes nitration reaction.

(iii) Methylbromide is treated with KCN.

A **[CBSE Comptt. Delhi/OD 2018]**

Ans. (i) Propene **1**

(ii) 4-nitrochlorobenzene and 2-nitrochlorobenzene / structures ½ + ½

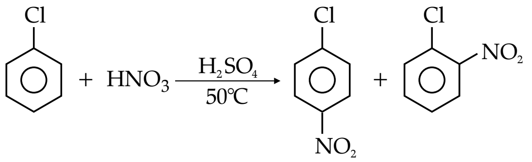
(iii) Methylcyanide / Ethanenitrile / structure **1**

[CBSE Marking Scheme 2018]

Detailed Answer:

(i) $CH_3 - CHBr - CH_3 + KOH \rightarrow CH_3 - CH = CH_2 + KBr + H_2O$

(ii)



(iii) $CH_3Br + KCN \rightarrow CH_3CN + KBr$

Q. 14. (i) Out of $(CH_3)_3C\text{-}Br$ and $(CH_3)_3C\text{-}I$, which one is more reactive towards S_N1 and why?

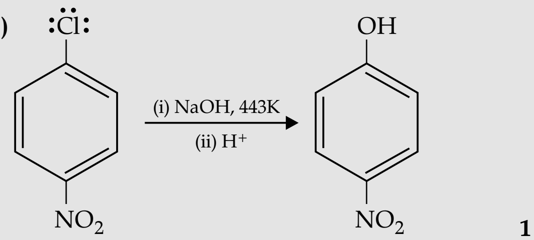
(ii) Write the product formed when p-nitrochlorobenzene is heated with aqueous NaOH at 443 K followed by acidification.

(iii) Why dextro and laevo – rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation? A **[CBSE Delhi Set 1 2019]**

Ans. (i) $(CH_3)_3C\text{–}I$, Due to large size of iodine / better leaving group / Due to lower electronegativity.

½ + ½

(ii)



1

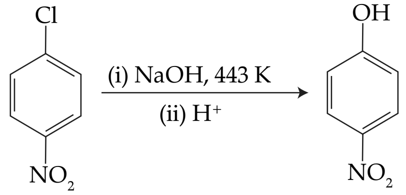
(iii) Because enantiomers have same boiling points / same physical properties.

[CBSE Marking Scheme, 2019] 1

Detailed Answer:

(i) Within a family, larger atoms are better nucleophiles. $I^- > Br^- > Cl^- > F^-$, therefore I^- is better leaving group than Br^-.

(ii)



p-nitrochlorobenzene p-nitrophenol

The presence of an electron withdrawing group ($-NO_2$) at ortho- and para- positions increases the reactivity of haloarenes.

(iii) Butan-2-ol has four different groups attached to the second tetrahedral carbon. Therefore, it is chiral molecule and the dextro and laevo – rotatory isomers of Butan-2-ol are enantiomers. The enantiomers possess identical physical properties like melting point, boiling point, solubility, refractive index etc. They only differ with respect to the rotation of plane polarised light. Therefore, dextro and laevo – rotatory isomers of Butan-2-ol are difficult to separate by fractional distillation.

AI Q. 15. Write the structures of main products when benzene diazonium chloride reacts with the following reagents :

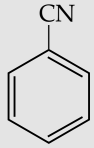
(i) CuCN

(ii) CH_3CH_2OH

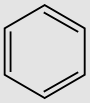
(iii) KI

A&E **[CBSE Delhi Set 2 2019]**

Ans. (i)



(ii)



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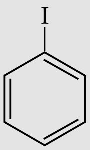
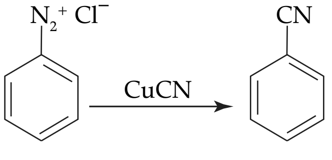


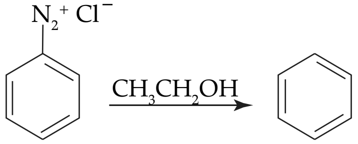
[CBSE Marking Scheme, 2019] 1 × 3

Detailed Answer:

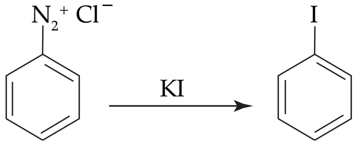
(i)



(ii)



(iii)



3

Visual Case based Questions (4 marks each)

Q.1. Read the passage given below and answer the following questions:

Nucleophilic substitution reaction of haloalkane can be conducted according to both S_N^1 and S_N^2 mechanisms. However, which mechanism it is based on is related to such factors as the structure of haloalkane, and properties of leaving group, nucleophilic reagent and solvent.

