CHAPTER 6

HALOALKANES AND HALOARENES

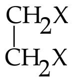
- Halogenated compunds persist in the environment due to their resistance to breakdown by soil bacteria.
- Haloalkanes are aliphatic hydrocarbons where a hydrogen atom is replaced by halogen, while haloarenes are aromatic hydrocarbons where hydrogen in the benzene ring is replaced with a halogen atom.
- Halogen atom is attached to sp^3 hybridized carbon atom in haloalkanes while in haloarenes it is attached to sp^2 hybridized 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,

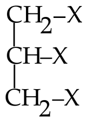
C_2H_5X

Monohaloalkane



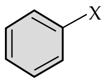
CH_2X-CH_2X

Dihaloalkane

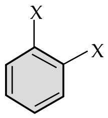


$CH_2X-CHX-CH_2X$

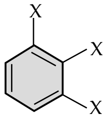
Trihaloalkane



Monohaloarene



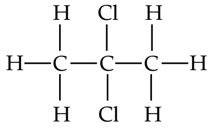
Dihaloarene



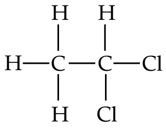
Trihaloarene

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)

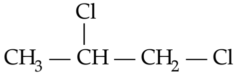


Ethylidene chloride
(1, 1–Dichloroethane)

(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)

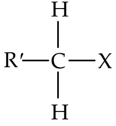


$CH_3-CH(Cl)-CH_2-Cl$

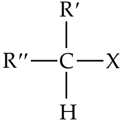
Propylene dichloride
(1, 2-Dichloropropane)

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

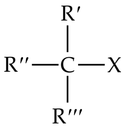
(i) Haloalkanes or alkyl halides (R—X): General formula is C_nH_{2n+1} X. They are further classified as primary, secondary and tertiary haloalkanes.



Primary haloalkane



Secondary haloalkane

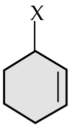


Tertiary haloalkane

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

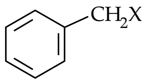
$CH_2=CH-CH-X$

Allyl halide
(3-Halo–1–propene)

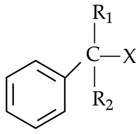


3-Halocylohex–1–ene

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



Benzyl halide (1°)



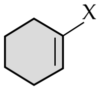
Here, $R_1=CH_3$, $R_2=H$ (2°)
or $R_1=R_2=CH_3$ (3°)

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

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

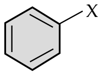
$CH_2=CH-X$

Vinyl halide



1–Halocylohex–1 –ene

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



Halobenzene

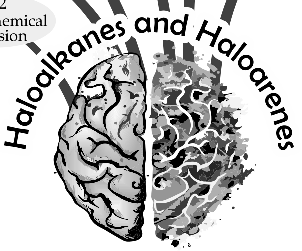
Nomenclature

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

Table 1

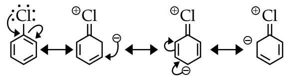
Structure	IUPAC Name	Common names
CH_3Cl	Chloromethane	Methyl chloride
CH_3CH_2Cl	Chloroethane	Ethyl chloride

HALOALKANES AND HALOARENES

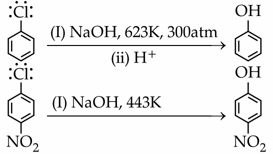


Haloarenes

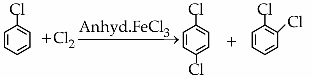
- Reactions :
  - (a) Nucleophilic substitution
    - (i) Resonance effect

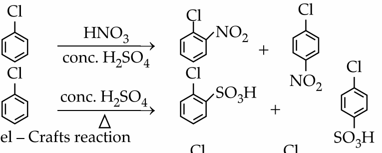


    - (ii) Hybridisation of C in C-X bond : Haloalkane –sp^3; Haloarence –sp^2
    - (iii) Phenyl cation unstabilised by resonance

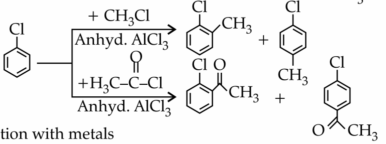


  - (b) Electrophilic substitution



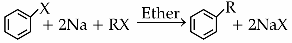


Friedel – Crafts reaction

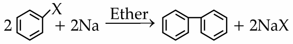


  - (c) Reaction with metals

Wurtz – Fitting reaction



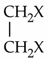
Fittig reaction



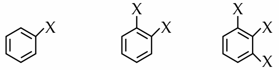
Classification

- No. of halogen atoms

C_2H_5X Monohaloalkane

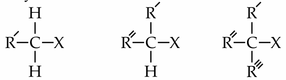


CH_2X-CH_2X Dihaloalkane

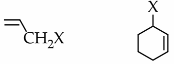


Monohaloarene Dihaloarene Trihaloarene

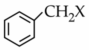
- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides



  - (b) Allylic halides

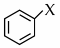


  - (c) Benzylic halides



- Compounds containing sp^2 C–X bond
  - (a) Vinylic halides

  - (b) Aryl halides

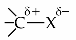


- Nomenclature

  Common name : Alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.

  IUPAC name : Numerals are used.
- Nature of C –X bond

  : Carbon –halogen bond is polarised.



Haloalkanes

=>Preparation

- From alcohol :

$$R{-}OH + HCl \xrightarrow{ZnCl_2} R{-}Cl + H_2O$$

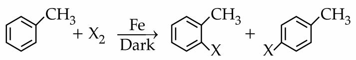
$$3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3$$

$$ROH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

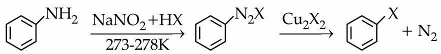
- From hydrocarbons :
  - (a) By free radical halogenation

$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

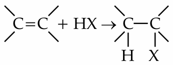
  - (b) By electrophilic substitution



  - (c) Sandmeyer's reaction



  - (d) From alkenes



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

- Halogen exchange :

$$R{-}X + NaI \rightarrow R - I + NaX$$

=>Properties

- Physical : Colourless, volatile, sweet smell.

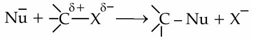
  Lower members are gases at room temperature while higher are solids.

  B.P : RI > RBr > RCl > RF.

  M.P : Para isomers have high m.p. than ortho and meta – isomers.

  Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.

  Solubility : Very slightly soluble in water.
- Chemical :
  - (a) Nucleophilic substitution

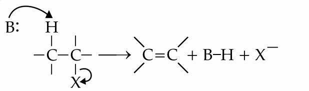


$$\bar{Nu} + \overset{\delta+}{C}{-}\overset{\delta-}{X} \longrightarrow C - Nu + X^-$$

$$\xrightarrow[\text{Tertiary, Secondary, Primary}]{\text{For } S_N2 \text{ reaction}}$$

$$\xleftarrow[\text{For } S_N1 \text{ reaction}]{}$$

  - (b) Elimination reaction



B = Base; X = Leaving group

  - (c) Reaction with metals

$$CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr$$

Wurtz reaction :

$$2RX + 2Na \xrightarrow{\text{Dry ether}} RR + 2NaX$$

Racemisation S_N1

- Chiral : Objects which are non-superimposable.
- Achiral : Objects which are superimposable.

S_N2 Stereochemical inversion

(a) Dextro (+/d)

(b) Laevo (–/*l*)

Polyhalogen compounds

Chloroform
- Solvent for fats, alkaloids, I etc.
- Production of freon.

Iodoform
- Antiseptic

Carbon tetrachloride
- Manufacture of refrigerants and propellants.
- Cleaning fluid.

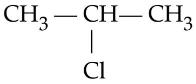
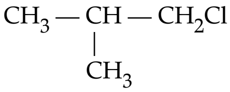
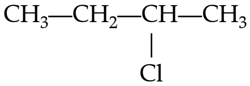
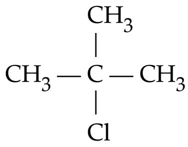
Freons
- For aerosol propellants, refrigeration and air conditioning purposes.

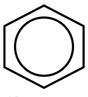
DDT
- As insecticide

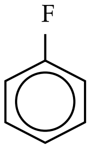
Dichloromethane
- Paint remover.
- Propellant in aerosols.
- Metal cleaning and finishing solvent.

Trace the Mind Map

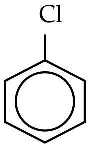
- First Level
- Second Level
- Third Level

$CH_3-CH_2-CH_2Cl$	1-Chloropropane	*n*-Propyl chloride
 $CH_3-\underset{\underset{Cl}{\vert}}{CH}-CH_3$	2-Chloropropane	Isopropyl chloride
$CH_3-CH_2-CH_2-CH_2Cl$	1-Chlorobutane	*n*-Butyl chloride
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2Cl$	1-Chloro-2-methyl propane	Isobutyl chloride
 $CH_3-CH_2-\underset{\underset{Cl}{\vert}}{CH}-CH_3$	2-Chlorobutane	*Sec.* butyl chloride
 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{Cl}{\vert}}{C}}-CH_3$	2-Chloro-2-methyl propane	*tert* 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

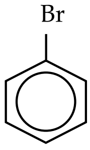

Benzene



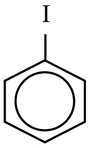
Fluorobenzene



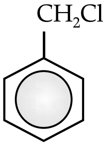
Chlorobenzene

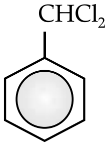


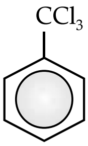
Bromobenzene

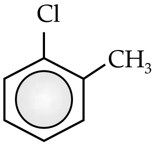


Iodobenzene









IUPAC name	1-Chloro –1 – phenylmethane	Dichlorophenyl methane	Trichlorophenyl methane	1– Chloro – 2 – methyl benzene
Common name	(Benzyl chloride)	(Benzyldene chloride) (Benzal chloride)	(Benzotrichloride)	(2 – Chlorotoluene)

Methods of Preparation of Haloalkenes

(a) From alcohols: Alkyl halides are prepared from alcohols, which are easily accessible. This method cannot be used to obtain aryl halides as the carbon-oxygen bond in phenols has a partial double bond character and it is difficult to break that bond.

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

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

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

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

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

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

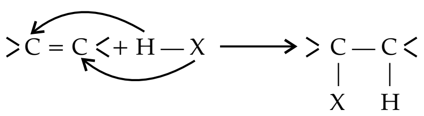
The reactions of primary and secondary alcohols with HX requires the presence of the anhydrous $ZnCl_2$.

(b) From hydrocarbons: By free radical halogenation.

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

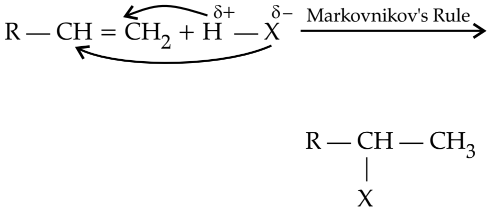
(c) From alkenes:

(i) Addition of hydrogen halide:



$$>C=C< + H-X \longrightarrow >\underset{X}{C}-\underset{H}{C}<$$

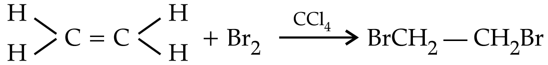
(X = Cl, Br, I)



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

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

(ii) Addition of Halogens:



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

vic-Dibromide

(d) Halide Exchange:

(i) Finkelstein Reaction: Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone is prepared by this reaction.

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

(ii) Swarts Reaction: The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/ bromide in the presence of a metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3 by this reaction.

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

- **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 from fluorine to iodine. 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 and iodine are coloured.

(i) Melting and boiling points: Due to polar and strong dipole-dipole interactions between the molecules of halogen derivatives have high B.P. and M.P. This increase in B.P. and M.P. than their parent hydrocarbon 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 intermolecular forces.

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

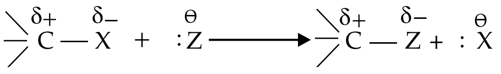
(iii) Solubility: Haloalkanes are insoluble in water but are soluble in organic solvents.

- **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 three types of chemical reactions with haloalkanes:

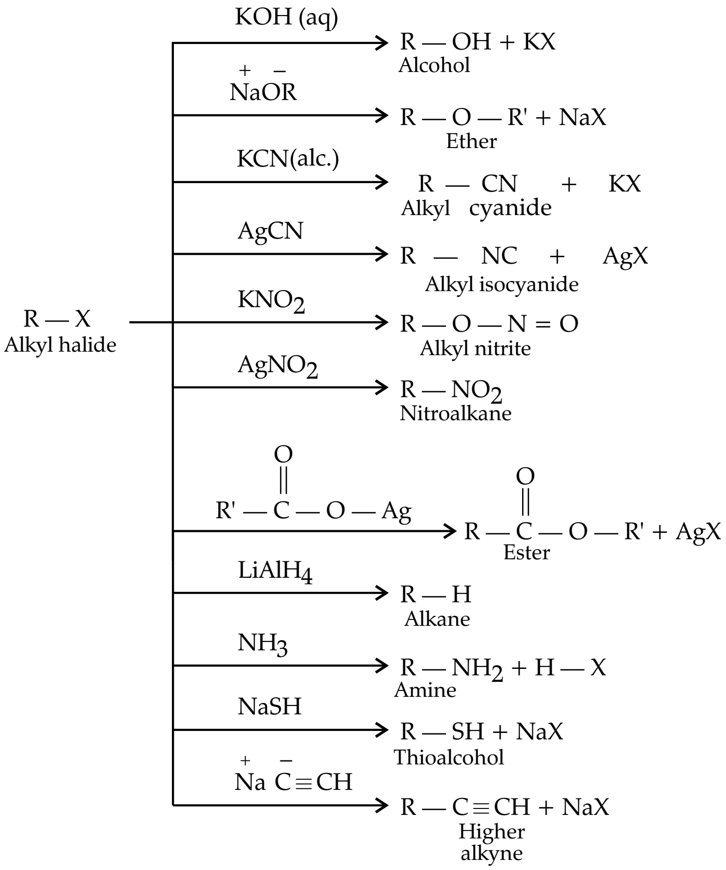
(a) Nucleophilic substitution reactions: When an atom or group of atoms is replaced by a nucleophile the reaction is called as nucleophilic substitution reaction, *e.g.,*



$$>\overset{\delta+}{C}-\overset{\delta-}{X} + :\overset{\ominus}{Z} \longrightarrow >\overset{\delta+}{C}-\overset{\delta-}{Z} + :\overset{\ominus}{X}$$

The following is the order of reactivity RCl < RBr < RI

$RCH_2X < R_2CHX < R_3CX$



(b) Reaction with metals: Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as organo-metallic compounds. The most important class of organo-metallic compounds is alkyl magnesium halide, RMgX, referred as Grignard Reagent which is prepared as below:

(1) Reaction with magnesium:

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

$$CH_3-CH_2-Br + Mg \xrightarrow{\text{Dry ether}} CH_3-CH_2-MgBr$$

Ethyl magnesium bromide

(2) Reduction with sodium (Wurtz reaction): Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide.