Influences of halogen : No matter which mechanism the nucleophilic substitution reaction is based on, the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair. Therefore, the weaker the alkalinity of leaving group is , the more stable the anion formed is and it will be more easier for the leaving group to leave the central carbon atom; that is to say, the reactant is more easier to be substituted. The alkalinity order of halogen ion is $I^- < Br^- < Cl^- < F^-$ and the order of their leaving tendency should be $I^- > Br^- > Cl^- > F^-$. Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is RI > RBr > RCl > RF. In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on $S_N{}^1$ mechanism. If the leaving group is not easy to leave, the reaction is based on $S_N{}^2$ mechanism.

Influences of solvent polarity: In $S_N{}^1$ reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilizing effect on the transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In $S_N{}^2$ 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 ($S_N{}^1$) of tertiary chlorobutane in 25° water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate ($S_N{}^2$) of 2-bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. In a word, the level of solvent polarity has influence on both $S_N{}^1$ and $S_N{}^2$ reactions, but with different results. Generally speaking, weak polar solvent is favorable for $S_N{}^2$ reaction, while strong polar solvent is favorable for $S_N{}^1$ reaction, because only under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation and halogen ion and solvents with a strong polarity is favorable for solvation of carbocation, increasing its stability. Generally speaking, the substitution reaction of tertiary haloalkane is based on $S_N{}^1$ mechanism in solvents with a strong polarity (for example, ethanol containing water). **(CBSE QB 2021)**

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) $S_N{}^1$ mechanism is favoured in which of the following solvents:
(a) benzene
(b) carbon tetrachloride
(c) acetic acid
(d) carbon disulphide

(ii) Nucleophilic substitution will be fastest in case of:
(a) 1-Chloro-2,2-dimethyl propane
(b) 1-Iodo-2,2-dimethyl propane
(c) 1-Bromo-2,2-dimethyl propane
(d) 1-Fluoro-2,2-dimethyl propane

(iii) $S_N{}^1$ reaction will be fastest in which of the following solvents?
(a) Acetone (dielectric constant 21)
(b) Ethanol (dielectric constant 24)
(c) Methanol (dielectric constant 32)
(d) Chloroform (dielectric constant 5)

(iv) Polar solvents make the reaction faster as they:
(a) destabilize transition state and decrease the activation energy
(b) destabilize transition state and increase the activation energy
(c) stabilize transition state and increase the activation energy
(d) stabilize transition state and decrease the activation energy

(v) $S_N{}^1$ reaction will be fastest in case of:
(a) 1-Chloro-2-methyl propane
(b) 1-Iodo-2-methyl propane
(c) 1-Chlorobutane
(d) 1-Iodobutane

Ans. (i) Correct option: (c)
(ii) Correct option: (b)
(iii) Correct option: (c)
(iv) Correct option: (c)
(v) Correct option: (b)

Q. 2. Read the passage given below and answer the following questions: (1 x 4 = 4)

Alkyl/Aryl halides may be classified as mono, di or polyhalogen compounds depending on one, two or more halogen atoms in their structures. Alkyl halides are prepared by free radical halogenation of alkanes, addition of halogen acids to alkenes and replacement of –OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by electrophilic substitution to arenes.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Complete the reaction:

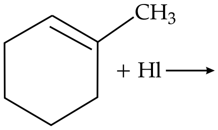
$H_3C\text{-}Br + AgF \rightarrow$

(a) $H_3C\text{-}Br + AgF \rightarrow H_3C\text{-}F + AgBr$
(b) $H_3C\text{-}Br + AgF \rightarrow Br\text{-}CH_2\text{-}F + AgH$
(c) $H_3C\text{-}Br + AgF \rightarrow [Ag(CH_3)]F + Br$
(d) None of the above

Ans. Correct option: (a)

Explanation: $H_3C\text{-}Br + AgF \rightarrow H_3C\text{-}F + AgBr$. **[1]**

(ii) Name the major monohalo product of the following reaction.



(a) 1-Iodo-1-methyl cyclohexane
(b) 1-Iodomethyl cyclohexane
(c) 1-Chloro cyclohexane
(d) None of the above

Ans. Correct option: (b)

Explanation: According to Markovnikov's rule, iodine will add to the carbon atom having less number of hydrogen atoms. **[1]**

(iii) 2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

Write the compound which is most reactive towards β-elimination reaction.

(a) 2-Bromopentane

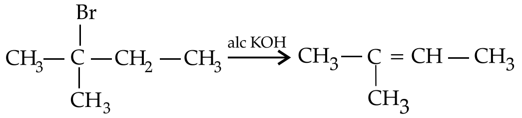
(b) 1- Bromopentane

(c) 2-Bromo-2-methylbutane

(d) None of the above

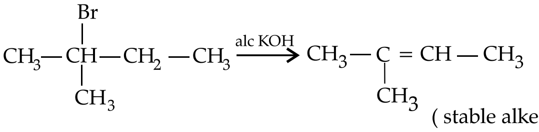
Ans. Correct option: (c)

Explanation :



$$CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3 \xrightarrow{\text{alc KOH}} CH_3-\underset{CH_3}{C}=CH-CH_3$$

(stable alkene with q a –H atoms)



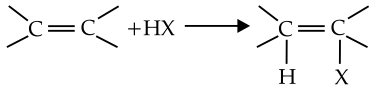
$$CH_3-\underset{CH_3}{\overset{Br}{CH}}-CH_2-CH_3 \xrightarrow{\text{alc KOH}} CH_3-\underset{CH_3}{C}=CH-CH_3$$

(stable alkene with q a –H atoms)

(iii) Which of the following is halogen exchange reaction?

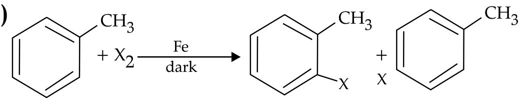
(a) RX + Nal $\longrightarrow$ RI + NaX

(b)



(c) $R-OH + HX \xrightarrow{ZnCl_2} R-X + H_2O$

(d)



Ans. Correct option: (a)

Explanation :

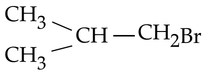
RX + Nal $\longrightarrow$ RI + NaX

It is halogen exchange reaction as in this reaction both R and Na exchanges halogens. [1]

OR

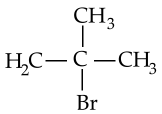
Arrange the following compounds in increasing order of their boiling points.

(i)



(ii) $CH_3CH_2CH_2CH_2Br$

(iii)



$$H_2C-\underset{Br}{\overset{CH_3}{C}}-CH_3$$

(a) (ii) < (iii) < (i)

(b) (i) < (ii) < (iii)

(c) (iii) < (i) < (ii)

(d) (iii) < (ii) < (i)

Ans. Correct option: (c)

Explanation :

boiling point of (i) is 364 K, boiling point of (ii) is 375 K. boiling point of (iii) is 346 K

As the branching increases in the isomeric alkyl halides, the boiling point decreases. **[1]**

AI Q. 3. Read the passage given below and answer the following questions: (1×4=4)

The objects which are non-superimposable on their mirror image (like a pair of hands) are said to be chiral and this property is known as chirality. Chiral molecules are optically active, while the objects, which are, superimposable on their mirror images are called achiral. These molecules are optically inactive. The above test of molecular chirality can be applied to organic molecules by constructing models and its mirror images or by drawing three dimensional structures and attempting to superimpose them in our minds. There are other aids, however, that can assist us in recognising chiral molecules. One such aid is the presence of a single asymmetric carbon atom.

In these questions a statement of assertion followed by a statement of reason is given . Choose the correct answer out of the following choices.

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.

(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.

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

(d) Assertion is wrong statement but Reason is correct statement.

(i) Assertion: The stereoisomers related to each other as non-superimposable mirror images are called enantiomers

Reason: Enantiomers possess identical physical properties.

Ans. Correct option: (b)

Explanation : The stereoisomers related to each other as non-superimposable mirror images are called enantiomers and they possess identical physical properties. **[1]**

(ii) Assertion: A racemic mixture containing two enantiomers in equal proportions will have zero optical rotation.

Reason: This is because the rotation due to one isomer will be cancelled by the rotation due to the other isomer. **[1]**

Ans. Correct option: (a)

(iii) Assertion: Butan-2-ol is a chiral molecule.

Reason: It has 4 different groups attached to carbon atom.

Explanation: A racemic mixture is an equimolar mixture of d and l forms. It is optically inactive due to external compensation as rotation of one form is cancelled by other form. **[1]**

Ans. Correct option: (a)

Explanation: Butan-2-ol is a chiral molecule as it has 4 different functional groups attached to the tetrahedral carbon atom. **[1]**

(iv) Assertion: Propan-2-ol is an achiral molecule.