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

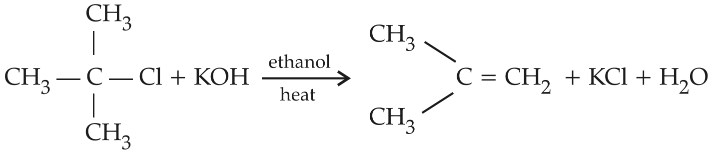
$$CH_3-CH_2-Cl + 2Na + Cl-CH_2-CH_3 \xrightarrow{\text{Dry ether}} \underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} + 2NaCl$$

(3) Reduction:

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

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

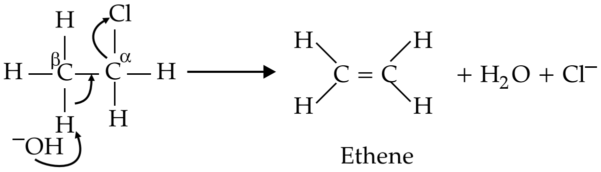
(4) Elimination reaction: Alkyl halides undergo β-elimination of hydrogen atom from β-carbon atom and halogen atom to form alkenes on being heated with KOH (alc.) or KNH_2, *e.g.*,



2-Chloro-2-methylpropane

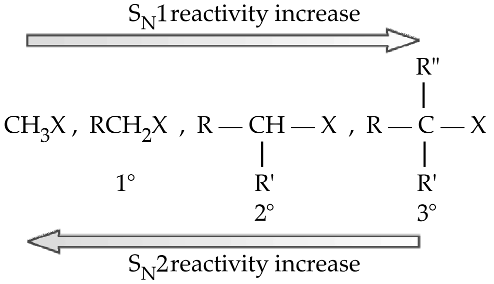
2-methylpropene

The reaction is called *dehydrohalogenation.*



Ethene

- **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 shows opposite order of reactivity in the two mechanisms.



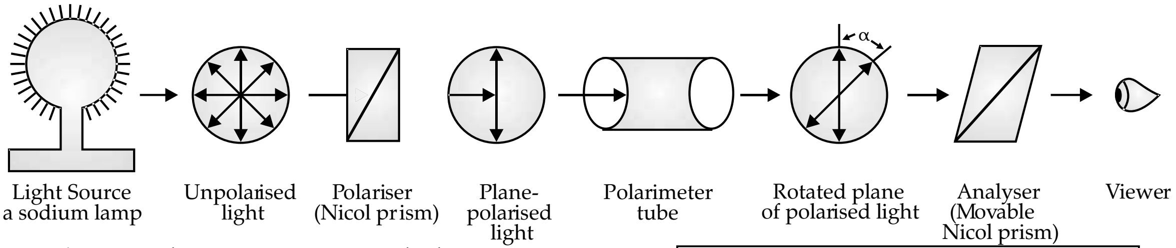
$$CH_3X,\ RCH_2X\ (1^\circ),\ R-\underset{R'}{CH}-X\ (2^\circ),\ R-\overset{R''}{\underset{R'}{C}}-X\ (3^\circ)$$

- **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.

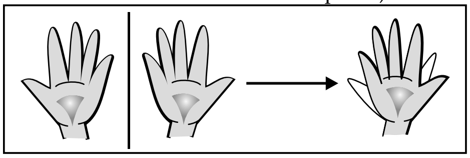
Specific rotation $[\alpha]_D^{t^\circ C}$

$$= \frac{\text{observed rotation } (\alpha_{obs})}{\text{length of tube } (d_m) \times \text{concentration of solution (g mol}^{-1})}$$

- **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:



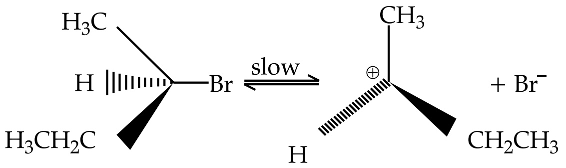
- **Enantiomers:** Those stereoisomers which are mirror images of each other but non-superimposable are called enantiomers, e.g., *d*(+) glucose and *l*(–) glucose are enantiomers.
- **Asymmetric molecule:** If all the four substituents attached to carbon are different, the resulting molecule will lack 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.*,



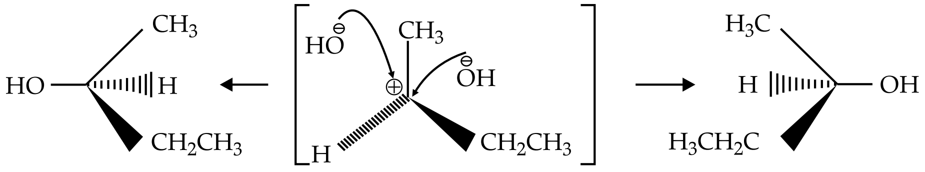
Non-superimposable hands

- **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-hybridized 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.



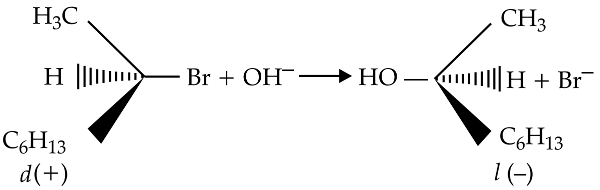
.(–)-2-Bromobutane



(+)-Butan-2-ol

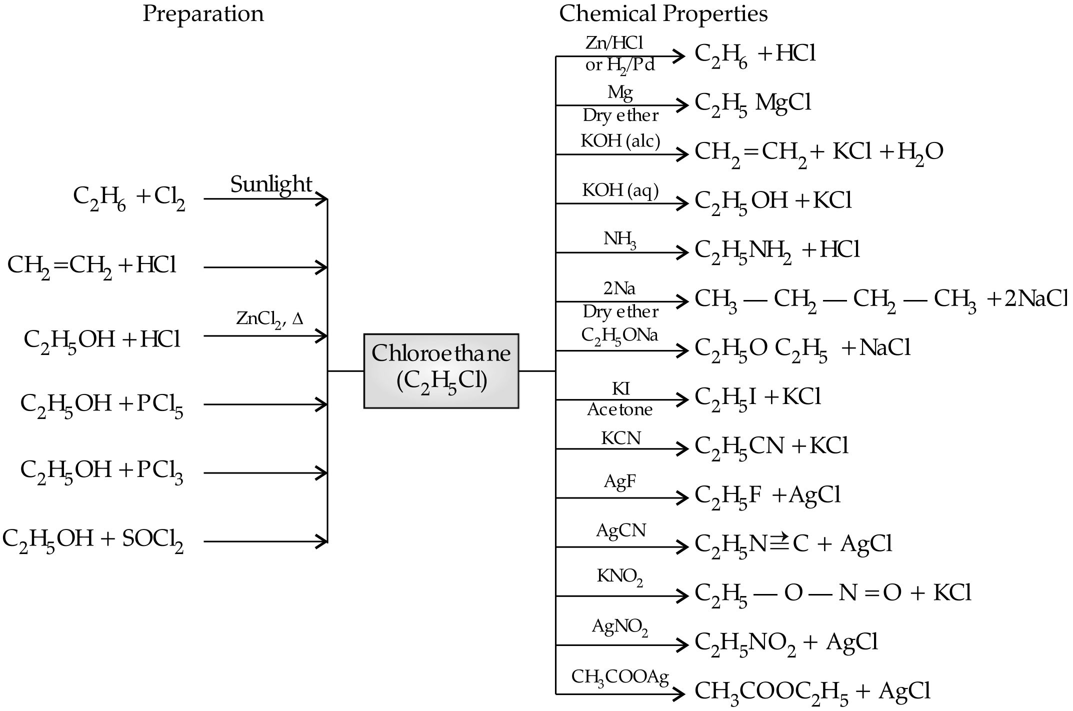
(-)-Butan-2-ol

- **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.

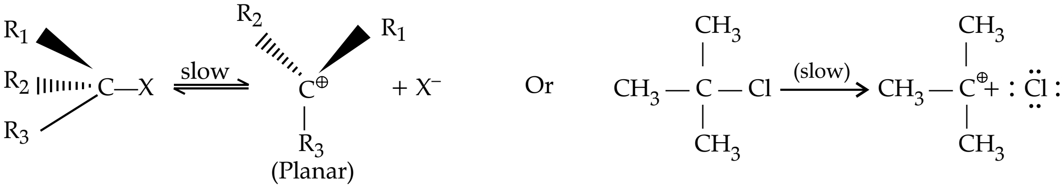
- **Important reactions of chloroethane:**



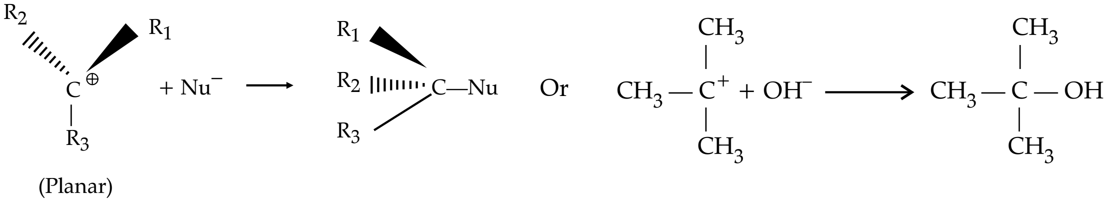
- **Mechanism of Nucleophilic substitution reaction:** Alkyl halides undergo two types of nucleophilic substitution reactions.

(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:

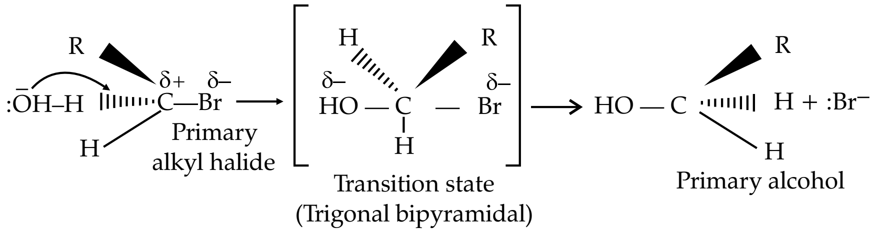


STEP II:



The slowest step is the 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 favours 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 takes place simultaneously.



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

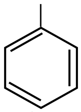
Mnemonics

Concept: S_N1 reaction
Mnemonics: Curt - 1
Interpretations: Carbocation intermediate

- Unimolecular Reaction.
- Racemic mixture is obtained.
- Two steps process.
- Ist order kinetics.

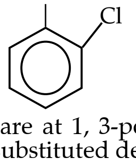
Haloarenes

- Haloarenes are the compounds formed by replacing one or more hydrogen atoms in an aromatic ring with halogen atoms. For example, monohalogen derivative

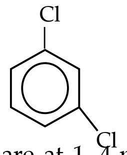


(X = F, Cl, Br, or I).

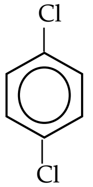
- When two halogens are at 1, 2- positions of benzene ring, it is called ortho-substituted derivative. e.g.,



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

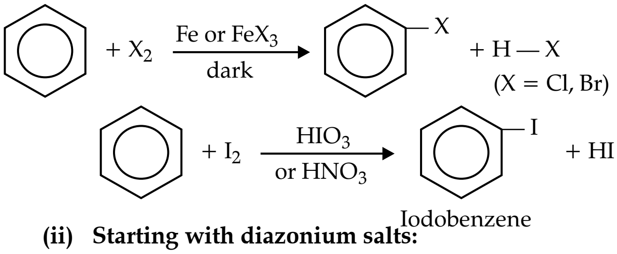


- When two halogens are at 1, 4-positions of benzene ring, it is called *para*-substituted derivative. e.g.,

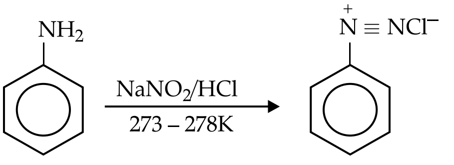


- **Methods of preparation of Haloarenes:**

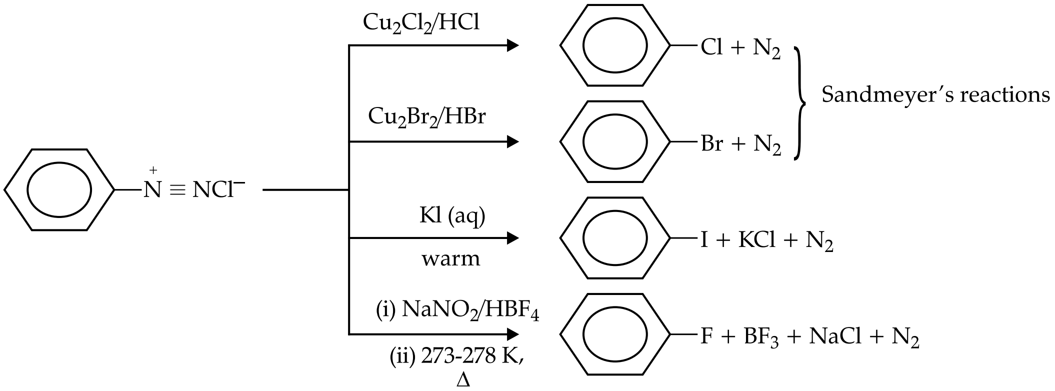
  (i) Reacting benzene directly with halogen:



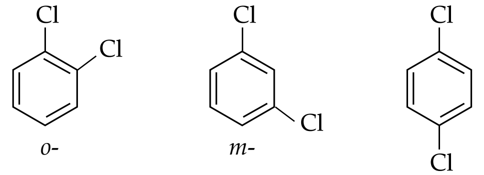
  (ii) Starting with diazonium salts:



Benzene diazonium chloride



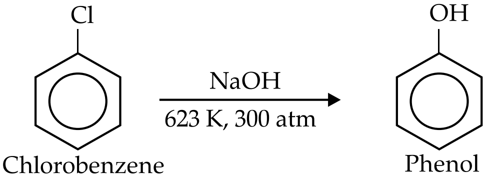
- **Physical properties of Haloarenes:** Isomeric haloarenes have similar boiling points. But para isomer has higher melting point than other two, i.e., *ortho*-and *meta*-because of the symmetry in *para*-isomer which occupies the crystal lattice better than *ortho* and *meta* isomers.



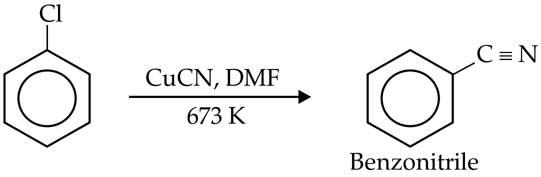
	o-	*m*-	*p*-
b.p. (K)	453	446	448
m.p. (K)	256	249	323

- **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.

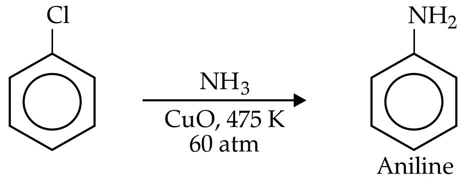
(i) Substitution by —OH group (Dow's process):



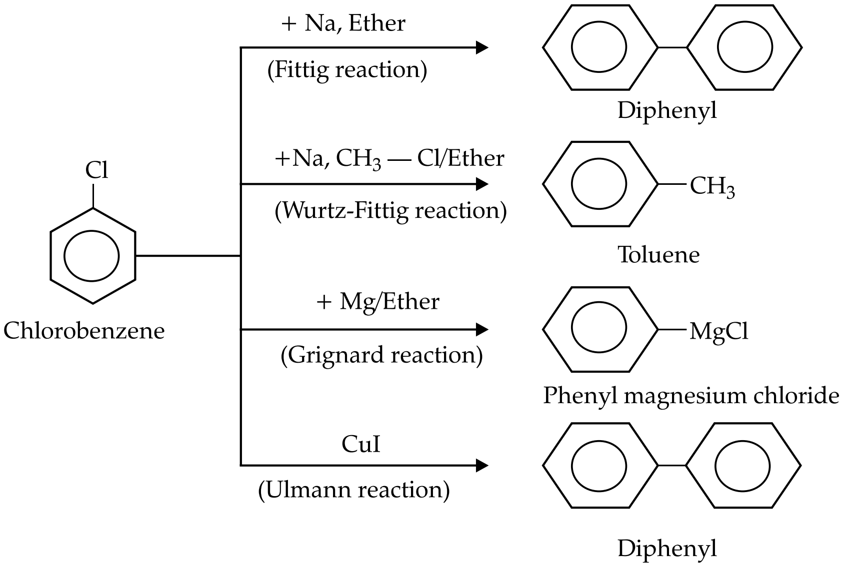
(ii) Substitution by —CN group:



(iii) Substitution by —NH_2 group:

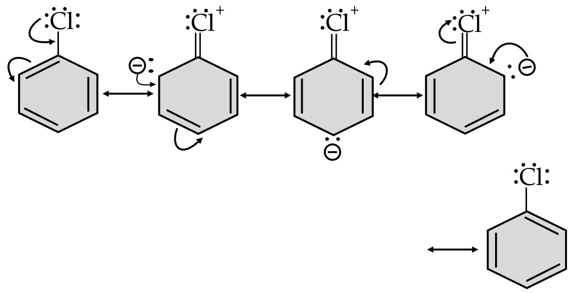


(iv) Reaction with metals:

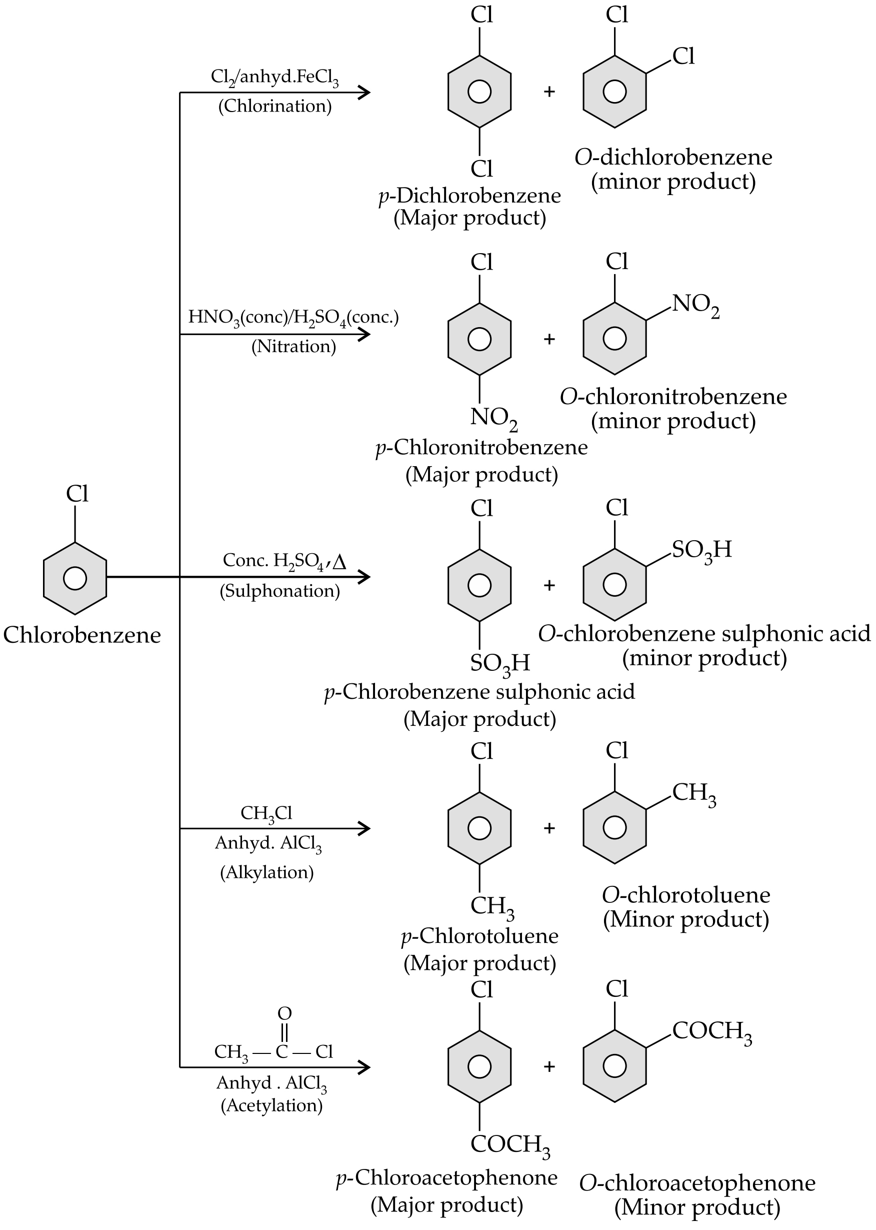


- **Nature of C—X bond in haloarene**: The C—X bond of aryl halide is less reactive than that of haloalkanes. One reason is that in aryl halide, halogen atom is attached to sp^2-hybrid carbon atom whereas in alkyl halides, it is attached to sp^3-hybrid carbon atom. Due to more electronegativity of sp^2-hybrid 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. It is widely used as solvent in pharmaceuticals and food industry.

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

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

It is extensively used as solvent for waxes, resins, rubber, fats, etc. It was earlier used as anaesthetic and swallowing agent, but due to formation of phosgene gas (poisonous gas), it is not used at present.

(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.

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

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

It is used as an antiseptic for dressing wounds.

(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.

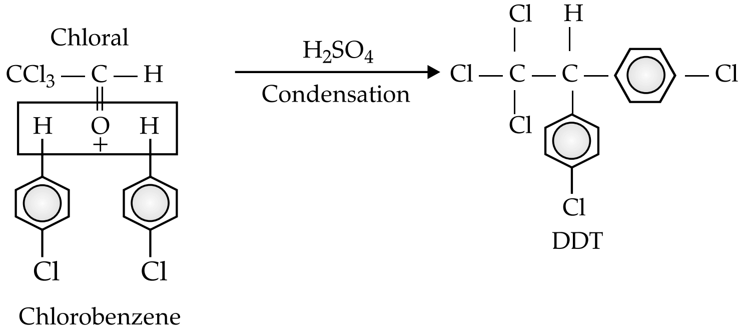
$$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + SCl_2$$

(Sulphur dichloride)

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

It is highly used as a solvent for fats, resins, etc. It is used in fire extinguisher.

(v) DDT: It is used as an insecticide. It creates pollution due to its extreme stability. It is non-biodegradable. It is manufactured by the condensation of chlorobenzene with chloral (trichloroacetaldehyde) in the presence of sulphuric acid. It is also called *p, p′*-dichloriodiphenyltrichloroethane. It is highly toxic to fish and due to stability, it gets deposited and stored in animal fat tissues. Thus it was banned in USA and India but still used in other countries of the world.



NCERT CORNER

Intext Questions

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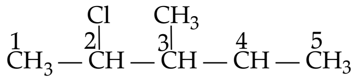
Q. 6.1. Write structures of the following compounds:

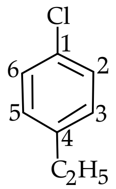
- **(i) 2-Chloro-3-methylpentane**
- **(ii) 1-Chloro-4-ethylcyclohexane**
- **(iii) 4-tert. -butyl-3-iodoheptane**
- **(iv) 1,4-Dibromobut-2-ene**
- **(v) 1-Bromo-4-sec. butyl-2-methylbenzene**

Ans. (i) 2-Chloro-3-methylpentane

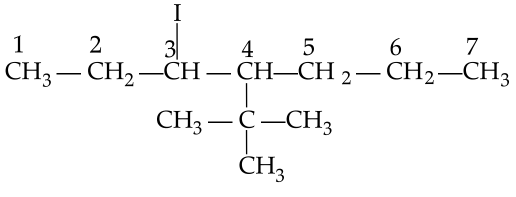


$$\overset{1}{CH_3}-\overset{\overset{Cl}{|}}{\underset{2}{CH}}-\overset{\overset{CH_3}{|}}{\underset{3}{CH}}-\overset{4}{CH}-\overset{5}{CH_3}$$

(ii) 1-Chloro-4-ethylcyclohexane



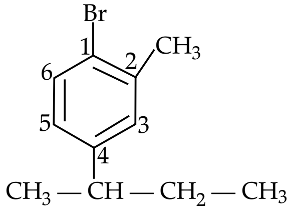
(iii) 4-tert. Butyl-3-iodoheptane



(iv) 1, 4-Dibromobut-2-ene

$$Br-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-Br$$

(v) 1-Bromo-4-sec. butyl-2-methylbenzene



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Q. 6.2. Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans. $2KI + H_2SO_4 \rightarrow 2KHSO_4 + 2HI$

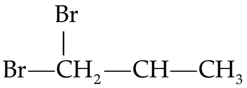
$$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + H_2O$$

In the presence of sulphuric acid (H_2SO_4), KI produces HI which is an oxidizing agent, it oxidizes HI (produced in the reaction to I_2).

As a result, the reaction between alcohol and HI to produce alkyl iodide cannot occur. Therefore, sulphuric acid is not used during the reaction of alcohols with KI. Instead, a non-oxidizing acid such as H_3PO_4 is used.

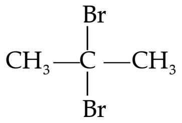
Q. 6.3. Write structures of different dihalogen derivatives of propane.

Ans. There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

(i)


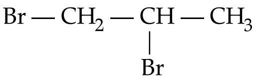
$$Br—CH_2—\underset{}{\overset{Br}{\overset{|}{C}}}H—CH_3$$

1, 1-Dibromopropane

(ii)


$$CH_3—\underset{\underset{Br}{|}}{\overset{Br}{\overset{|}{C}}}—CH_3$$

2, 2-Dibromopropane

(iii)


$$Br — CH_2 — \underset{\underset{Br}{|}}{C}H — CH_3$$

1, 2-Dibromopropane

(iv) $Br—CH_2—CH_2—CH_2—Br$

1, 3-Dibromopropane

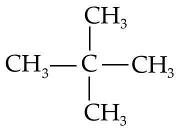
Q. 6.4. Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(i) A single monochloride.

(ii) Three isomeric monochlorides.

(iii) Four isomeric monochlorides.

Ans. (i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula C_5H_{12}. This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.



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

Neopentane

(ii) To have three isomeric monochlorides, the isomer of the alkane of themolecular formula

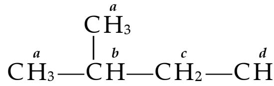
$$\overset{1}{C}H_3 — \overset{2}{C}H_2 — \overset{3}{C}H_2 — \overset{4}{C}H_2 — \overset{5}{C}H_3$$

n-Pentane

C_5H_{12} should contain three different types of H-atoms.

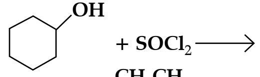
Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H-atoms labelled as *a*, *b* and *c* in *n*-pentane.

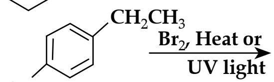
(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c*, and *d* in 2-methylbutane.

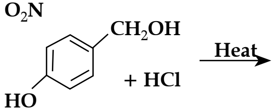


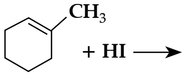
$$\overset{a}{C}H_3—\overset{\overset{a}{C}H_3}{\overset{|}{\overset{b}{C}}}H—\overset{c}{C}H_2—\overset{d}{C}H_3$$

Q. 6.5. Draw the structures of major monohalo products in each of the following reactions:

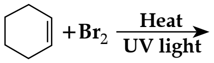
(i)


(ii)


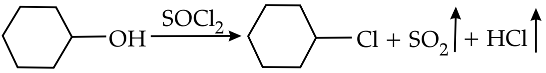
(iii)


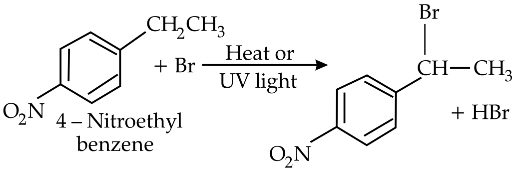
(iv)


(v) $CH_3CH_2Br + NaI \longrightarrow$

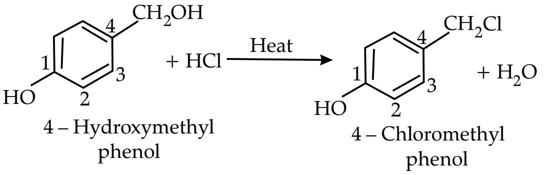
(vi)


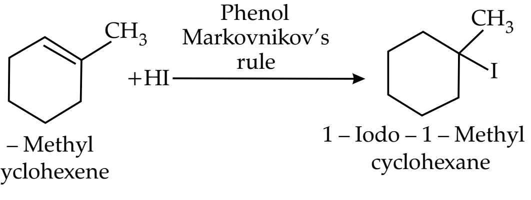
Ans.

(i)


(ii)


1 – Bromo – 1 – (4 – Nitrophenyl) ethane

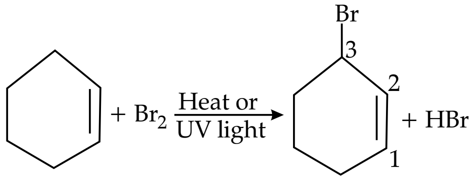
(iii)


(iv)


(v) $CH_3CH_2Br + NaI \rightarrow CH_3CH_2I + NaBr$

Bromoethane Iodoethane

(vi)



Cyclohexene 3 – Bromocyclohexene

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Q. 6.6. Arrange each set of compounds in order of increasing boiling points.