Reason: Carbon is called asymmetric carbon or stereocentre.

Ans. Correct option: (c)

Explanation: Propan-2-ol is an achiral molecule as it does not contain an asymmetric carbon, as all the four groups attached to the tetrahedral carbon are not different. **[1]**

Q. 4. Read the passage given below and answer the following questions: (1×4=4)

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

(i) In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring.

(ii) In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2 -hybridised.

(iii) In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance.

The following questions are Multiple Choice Questions. Choose the most appropriate answer :

(a) A primary alkyl halide would prefer to undergo ________.

(i) S_N1 reaction
(ii) S_N2 reaction
(iii) α-Elimination
(iv) Racemisation

Ans. Correct option: (ii)

Explanation: A primary alkyl halide would prefer to undergo S_N^2 reaction. **[1]**

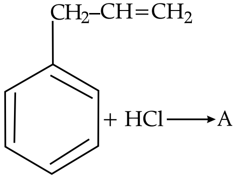
(b) Which of the following alkyl halides will undergoes S_N1 reaction most readily?

(i) $(CH_3)_3C$—F
(ii) $(CH_3)_3C$—Cl
(iii) $(CH_3)_3C$—Br
(iv) $(CH_3)_3C$—I

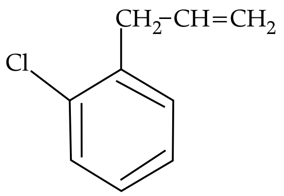
Ans. Correct option: (d)

Explanation: $(CH)_3C$-I being a tertiary alkyl halide will most readily undergo S_N1 reaction. **[1]**

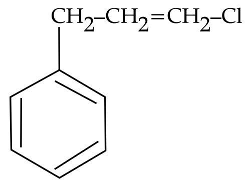
(c) What is 'A' in the following reaction?



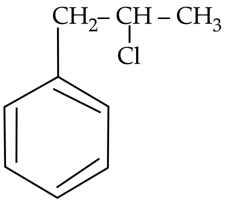
(i)



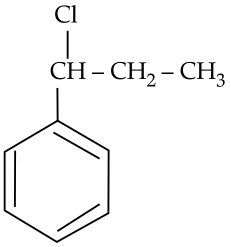
(ii)



(iii)

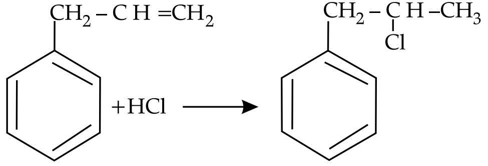


(iv)



Ans. Correct option:(c)

Explanation:



[1]

(d) Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows ________.

(i) S_N1 mechanism
(ii) S_N2 mechanism
(iii) Any of the above two depending upon the temperature of reaction
(iv) Saytzeff rule.

Ans. Correct option: (iv)

Explanation:

C_6H_5-CH_2 is stable cation so favours the progress of reaction by S_N1 mechanism. **[1]**

Self-Asessment Test-10

Time : 1 Hour **Max. Marks : 25**

Q.1. Read the passage given below and answer the following questions : (1 × 4 = 4)

The reaction in which a nucleophile replaces already existing nucleophile in a molecule is called nucleophilic substitution reaction. Haloalkanes are substrate in these reactions. In this type of reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.

In these questions, a statement of assertion followed by a statement of reason is given.

Choose the correct answer out of the following choices.

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

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

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

(d) Assertion is wrong statement but reason is correct statement

(i) Assertion : Chlorobenzene is formed by reaction of chlorine with the benzene in presence of $AlCl_3$.

Reason : $[AlCl_4]^-$ is the species that attacks the benzene ring in this reaction.

(ii) Assertion : Electrophilic substitution reactions occurs slowly in haloarenes.

Reason : The reason for this effect is –R effect of the benzene ring.

(iii) Assertion : Haloalkanes, though polar are, insoluble in water.

Reason : Haloalkanes do not form hydrogen bond with water.

(iv) Assertion : In monohaloarenes , further electrophilic substitution occurs at the ortho and para positions.

Reason : Halogen atom is a ring deactivator.

OR

Assertion : It is difficult to replace chlorine by –OH in chlorobenzene in comparison to that in chloroethane.

Reason : Carbon-chlorine (C-Cl) bond in chlorobenzene has a partial double bond character due to resonance.

Following questions (No. 2 to 5) are Multiple Choice Questions carrying 1 mark each.