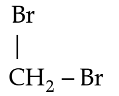
(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

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

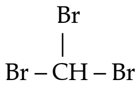
Ans.(i)

$CH_3 - Cl$ Chloromethane

$CH_3 - Br$ Bromomethane


$\overset{\substack{Br\\|}}{C}H_2 - Br$

Dibromomethane


$Br - \overset{\substack{Br\\|}}{C}H - Br$

Bromoform

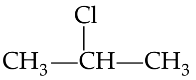
For alkyl halides containing the same alkyl group, the boiling point increases with an increase in the atomic mass of the halogen atom.

Since, the atomic mass of Br is greater than that of Cl, the boiling point of bromomethane is higher than that of chloromethane.

Further, for alkyl halides containing the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of Dibromomethane is higher than that of chloromethane and bromomethane, but lower than that of bromoform. Hence, the given set of compounds can be arranged in the order of their increasing boiling points as:

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

(ii)


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

Isopropyl chloride

$Cl—CH_2—CH_2—CH_3$

1 – Chloropropane

$Cl—CH_2—CH_2—CH_2—CH_3$

1 – Chlorobutane

For alkyl halides containing the same halide, the boiling point increases with an increase in the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than that of isopropyl chloride and 1-chloropropane.

Further, the boiling point decreases with an increase in branching in the chain. Thus, the boiling point of isopropyl alcohol is lower than that of 1-chloropropane. Hence, the given set of compounds can be arranged in the increasing order of their boiling points as: Isopropyl chloride < 1-Chloropropane < 1-chlorobutane.

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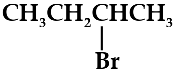
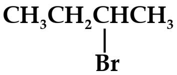
Q. 6.7. Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.

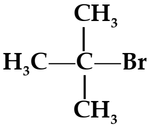
(i) $CH_3CH_2CH_2CH_2Br$ **or**


$CH_3CH_2\underset{\substack{|\\Br}}{C}HCH_3$

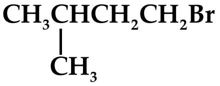
(ii)


$CH_3CH_2\underset{\substack{|\\Br}}{C}HCH_3$

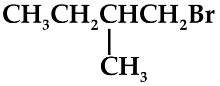
or


$H_3C—\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}—Br$

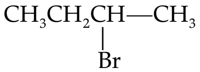
(iii)


$CH_3\underset{\substack{|\\CH_3}}{C}HCH_2CH_2Br$

or


$CH_3CH_2\underset{\substack{|\\CH_3}}{C}HCH_2Br$

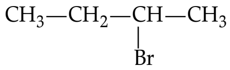
Ans. (i) $CH_3CH_2CH_2CH_2Br$


$CH_3CH_2\underset{\substack{|\\Br}}{C}H—CH_3$

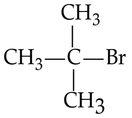
1 - Bromobutane(1°) **2 - Bromobutane(2°)**

2-Bromobutane is a 2° alkylhalide whereas 1-bromobutane is a 1° alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.

(ii)


$CH_3—CH_2—\underset{\substack{|\\Br}}{C}H—CH_3$

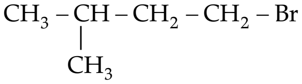
2 - Bromobutane(2°)


$CH_3—\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}—Br$

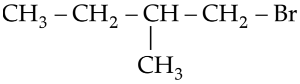
2 - Bromo - 2 - methylpropane(3°)

2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3° alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.

(iii)


$CH_3 - \underset{\substack{|\\CH_3}}{C}H - CH_2 - CH_2 - Br$

1 - Bromo - 3 - methylbutane(1°)

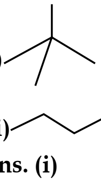

$CH_3 - CH_2 - \underset{\substack{|\\CH_3}}{C}H - CH_2 - Br$

1 - Bromo - 2 - methylpropane(1°)

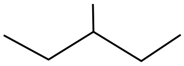
Both the alkyl halides are primary. However, the substituent $-CH_3$ is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo- 2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by S_N2 mechanism.

Q. 6.8. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

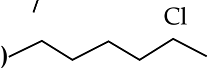
(i)



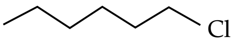
and



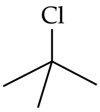
(ii)



and

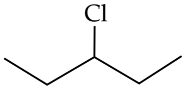


Ans. (i)



2 – Chloro – 2 – methylpropane (3°)

(I)

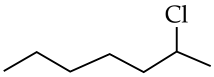


3 – Chloropentane (2°)

(II)

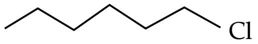
S_N1 reaction proceeds via the formation of carbocation. The alkyl halide (I) is 3° while (II) is 2°. Therefore, (I) forms 3° carbocation while (II) forms 2° carbocation. Greater the stability of the carbocation, faster is the rate of S_N1 reaction. Since, 3° carbocation is more stable than 2° carbocation. (I), i.e., 2−chloro-2-methylpropane, undergoes faster S_N1 reaction than (II), i.e., 3- chloropentane.

(ii)



2 – Chloroheptane (2°)

(I)

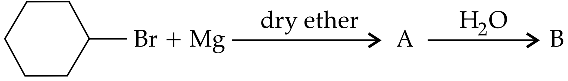


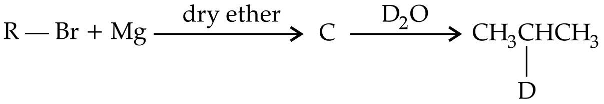
1 –Chlorohexane (1°)

(II)

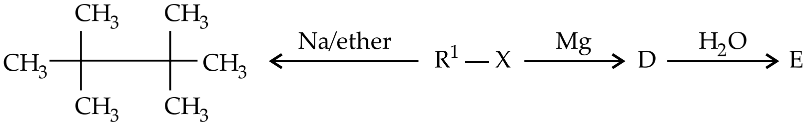
The alkyl halide (I) is 2° while (II) is 1°. 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2−chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

Q. 6.9. Identify A, B, C, D, E, R and R$_1$ in the following:



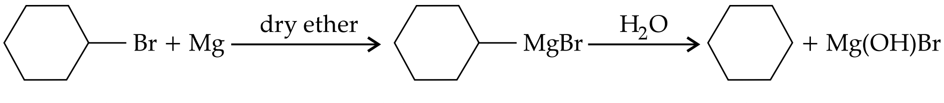


$$\mathrm{R-Br + Mg \xrightarrow{dry\ ether} C \xrightarrow{D_2O} CH_3\underset{\underset{D}{|}}{C}HCH_3}$$



$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xleftarrow{Na/ether} R^1-X \xrightarrow{Mg} D \xrightarrow{H_2O} E}$$

Ans.

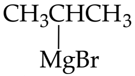


Bromocyclohexane

Cyclohexylmagnesium bromide (A)

Cyclohexane (B)

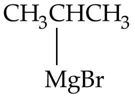
Since D of D_2O gets attached to the carbon atom to which MgBr is attached, C is



$$\mathrm{CH_3\underset{\underset{MgBr}{|}}{C}HCH_3}$$

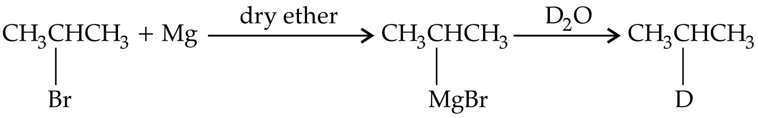
Isopropylmagnesium bromide

Therefore, the compound R − Br is



$$\mathrm{CH_3\underset{\underset{MgBr}{|}}{C}HCH_3}$$

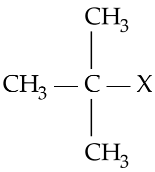
2 – Bromopropane



$$\mathrm{CH_3\underset{\underset{Br}{|}}{C}HCH_3 + Mg \xrightarrow{dry\ ether} CH_3\underset{\underset{MgBr}{|}}{C}HCH_3 \xrightarrow{D_2O} CH_3\underset{\underset{D}{|}}{C}HCH_3}$$

(C)

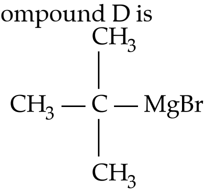
When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product. This is known as Wurtz reaction. Therefore, the halide, R^1−X, is



$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-X}$$

tert-Butylhalide

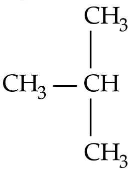
Therefore, compound D is



$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-MgBr}$$

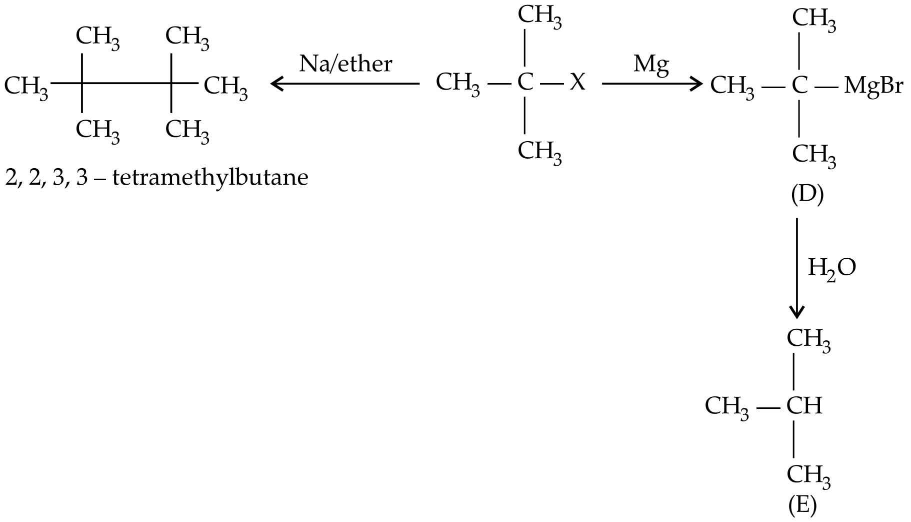
tert-Butylhalide

And, compound E is



$$\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}H}$$

2-Methylpropane

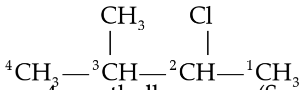


Exercise Questions

Q. 1. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:
[NCERT Ex. Q.6.1, Page 189]

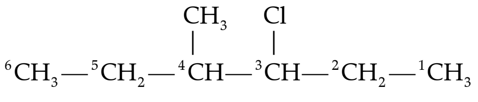
(i) $(CH_3)_2CHCH(Cl)CH_3$
(ii) $CH_3CH_2CH(CH_3)\ CH(C_2H_5)\ Cl$
(iii) $CH_3CH_2C(CH_3)_2CH_2I$
(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$
(v) $CH_3CH(CH_3)\ CH(Br)CH_3$
(vi) $CH_3C(C_2H_5)_2CH_2Br$
(vii) $CH_3C(Cl)(C_2H_5)\ CH_2CH_3$
(viii) $CH_3CH{=}C(Cl)CH_2CH(CH_3)_2$
(ix) $CH_3CH{=}CHC(Br)(CH_3)_2$
(x) *p*-$ClC_6H_4CH_2CH(CH_3)_2$
(xi) *m*-$ClCH_2C_6H_4CH_2C(CH_3)_3$
(xii) *o*-$Br\text{-}C_6H_4CH(CH_3)\ CH_2CH_3$

Ans. (i) 2−Chloro−3−methylbutane (Secondary alkyl halide)



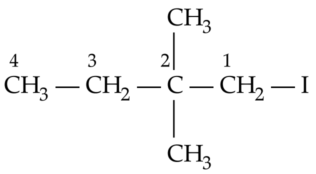
$${}^4CH_3-{}^3\overset{\overset{CH_3}{|}}{C}H-{}^2\overset{\overset{Cl}{|}}{C}H-{}^1CH_3$$

(ii) 3−Chloro−4−methylhexane (Secondary alkyl halide)



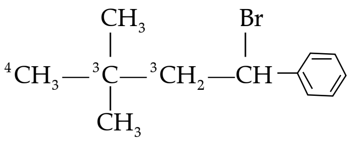
$${}^6CH_3-{}^5CH_2-{}^4\overset{\overset{CH_3}{|}}{C}H-{}^3\overset{\overset{Cl}{|}}{C}H-{}^2CH_2-{}^1CH_3$$

(iii) 1−Iodo−2, 2 –dimethylbutane (Primary alkyl halide)

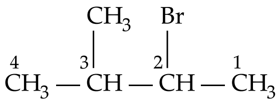


$$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{1}{CH_2}-I$$

(iv) 1−Bromo−3, 3−dimethyl−1−phenylbutane (Secondary benzyl halide)

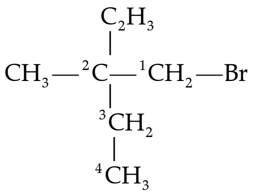


(v) 2−Bromo−3−methylbutane (Secondary alkyl halide)



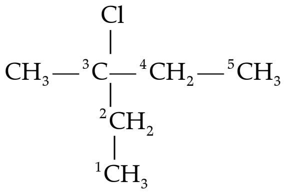
$$\overset{4}{CH_3}-\overset{\overset{CH_3}{|}}{\overset{3}{C}H}-\overset{\overset{Br}{|}}{\overset{2}{C}H}-\overset{1}{CH_3}$$

(vi) 1−Bromo−2−ethyl−2−methylbutane (Primary alkyl halide)



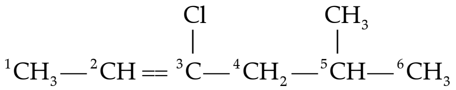
$$CH_3-{}^2\underset{\underset{\underset{{}^4CH_3}{|}}{{}^3CH_2}}{\overset{\overset{C_2H_3}{|}}{C}}-{}^1CH_2-Br$$

(vii) 3−Chloro−3−methylpentane (Tertiary alkyl halide)



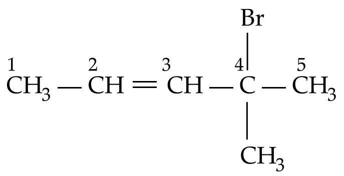
$$CH_3-{}^3\underset{\underset{\underset{{}^1CH_3}{|}}{{}^2CH_2}}{\overset{\overset{Cl}{|}}{C}}-{}^4CH_2-{}^5CH_3$$

(viii) 3−Chloro−5−methylhex−2−ene(Vinyl halide)



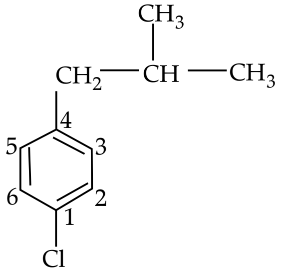
$${}^1CH_3-{}^2CH={}^3\overset{\overset{Cl}{|}}{C}-{}^4CH_2-{}^5\overset{\overset{CH_3}{|}}{C}H-{}^6CH_3$$

(ix) 4−Bromo−4−methylpent−2−ene (Allyl halide)

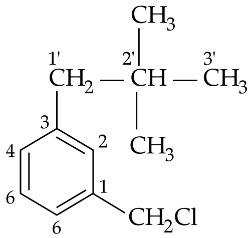


$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{\overset{4}{C}}}-\overset{5}{CH_3}$$

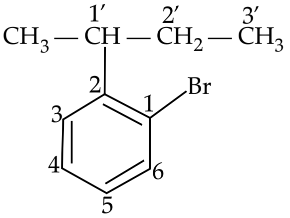
(x) 1−Chloro−4−(2−methylpropyl) benzene (Aryl halide)



(xi) 1−Chloromethyl−3−(2, 2−dimethylpropyl) benzene (Primary benzyl halide)



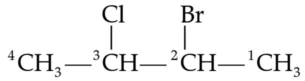
(xii) 1−Bromo−2−(1−methylpropyl) benzene (Aryl halide)



Q. 2.Give the IUPAC names of the following compounds: **[NCERT Ex. Q.6.2, Page 189]**

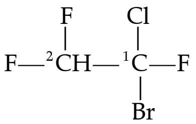
- **(i)** $CH_3CH(Cl)CH(Br)CH_3$
- **(ii)** $CHF_2CBrClF$
- **(iii)** $ClCH_2C \rightarrow CCH_2Br$
- **(iv)** $(CCl_3)_3CCl$
- **(v)** $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$
- **(vi)** $(CH_3)_3CCH{=}CClC_6H_4I\text{-}p$

Ans. (i) 2−Bromo−3−chlorobutane



$${}^{4}CH_3-{}^{3}\overset{Cl}{C}H-{}^{2}\overset{Br}{C}H-{}^{1}CH_3$$

(ii) 1−Bromo−1−chloro−1, 1, 2−trifluoroethane

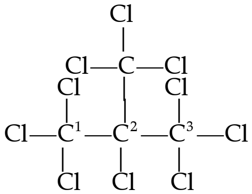


$$F-{}^{2}\overset{F}{C}H-{}^{1}\underset{Br}{\overset{Cl}{C}}-F$$

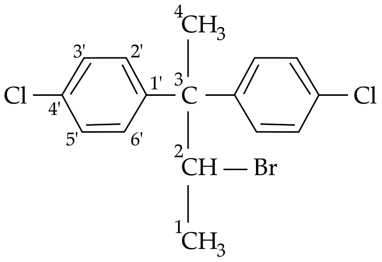
(iii) 1−Bromo−4−chlorobut−2−yne

$$Cl-\overset{4}{C}H_2-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_2-Br$$

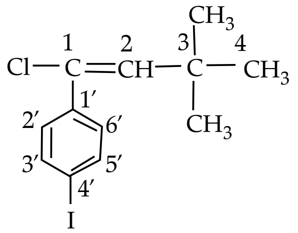
(iv) 2−(Trichloromethyl) −1,1,1,2,3,3,3−heptachloropropane



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



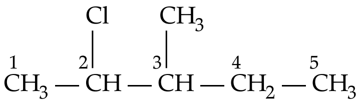
(vi) 1−chloro−1−(4−iodophenyl)−3, 3−dimethylbut−1−ene



Q. 3. Write the structures of the following organic halogen compounds. **[NCERT Ex. Q.6.3, Page 189]**

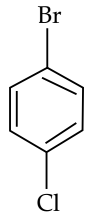
- **(i) 2-Chloro-3-methylpentane**
- **(ii) *p*-Bromochlorobenzene**
- **(iii) 1-Chloro-4-ethylcyclohexane**
- **(iv) 2-(2-Chlorophenyl)-1-iodooctane**
- **(v) Perfluorobenzene**
- **(vi) 4-tert-butyl-3-iodoheptane**
- **(vii) 1-Bromo-4-sec-butyl-2-methylbenzene**
- **(viii) 1,4-Dibromobut-2-ene**

Ans. (i) 2-Chloro-3-methylpentane

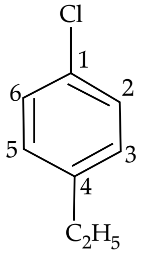


$$\overset{1}{C}H_3-\overset{Cl}{\overset{2}{C}}H-\overset{CH_3}{\overset{3}{C}}H-\overset{4}{C}H_2-\overset{5}{C}H_3$$

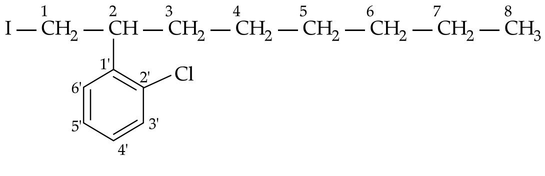
(ii) *p*-Bromochlorobenzene



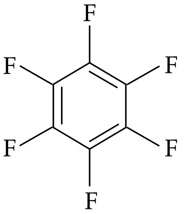
(iii) 1-Chloro-4-ethylcyclohexane



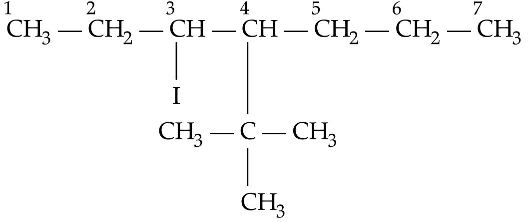
(iv) 2-(2-Chlorophenyl)-1-iodooctane



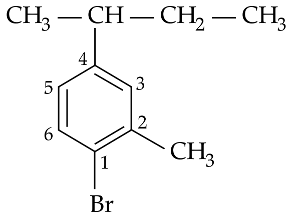
(v) Perfluorobenzene



(vi) 4-tert-butyl-3-iodoheptane



(vii) Bromo-4-sec-butyl-2-methylbenzene



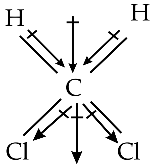
(viii) 1, 4-Dibromobut-2-ene

$$Br-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-Br$$

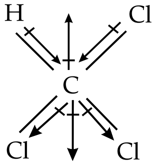
Q. 4. Which one of the following has the highest dipole moment? [NCERT Ex. Q.6.4, Page 189]

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

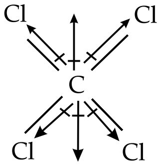
Ans. (i) Dichlormethane (CH_2Cl_2), $\mu = 1.60D$



(ii) Chloroform ($CHCl_3$), $\mu = 1.08D$



(iii) Carbon tetrachloride (CCl_4), $\mu = 0D$



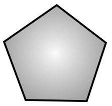
CCl_4 is a symmetrical molecule. Therefore, the dipole moments of all four C−Cl bonds cancel each other. Hence, its resultant dipole moment is zero.

As shown in the above figure, in $CHCl_3$, the resultant of dipole moments of two C−Cl bonds is opposed by the resultant of dipole moments of one C−H bond and one C−Cl bond. Since the resultant of one C−H bond and one C−Cl bond dipole moments is smaller than two C−Cl bonds, the opposition is to a small extent. As a result, $CHCl_3$ has a small dipole moment of 1.08 D.On the other hand, in case of CH_2Cl_2, the resultant of the dipole moments of two C−Cl bonds is strengthened by the resultant of the dipole moments of two C−H bonds. As a result, CH_2Cl_2 has a higher dipole moment of 1.60 D than $CHCl_3$, i.e., CH_2Cl_2 has the highest dipole moment. Hence, the given compounds can be arranged in the increasing order of their dipole moments as:

$$CCl_4 < CHCl_3 < CH_2Cl_2$$

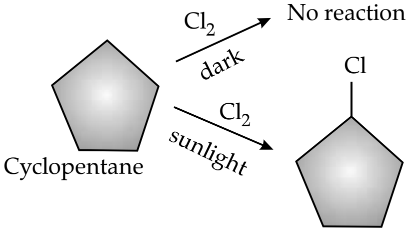
Q. 5. A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon. [NCERT Ex. Q.6.5, Page 189]

Ans. A hydrocarbon with the molecular formula, C_5H_{10} belongs to the group with a general molecular formula C_nH_{2n}. Therefore, it may either be an alkene or a cycloalkane. Since, hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane. Further, the hydrocarbon gives a single monochloro compound, C_5H_9Cl by reacting with chlorine in bright sunlight. Since a single monochloro compound is formed, the hydrocarbon must contain H−atoms that are all equivalent. Also, as all H−atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.



Cyclopentane (C_5H_{10})

The reactions involved in the question are:



Mono chlorocyclopentane (C_5H_{10})

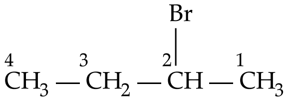
Q. 6. Write the isomers of the compound having formula C_4H_9Br. [NCERT Ex. Q.6.6, Page 189]

Ans. There are four isomers of the compound having the formula C_4H_9Br. These isomers are given below.

(a) 1−Bromobutane

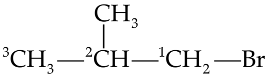
$$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-Br$$

(b) 2−Bromobutane



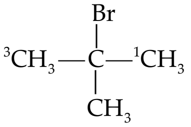
$$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{\underset{}{CH}}(Br)-\overset{1}{CH_3}$$

(c) 1−Bromo−2−methylpropane



$$^3CH_3-{}^2CH(CH_3)-{}^1CH_2-Br$$

(d) 2−Bromo−2−methylpropane



$$^{3}CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-{}^{1}CH_3$$

Q. 7.Write the equations for the preparation of 1−iodobutane from [NCERT Ex. Q.6.7, Page 189]

(i) 1-butanol

(ii) 1-chlorobutane

(iii) but-1-ene.

Ans.

(i) $$\underset{\text{I - Butanol}}{CH_3-CH_2-CH_2-CH_2-OH} + HI \xrightarrow{ZnCl_2} \underset{\text{I- Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I} + H_2O$$

(ii) $$\underset{\text{I – Chlorobutane}}{CH_3-CH_2-CH_2-CH_2-Cl} + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{dry acetone}} NaCl + \underset{\text{1– Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I}$$

(iii) $$CH_3-CH_2-CH=CH_2 + HBr \xrightarrow[\text{(Anti-Markovnikov's addition)}]{\text{Peroxide}} \underset{\text{I – Bromobutane}}{CH_3-CH_2-CH_2-CH_2-Br}$$

$$\underset{\text{I – Bromobutane}}{CH_3-CH_2-CH_2-CH_2-Br} \xrightarrow{\text{NaI/dry acetone}} NaBr + \underset{\text{1– Iodobutane}}{CH_3-CH_2-CH_2-CH_2-I}$$

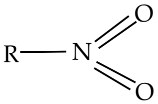
Q. 8.What are ambident nucleophiles? Explain with an example. [NCERT Ex. Q.6.8, Page 189]

Ans. Ambident nucleophiles are nucleophiles having two nucleophilic sites. Thus, ambident nucleophiles have two sites through which they can attack. For example, nitrite ion is an ambident nucleophile.

$$[^{-}O-\ddot{N}=O]$$

Nitrite ion can attack through oxygen resulting in the formation of alkyl nitrites. Also, it can attack through nitrogen resulting in the formation of nitroalkanes.

Alkylnitrite



Nitroalkane

Q. 9.Which compound in each of the following pairs will react faster in S_N2 reaction with $-OH$? [NCERT Ex. Q.6.9, Page 190]

(i) CH_3Br or CH_3I

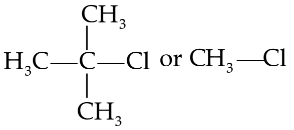
(ii) $(CH_3)_3CCl$ or CH_3Cl

Ans. (i) In the S_N2 mechanism, the reactivity of halides for the same alkyl group increases in the order. This happens because as the size increases, the halide ion becomes a better leaving group.

$$R-F << R-Cl < R-Br < R-I$$

Therefore, CH_3I will react faster than CH_3Br in S_N2 reactions with OH^-.

(ii)



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl \text{ or } CH_3-Cl$$

The S_N2 mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in case of $(CH_3)_3CCl$, the attack of the nucleophile at the carbon atom is hindered because of the presence of bulky substituents on that carbon atom bearing the leaving group. On the other hand, there are no bulky substituents on the carbon atom bearing the leaving group in CH_3Cl. Hence, CH_3Cl reacts faster than $(CH_3)_3CCl$ in S_N2 reaction with $-OH$.

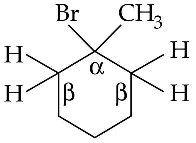
Q. 10. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene: [NCERT Ex. Q.6.10, Page 190]

(i) 1-Bromo-1-methylcyclohexane

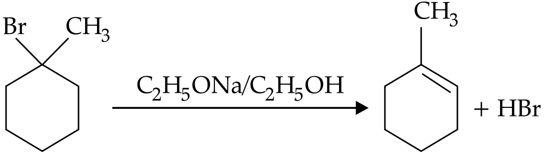
(ii) 2-Chloro-2-methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

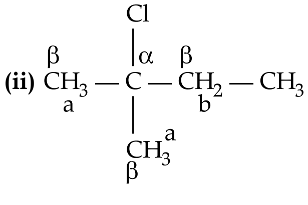
Ans. (i) 1−bromo−1−methylcyclohexane



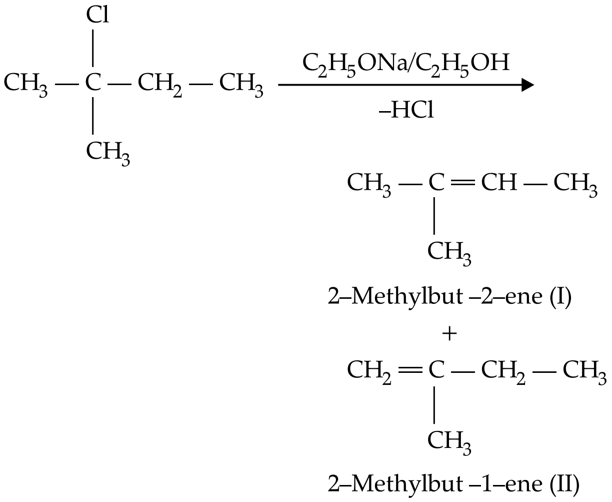
In the given compound, all β-hydrogen atoms are equivalent. Thus, dehydrohalogenation of this compound gives only one alkene.