Q. 2. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

(i) Electrophilic elimination reaction

(ii) Electrophilic substitution reaction

(iii) Free radical addition reaction

(iv) Nucleophilic substitution reaction U

[NCERT exemplar page 134]

Q. 3. Which is the correct increasing order of boiling points of the following compounds?

1-Bromoethane, 1-Bromopropane, 1-Bromobutane, Bromobenzene

(a) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane

(b) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane

(c) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene

(d) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene A&E

[NCERT exemplar page 140]

Q.4. Which reagent will you use for the following reaction ?

$$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

(a) Cl_2 / UV light

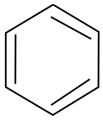
(b) NaCl + H_2SO_4

(c) Cl_2 gas in dark

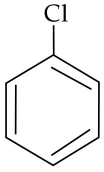
(d) Cl_2 gas in presence of iron in dark

Q. 5. Arrange the following compounds in the increasing order of their densities.

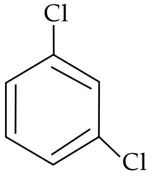
(i)



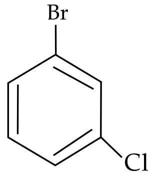
(ii)



(iii)



(iv)



(a) (i) < (ii) < (iii) < (iv)

(b) (i) < (iii) < (iv) < (ii)

(c) (iv) < (iii) < (ii) < (i)

(d) (ii) < (iv) < (iii) < (i) A&E

[NCERT Exemplar page 135]

AI **Q. 6. Assertion:** Ethylidene chloride is a gem- dihalide.

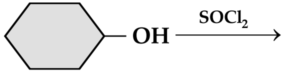
Reason: 2 Halogen atoms are present on two carbon atoms. **[R]**

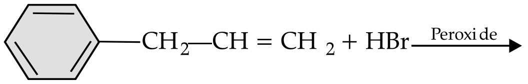
Q.7. Assertion: 2-Bromopentane is a haloalkane.

Reason: Haloalkanes contain halogen atom (s) attached to the sp^3 hybridised carbon atom of an alkyl group. **[R]**

Q.No. 8 & 9 are Short Answer Type-I carrying 2 marks each.

Q.8. Draw the structure of major monohalo product in each of the following reactions:





$C_6H_5-CH_2-CH=CH_2 + HBr \xrightarrow{Peroxide}$ $\boxed{A}$

Q.9. Which halogen comound in each of the following pairs will react faster in S_N2 reaction:

(a) CH_3Br or CH_3I

(b) $(CH_3)_3C-Cl$ or CH_3-Cl $\boxed{A}$

Q.No. 10 & 11 are Short Answer Type-II carrying 3 marks each.

Q.10. What happens when:

(i) CH_3-Cl is treated with aqueous KOH?

(ii) CH_3-Cl is treated with KCN?

(iii) CH_3-Br is treated with Mg in the presence of dry ether? $\boxed{U}$

Q.11. Write the major products in the following equations :

(i) $CH_3 - CH_2OH \xrightarrow{PCl_5} ?$ $\boxed{R}$

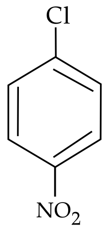
AI (ii) Write the structure of 1-bromo-4-chlorobut-2-ene. $\boxed{A}$

(iii) Write down the structure and IUPAC name for neo-pentylbromide

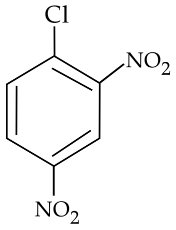
Q.No 12 is a Long Answer Type Carrying 5 marks each.

Q.12. (a) Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved. $\boxed{A}$

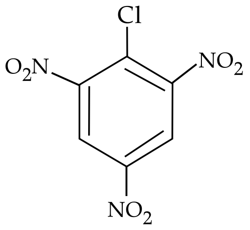
(b) Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:



[I]



[II]



[III] $\boxed{A\&E}$

(c) (i) Why iodoform has appreciable antiseptic property? $\boxed{R}$

OR

(a) (i) Allyl chloride can be distinguished from vinyl chloride by NaOH and silver nitrate test. Comment.

(ii) Alkyl halide reacts with lithium aluminium hydride to give alkane. Name the attacking reagent which will bring out this change. $\boxed{A}$

(b) Identify the products A and B formed in the following reaction:

$CH_3-CH_2-CH=CH-CH_3 + HCl \rightarrow A + B$

(c) Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent? $\boxed{A}$