(ii)



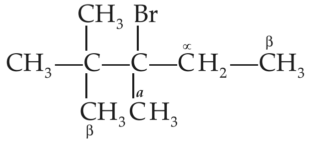
In the given compound, there are two different sets of equivalent β-hydrogen atoms labelled as *a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.



$$CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_2-CH_3 \xrightarrow[-HCl]{C_2H_5ONa/C_2H_5OH} \underset{\text{2–Methylbut –2–ene (I)}}{CH_3-\underset{CH_3}{C}=CH-CH_3} + \underset{\text{2–Methylbut –1–ene (II)}}{CH_2=\underset{CH_3}{C}-CH_2-CH_3}$$

Saytzeff's rule implies that in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced. Therefore, alkene (I) i.e., 2-methylbut-2-ene is the major product in this reaction.

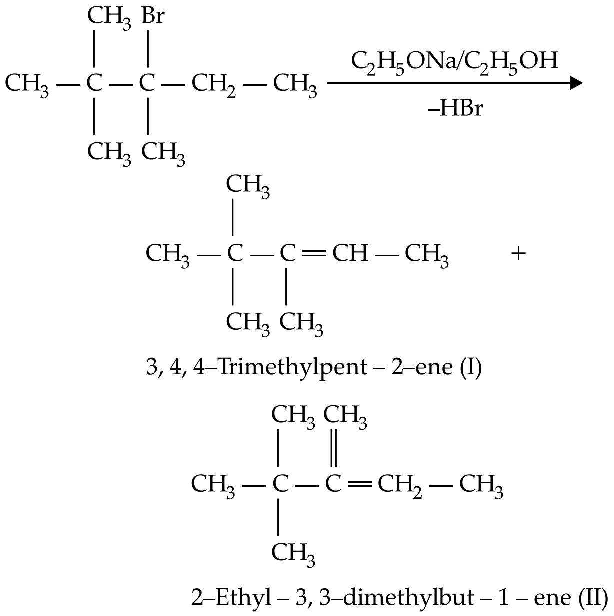
(iii)



$$CH_3-\underset{\underset{\beta}{CH_3}}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{Br}{C}}-\overset{\alpha}{C}H_2-\overset{\beta}{C}H_3$$

2, 2, 3-trimethyl-3-bromopentane

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



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

$$\underset{\text{3, 4, 4–Trimethylpent – 2–ene (I)}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{C}=CH-CH_3} + \underset{\text{2–Ethyl – 3, 3–dimethylbut – 1 – ene (II)}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\overset{CH_3}{\|}}{C}=CH_2-CH_3}$$

According to Saytzeff's rule, in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to the doubly bonded carbon atom is preferably formed. Hence, alkene (I), i.e., 3,4,4-trimethylpent-2-ene is the major product in this reaction.

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

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

[NCERT Ex. Q.6.11, Page 190]

Ans.

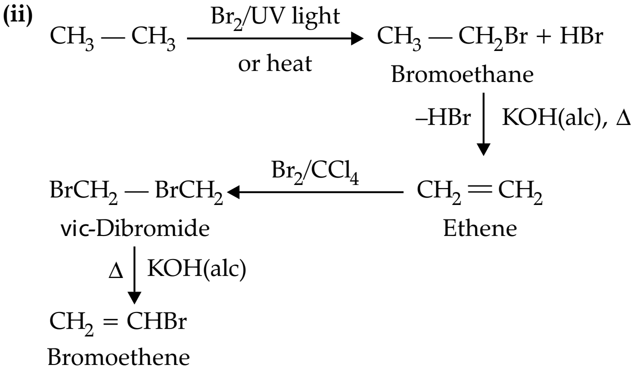
(i)

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{SOCl_2,\text{ Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2\uparrow + HCl$$

$$\underset{\text{Ethyne}}{HC=CH} + NaNH_2 \xrightarrow{\text{Liq. }NH_3} \underset{\text{Sodium acetylide}}{HC=\overset{-}{C}\overset{+}{Na}}$$

$$\underset{\text{Chloroethane}}{CH_3CH_2-Cl} + HC=\overset{-}{C}\overset{+}{Na} \rightarrow \underset{\text{But - 1 - yne}}{CH_3CH_2C=CH} + NaCl$$

(ii)



$$CH_3-CH_3 \xrightarrow[\text{or heat}]{Br_2/\text{UV light}} \underset{\text{Bromoethane}}{CH_3-CH_2Br} + HBr \xrightarrow[-HBr]{KOH(alc), \Delta} \underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow{Br_2/CCl_4} \underset{\text{vic-Dibromide}}{BrCH_2-BrCH_2} \xrightarrow[\Delta]{KOH(alc)} \underset{\text{Bromoethene}}{CH_2=CHBr}$$

(iii) $CH_3-CH_3=CH_2+HBr\xrightarrow{\text{Peroxide}}CH_3-CH_2-CH_2Br$

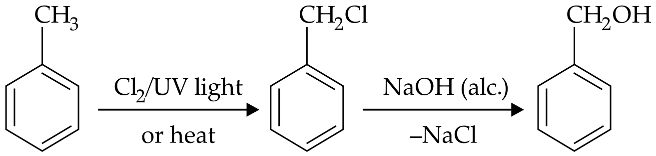
Propene　　1–Bromopropane

$\downarrow$ $AgNO_2$

$AgBr+CH_3-CH_2-CH_2NO_2$

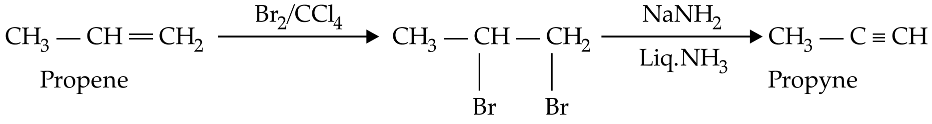
1–Nitropropane

(iv)



Toluene　　Benzyl chloride　　Benzyl alcohol

(v)



$$CH_3-CH=CH_2\xrightarrow{Br_2/CCl_4}CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}}\xrightarrow[\text{Liq.}NH_3]{NaNH_2}CH_3-C\equiv CH$$

Propene　　1,2-Dibromopropane　　Propyne

(vi) $CH_3-CH_2-OH\xrightarrow[-POCl_3,\ -HCl]{PCl_5}CH_3-CH_2-Cl$

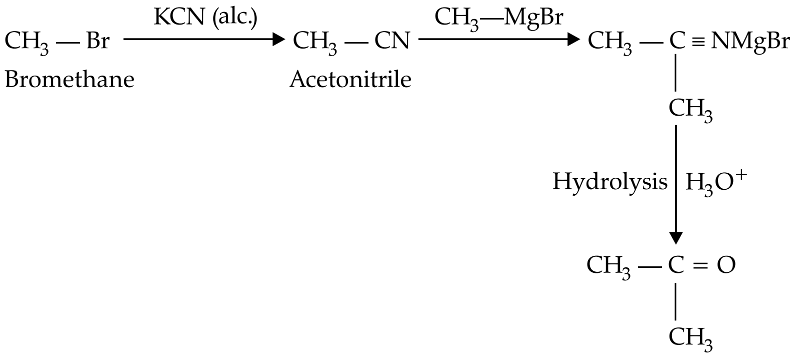
Ethanol　　Chloroethane

$\downarrow$ AgF

CH_3-CH_2-F

Ethyl fluoride

(vii)



$$CH_3-Br\xrightarrow{\text{KCN (alc.)}}CH_3-CN\xrightarrow{CH_3-MgBr}CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}\equiv NMgBr$$

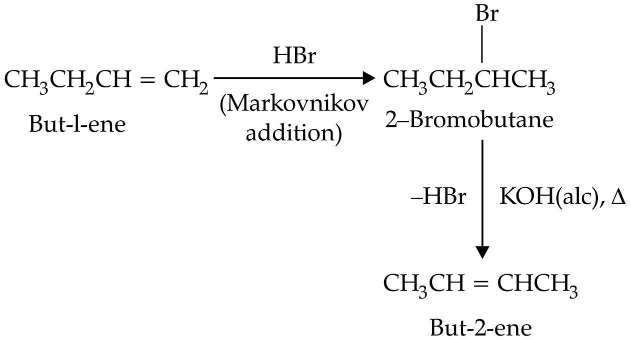
Bromethane　　Acetonitrile

Hydrolysis $\downarrow$ H_3O^+

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O$$

Propanone

(viii)



$$CH_3CH_2CH=CH_2\xrightarrow[\text{(Markovnikov addition)}]{HBr}CH_3CH_2\overset{\displaystyle Br}{\overset{|}{C}H}CH_3$$

But-l-ene　　2–Bromobutane

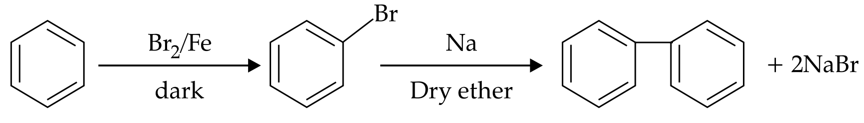
–HBr $\downarrow$ KOH(alc), Δ

$CH_3CH=CHCH_3$

But-2-ene

(ix) $$\underset{\text{1-chlorobutane}}{2CH_3CH_2CH_2CH_2Cl} + 2Na \xrightarrow[\text{Wurtz reaction}]{\text{Dry ether}} \underset{\text{(n-octane)}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3} + 2NaCl$$

(x)



Benzene Bromobenzene Diphenyl

Q. 12. Explain why:

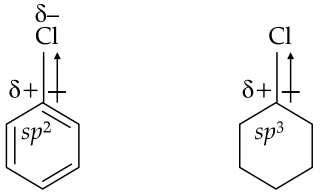
(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

[NCERT Ex. Q.6.12, Page 190]

Ans. (i)



Chlorobenzene Cyclohexyl chloride

In chlorobenzene, the Cl-atom is linked to a *sp*^{2} hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to a *sp*^{3} hybridized carbon atom. Now, *sp*^{2} hybridized carbon has more s-character than *sp*^{3} hybridized carbon atom. Therefore, the former is more electronegative than the latter.

Therefore, the density of electrons of C–Cl bond near the Cl-atom is less in chlorobenzene than in cyclohexyl chloride.Moreover, the –R effect of the benzene ring of chlorobenzene decreases the electron density of the C–Cl bond near the Cl-atom. As a result, the polarity of the C–Cl bond in chlorobenzene decreases. Hence, the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(ii) To be miscible with water, the solute-water force of attraction must be stronger than the solute solute and water-water forces of attraction. Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the alkyl halide-alkyl halide and water-water forces of attraction. Hence, alkyl halides (though polar) are immiscible with water.

(iii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes.Therefore, grignard reagents should be prepared under anhydrous conditions.

$$\underset{\text{Grigrard reagent}}{\overset{\delta-}{R}\overset{\delta+}{Mg}\overset{\delta-}{X}} + H_2O \longrightarrow \underset{\text{Alkane}}{R-H} + Mg(OH)X$$

Q. 13. Give the uses of Freon-12, DDT, carbon tetrachloride and iodoform. [NCERT Ex. Q.6.13, Page 190]

Ans.Uses of Freon–12

Freon-12 (dichlorodifluoromethane, CF_2Cl_2) is commonly known as CFC. It is used as a refrigerant in refrigerators and air conditioners. It is also used in aerosol spray propellants such as body sprays, hair sprays, etc. However, it damages the ozone layer. Hence, its manufacture was banned in the United States and many other countries in 1994.

Uses of DDT

DDT (*p, p*–dichlorodiphenyltrichloroethane) is one of the best-known insecticides. It is very effective against mosquitoes and lice. But due its harmful effects, it was banned in the United States in 1973.

Uses of carbontetrachloride (CCl_4)

(i) It is used for manufacturing refrigerants and propellants for aerosol cans.

(ii) It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

(iii) It is used as a solvent in the manufacture of pharmaceutical products.

(iv) Until the mid-1960's, carbon tetrachloride was widely used as a cleaning fluid, a degreasing agent in industries, a spot reamer in homes, and a fire extinguisher.

Uses of iodoform (CHI_3)

Iodoform was used earlier as an antiseptic, but now it has been replaced by other formulations containing iodine-due to its objectionable smell. The antiseptic property of iodoform is only due to the liberation of free iodine when it comes in contact with the skin.

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

[NCERT Ex. Q.6.14, Page 190]

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$

(ii) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}$

(iv) $CH_3CH_2Br + KCN \xrightarrow{\text{aq. ethanol}}$

(v) $C_6H_5ONa + C_2H_5Cl \rightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \rightarrow$

(vii) $CH_3CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}}$

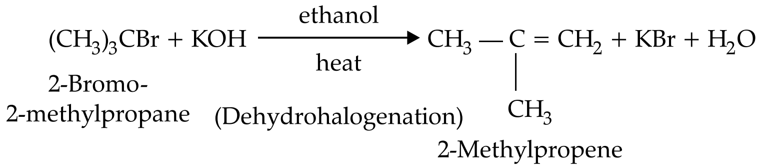
(viii) $CH_3CH{=}C(CH_3)_2 + HBr \rightarrow$

Ans.

(i) $$\underset{\text{1 – Chloropropane}}{CH_3CH_2CH_2Cl} + NaI \xrightarrow[\text{heat}]{\text{acetone}} \underset{\text{1 – Iodopropane}}{CH_3CH_2CH_2I} + NaCl$$

(Finkelstein reaction)

(ii)



$$\underset{\text{2-Bromo-2-methylpropane}}{(CH_3)_3CBr} + KOH \xrightarrow[\text{heat}]{\text{ethanol}} \underset{\text{2-Methylpropene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2} + KBr + H_2O$$

(Dehydrohalogenation)

(iii) $$\underset{\text{2 – Bromobutane}}{CH_3CH(Br)CH_2CH_3} + NaOH \xrightarrow{\text{Water}} \underset{\text{Butan– 2 – ol}}{CH_3CH(OH)CH_2CH_3} + NaBr$$

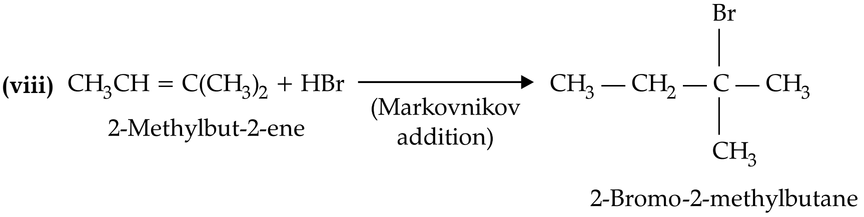
(iv) $$\underset{\text{Bromobutane}}{CH_3CH_2Br} + KCN \xrightarrow[\text{(Nucleophilic substitution)}]{\text{aq. ethanol}} \underset{\text{Cyanoethane}}{CH_3H_2CN} + KBr$$

(v) $$\underset{\text{Sodium phenoxide}}{C_6H_5ONa} + \underset{\text{Chloroethane}}{C_2H_5Cl} \xrightarrow[\text{(Williamson synthesis)}]{} \underset{\text{Phenetole}}{C_6H_5-O-C_2H_5} + NaCl$$

(vi) $$\underset{\text{1 – Propanol}}{CH_3CH_2CH_2OH} + SOCl_2 \longrightarrow \underset{\text{1 – Chloropropane}}{CH_3CH_2CH_2Cl} + SO_2\uparrow + HCl$$

(vii) $$\underset{\text{But – 1 – ene}}{CH_3CH_2CH=CH_2} + HBr \xrightarrow[\text{(Anti–Markovnikov's addition)}]{\text{Peroxide}} \underset{\text{1 – Bromobutane}}{CH_3CH_2CH_2CH_2-Br}$$

(viii)



$$\underset{\text{2-Methylbut-2-ene}}{CH_3CH=C(CH_3)_2} + HBr \xrightarrow[\text{(Markovnikov addition)}]{} CH_3-CH_2-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

2-Bromo-2-methylbutane

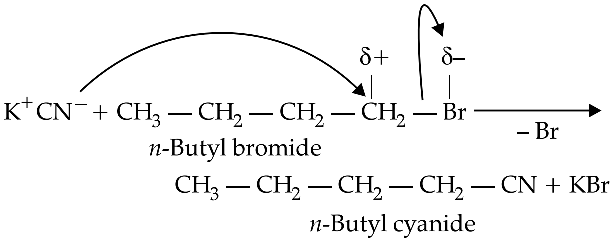
Q. 15. Write the mechanism of the following reaction: **[NCERT Ex. Q.6.15, Page 190]**

$$nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$$

Ans. The given reaction is:

$$nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$$

The given reaction is an S_N2 reaction. In this reaction, CN^- acts as the nucleophile and attacks the carbon atom to which Br is attached. CN^- ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



$$K^+CN^- + \underset{n\text{-Butyl bromide}}{CH_3-CH_2-CH_2-\overset{\delta+}{CH_2}-\overset{\delta-}{Br}} \xrightarrow[-\,Br]{} \underset{n\text{-Butyl cyanide}}{CH_3-CH_2-CH_2-CH_2-CN} + KBr$$

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

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

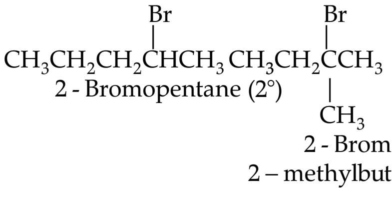
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2- methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1Bromo-3- methylbutane. **[NCERT Ex. Q.6.16, Page 190]**

Ans. (i)

$CH_3CH_2CH_2CH_2CH_2-Br$

1 – Bromopentane (1°)



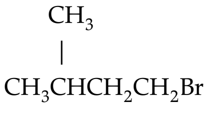
$$\underset{\text{2 - Bromopentane (2°)}}{CH_3CH_2CH_2\overset{\overset{Br}{|}}{C}HCH_3} \quad \underset{\text{2 - Bromo - 2 – methylbutane (3°)}}{CH_3CH_2\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3}$$

An S_N2 reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards S_N2 displacement decreases. Due to the presence of substituent, hindrance to the approaching nucleophile increases in the following order.

1- Bromopentane < 2-bromopentane < 2-Bromo-2-methylbutane

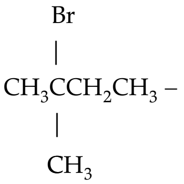
Hence, the increasing order of reactivity towards S_N2 displacement is: 2-Bromo-2- methylbutane < 2-Bromopentane < 1-Bromopentane

(ii)



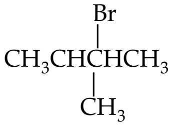
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2Br$

1 - Bromo - 3 - methylbutane(1°)



$CH_3\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_3$ –

2 - Bromo - 2 methylbutane(3°)



$CH_3CH\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}HCH_3$

2 - Bromo - 3 methylbutane(2°)

Since steric hindrance in alkyl halides increases in the order of 1° < 2° < 3°, the increasing order of reactivity towards S_N2 displacement is 3° < 2° < 1°.

Hence, the given set of compounds can be arranged in the increasing order of their reactivity towards S_N2 displacement as:

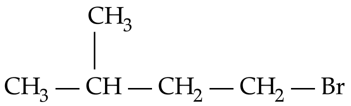
2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane.

[2- Bromo-3-methylbutane is incorrectly given in NCERT]

(iii)

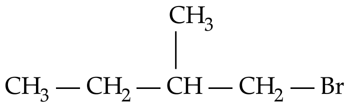
$CH_3 — CH_2 — CH_2 — CH_2 — Br$

1– Bromobutane



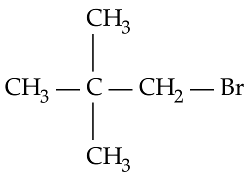
$CH_3 — \overset{\overset{CH_3}{|}}{C}H — CH_2 — CH_2 — Br$

1– Bromo – 3 – methylbutane



$CH_3 — CH_2 — \overset{\overset{CH_3}{|}}{C}H — CH_2 — Br$

1– Bromo – 2 – methylbutane



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

1–Bromo – 2, 2 – dimethylpropar

The steric hindrance to the nucleophile in the S_N2 mechanism increases with a decrease in the distance of the substituents from the atom containing the leaving group. Further, the steric hindrance increases with an increase in the number of substituents. Therefore, the increasing order of steric hindrances in the given compounds is as below:

1-Bromobutane < 1-Bromo-3-methylbutane < 1-Bromo-2-methylbutane < 1-Bromo-2, 2-dimethylpropane

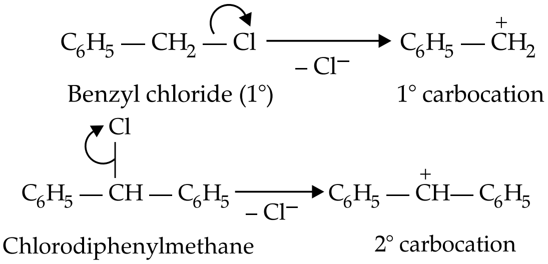
Hence, the increasing order of reactivity of the given compounds towards S_N2 displacement is:

1-Bromo-2, 2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3- ethylbutane < 1- Bromobutane

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

[NCERT Ex. Q.6.17, Page 190]

Ans.

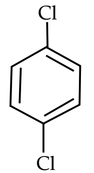


Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. Now, $C_6H_5CH_2Cl$ forms 1°-carbocation, while $C_6H_5CHClC_6H_5$ forms 2°-carbocation, which is more stable than 1°-carbocation. Hence, $C_6H_5CHClC_6H_5$ is hydrolyzed more $C_6H_5CH_2Cl$ easily than by aqueous KOH.

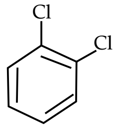
Q. 18. *p*-Dichlorobenzene has higher m.p. and lower solubility than those of *o*- and *m*-isomers. Discuss.

[NCERT Ex. Q.6.18, Page 190]

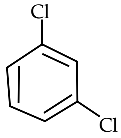
Ans.



p- Dichlorobenzene



o- Dichlorobenzene



m- Dichlorobenzene

p-Dichlorobenzene is more symmetrical than *o*-and *m*-isomers. For this reason, it fits more closely than *o*-and *m*-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of *p*-dichlorobenzene. As a result, *p*-dichlorobenzene has a higher melting point and lower solubility than *o*-and *m*-isomers.

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

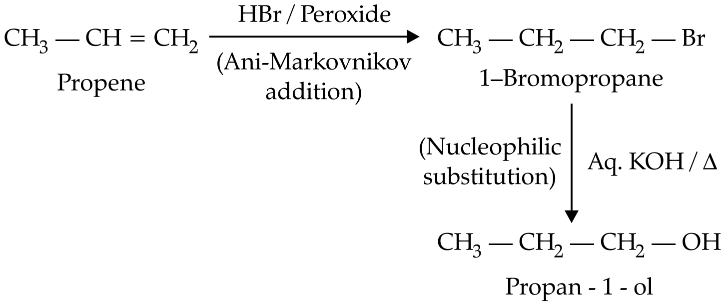
- **(i) Propene to propan-1-ol**
- **(ii) Ethanol to but-1-yne**
- **(iii) 1-Bromopropane to 2-bromopropane**
- **(iv) Toluene to benzyl alcohol**
- **(v) Benzene to 4-bromonitrobenzene**
- **(vi) Benzyl alcohol to 2-phenylethanoic acid**
- **(vii) Ethanol to propanenitrile**
- **(viii) Aniline to chlorobenzene**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

(xiii) **2-Chloropropane to 1-propanol**
(xiv) **Isopropyl alcohol to iodoform**
(xv) **Chlorobenzene to *p*-nitrophenol**
(xvi) **2-Bromopropane to 1-bromopropane**
(xvii) **Chloroethane to butane**
(xviii) **Benzene to diphenyl**
(xix) ***tert*-Butyl bromide to isobutyl bromide**
(xx) **Aniline to phenylisocyanide**

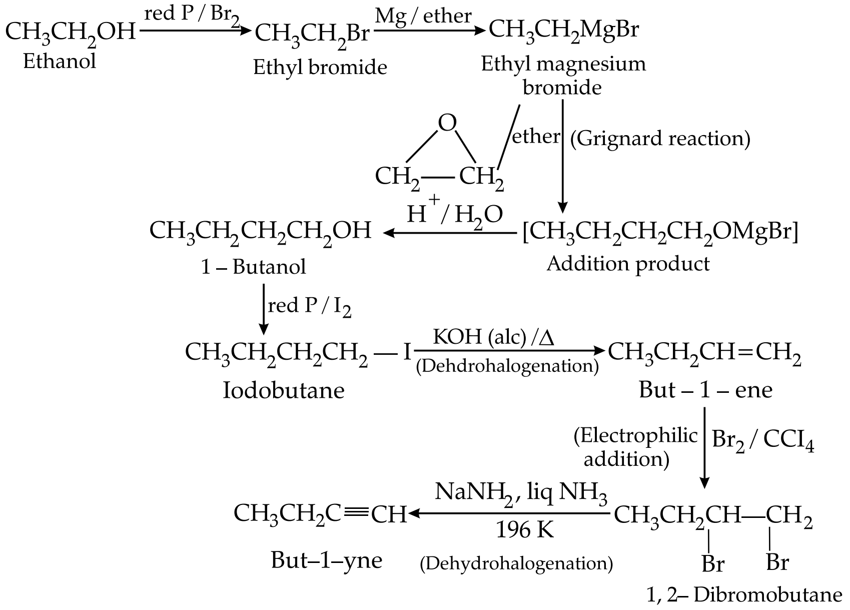
[NCERT Ex. Q.6.19, Page 190-191]

Ans.

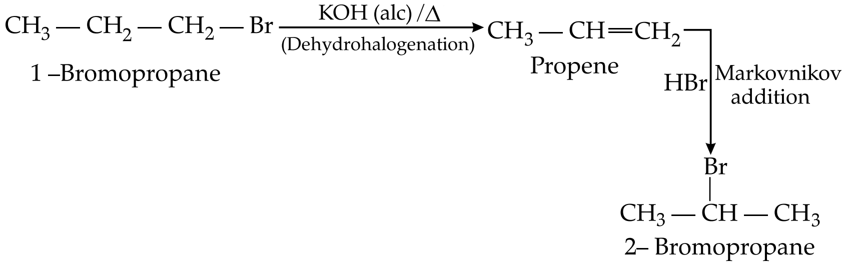
(i)



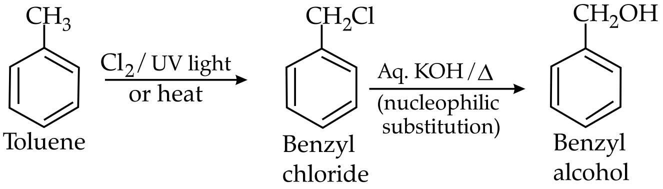
(ii)



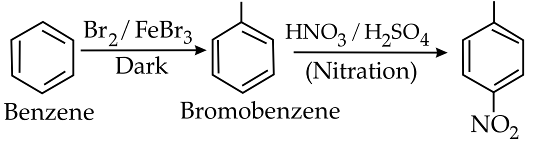
(iii)



(iv)

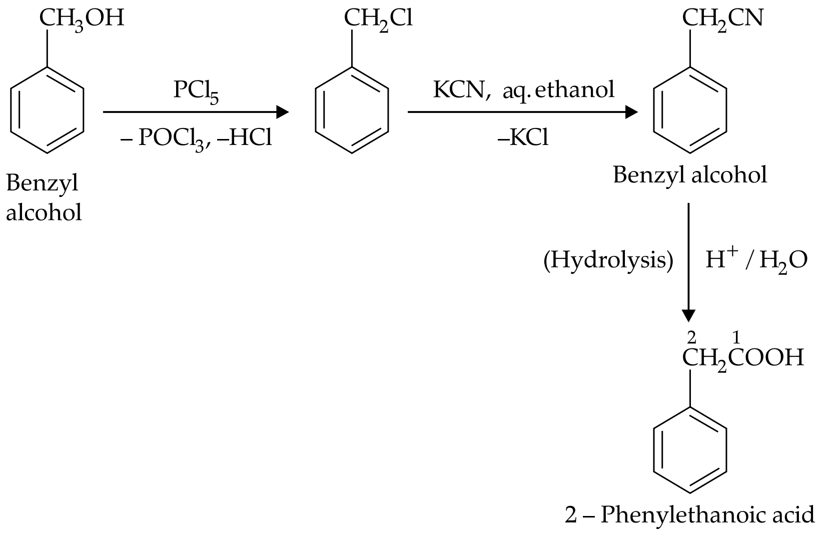


(v)



4 – Bromonitrobenzene

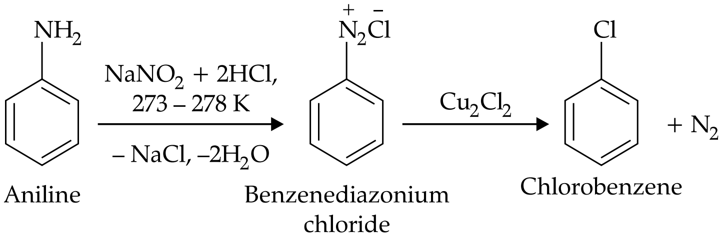
(vi)



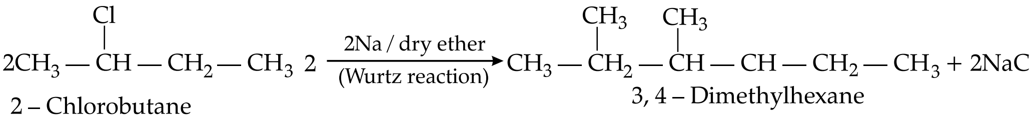
(vii)

$$\underset{\text{Ethanol}}{CH_3 — CH_2 — OH} \xrightarrow{\text{red P / Br}_2} \underset{\text{Bromoethane}}{CH_3 — CH_2 — Br} \xrightarrow{\text{KCN, Aq. ethanol}} \underset{\text{Propanenitrile}}{CH_3 — CH_2 — CN}$$

(viii)

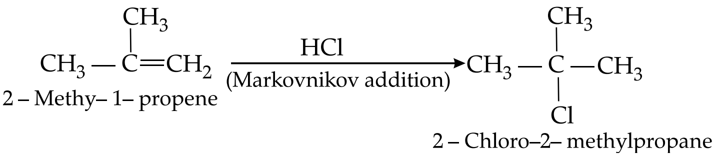


(ix)



$$\underset{\text{2 – Chlorobutane}}{2CH_3 — \overset{\displaystyle Cl}{\overset{|}{C}H} — CH_2 — CH_3}\ 2 \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na / dry ether}} \underset{\text{3, 4 – Dimethylhexane}}{CH_3 — \overset{\displaystyle CH_3}{\overset{|}{C}H_2} — \overset{\displaystyle CH_3}{\overset{|}{C}H} — CH — CH_2 — CH_3} + 2NaC$$

(x)



$$\underset{\text{2 – Methy– 1– propene}}{CH_3 — \overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2} \xrightarrow[\text{(Markovnikov addition)}]{\text{HCl}} \underset{\text{2 – Chloro–2– methylpropane}}{CH_3 — \underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} — CH_3}$$

(xi)

$$\underset{\text{Ethylchloride}}{CH_3 — CH_2 — Cl} \xrightarrow[\text{(Nucleophilic substitution)}]{\text{KCN,aq.ethanol}} \underset{\text{Propanenitrile}}{CH_3 — CH_2 — CN} + KCl$$

$$\text{(Hydrolysis)} \Big\downarrow H^+ / H_2O$$

$$\underset{\text{Propanoic acid}}{CH_3 — CH_2 — COOH}$$

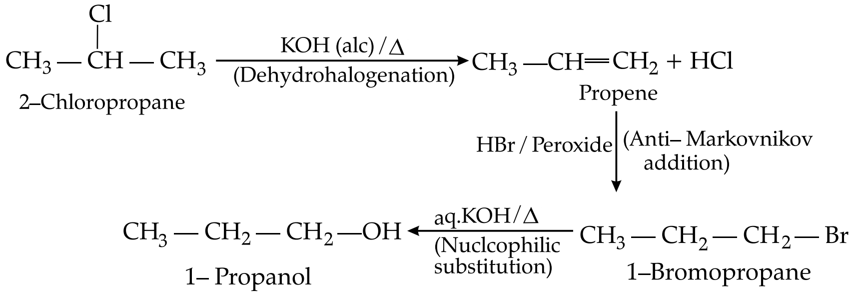
(xii)

$$\underset{\text{But–1– ene}}{CH_3 —CH_2 — CH{=}CH_2} \xrightarrow[\text{(Anti–Markovnikov addition)}]{\text{HBr / Peroxide}} \underset{\text{1–Bromobutane}}{CH_3 — CH_2 —CH_2 —CH_2 —Br}$$

$$\begin{matrix}\text{Finkelstein}\\\text{reaction}\end{matrix} \Big\downarrow \text{NaI, dry acetone}$$

$$\underset{n\text{– Butyliodide}}{CH_3—CH_2—CH_2—CH_2—I}$$

(xiii)

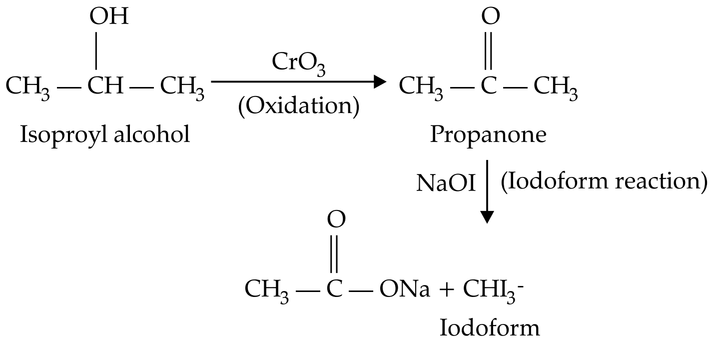


$$CH_3-\overset{\displaystyle Cl}{\overset{|}{C}}H-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc) / }\Delta} CH_3-CH=CH_2 + HCl$$

$$CH_3-CH=CH_2 \xrightarrow[\text{(Anti– Markovnikov addition)}]{\text{HBr / Peroxide}} CH_3-CH_2-CH_2-Br$$

$$CH_3-CH_2-CH_2-OH \xleftarrow[\text{(Nuclcophilic substitution)}]{\text{aq.KOH/}\Delta} CH_3-CH_2-CH_2-Br$$

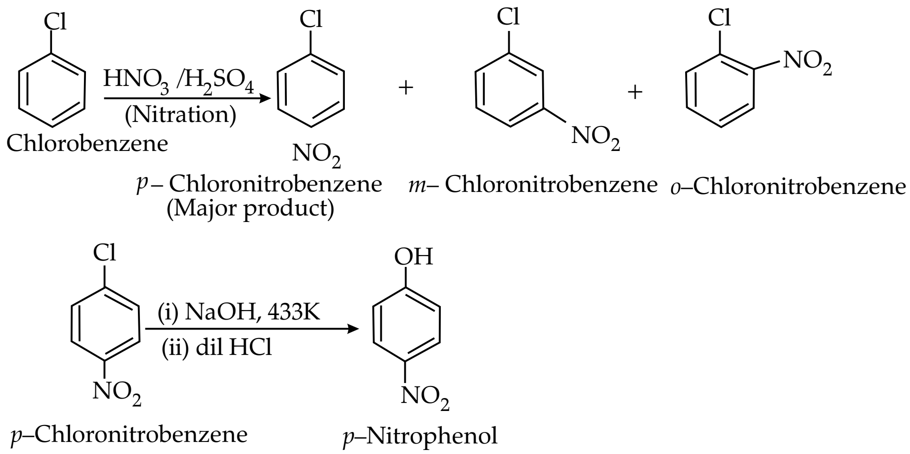
(xiv)



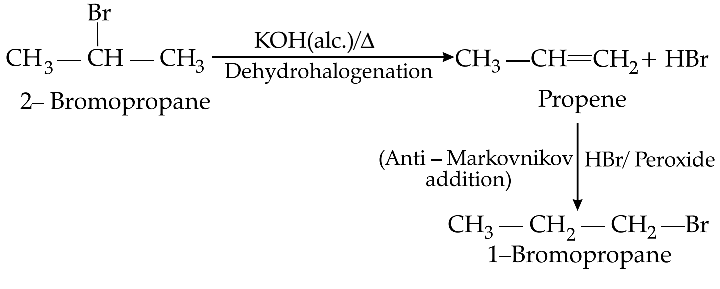
$$CH_3-\overset{\displaystyle OH}{\overset{|}{C}}H-CH_3 \xrightarrow[\text{(Oxidation)}]{CrO_3} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{(Iodoform reaction)}]{NaOI} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-ONa + CHI_3{}^{-}$$

(xv)



(xvi)



$$CH_3-\overset{\displaystyle Br}{\overset{|}{C}}H-CH_3 \xrightarrow[\text{Dehydrohalogenation}]{\text{KOH(alc.)/}\Delta} CH_3-CH=CH_2 + HBr$$

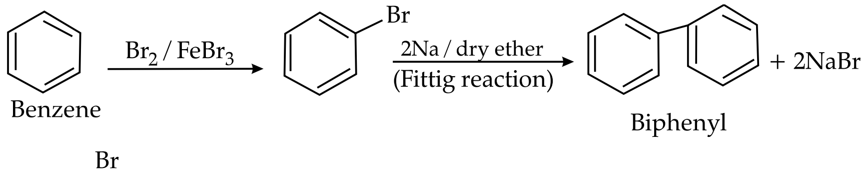
$$CH_3-CH=CH_2 \xrightarrow[\text{(Anti – Markovnikov addition)}]{\text{HBr/ Peroxide}} CH_3-CH_2-CH_2-Br$$

(xvii)

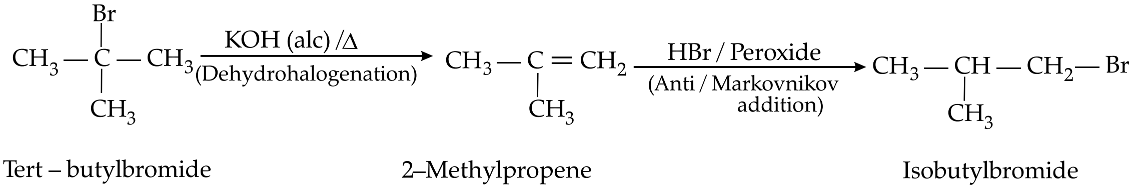
$$CH_3-CH_2-Cl \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/ dry ether}} CH_3-CH_2-CH_2-CH_3 + 2NaCl$$

Chloroethane Butane

(xviii)

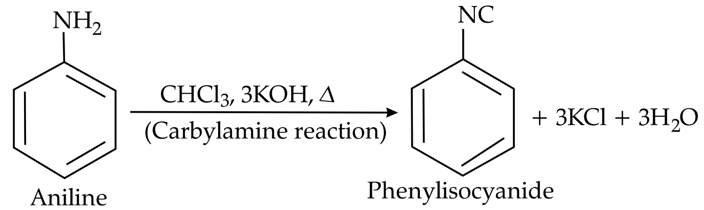


(xix)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Br}{\overset{|}{C}}}}-CH_3 \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc) /}\Delta} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow[\text{(Anti / Markovnikov addition)}]{\text{HBr / Peroxide}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-Br$$

(xx)



Aniline

Phenylisocyanide

Q. 20. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain. [NCERT Ex. Q.6.20, Page 191]

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

$$\underset{\text{Alkyl chloride}}{R-Cl} + KOH_{(aq)} \longrightarrow \underset{\text{Alcohol}}{R-OH} + KCl$$

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

$$\underset{\text{Alkyl chloride}}{R-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-Cl} + KOH_{(alc)} \longrightarrow \underset{\text{Alkene}}{R-CH{=}CH_2} + KCl + H_2O$$

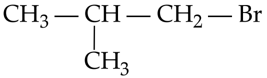
OH^- ion is a much weaker base than RO^- ion. Also, OH^- ion is highly solvated in an aqueous solution and as a result, the basic character of OH^- ion decreases. Therefore, it cannot abstract a hydrogen from the β-carbon.

Q. 21. Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when *n*-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions. [NCERT Ex. Q.6.21, Page 191]

Ans. There are two primary alkyl halides having the formula, C_4H_9Br. They are *n*-bulyl bromide and isobutyl bromide.

$$CH_3-CH_2-CH_2-CH_2-Br$$

n– Butylbromide



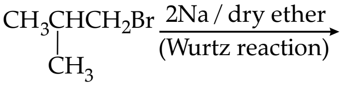
$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{CH}-CH_2-Br}$$

Isobutyl bromide

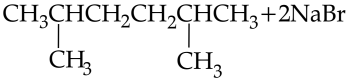
Therefore, compound (a) is either *n*–butyl bromide or isobutyl bromide.

Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, C_8H_{18}, which is different from the compound formed when *n*–butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

$$\underset{n\text{– Butyl bromide}}{2CH_3CH_2CH_2CH_2Br} \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/ dry ether}} \underset{n\text{– Octane}}{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3} + 2NaBr$$

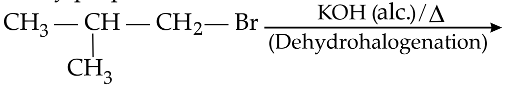


$$\underset{\substack{\text{Isobutyl bromide}\\\text{(a)}}}{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2Br} \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na / dry ether}}$$

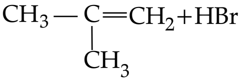


$$\underset{\substack{\text{2, 5 – Dimethylhexane}\\\text{(b)}}}{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3} + 2NaBr$$

Thus, compound (d) is 2, 5–dimethylhexane. It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence,compound (b) is 2–methylpropene.

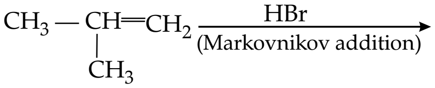


$$\underset{\substack{\text{Isobutyl bromide}\\\text{(a)}}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-Br} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH (alc.)/}\Delta}$$

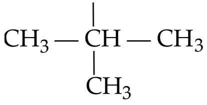


$$\underset{\substack{\text{2– Methylpropene}\\\text{(b)}}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2} + HBr$$

Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2–bromo–2–methylpropane.



$$\underset{\substack{\text{2– Methylpropene}\\\text{(b)}}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}{=}CH_2} \xrightarrow[\text{(Markovnikov addition)}]{\text{HBr}}$$



$$\underset{\substack{\text{2– Bromo –2– Methylpropane}\\\text{(c)}}}{CH_3-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}-CH_3}$$

Q. 22. What happens when

(i) *n*-butyl chloride is treated with alcoholic KOH,

(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

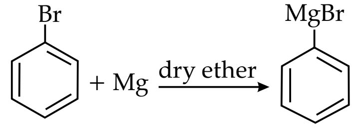
(vi) methyl chloride is treated with KCN.

[NCERT Ex. Q.6.22, Page 191]

Ans. (i) When $n-$butyl chloride is treated with alcoholic KOH, the formation of but$-1-$ene takes place. This reaction is a dehydrohalogenation reaction.

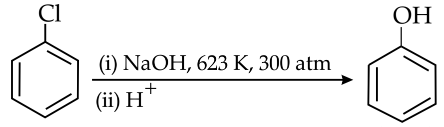
$$\underset{n\text{– Butyl chloride}}{CH_3-CH_2-CH_2-CH_2-Cl} \xrightarrow[\text{Dehydrohalogenation}]{\text{KOH (alc.)}/\Delta} \underset{\text{But–1–ene}}{CH_3-CH_2-CH{=}CH_2+KCl+H_2O}$$

(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.



Bromobenzene Phenylmagnesium bromide

(iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.



Chlorobenzene Phenol

(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} \xrightarrow[\text{(Hydrolysis)}]{\text{KOH}} \underset{\text{Ethanol}}{CH_3-CH_2-OH+KCl}$$

(v) When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction.

$$\underset{\text{Methyl bromide}}{2CH_3-Br} + 2Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3+2NaBr}$$

(vi) When methyl chloride is treated with KCN, it undergoes a substitution reaction to give methyl cyanide.

$$\underset{\text{Methy chloride}}{CH_3-Cl} + KCN \xrightarrow[\text{substitution}]{\text{Nucleophilic}} \underset{\text{Methyl cyanide}}{CH_3-CN+KCl}$$