DAY THIRTY

Haloalkanes and Haloarenes

Learning & Revision for the Day

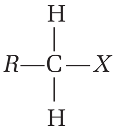
- Haloalkanes
- Haloarenes
- Polyhalogen Compounds

The replacement of hydrogen atom(s) from a hydrocarbon (aliphatic or aromatic) by halogen atom(s) results in the formation of **haloalkanes** (alkyl halides) or **haloarenes** (aryl halides). These may be classified as mono, di or trihalo compounds depending upon the number of halogen atoms.

Haloalkanes

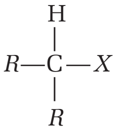
These are the compounds in which halogen atom (i.e. Cl, Br, I) is directly attached to sp^3-hybridised C-atom of alkyl group.

e.g.



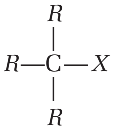
$$R-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-X$$

1° (primary)



$$R-\overset{\displaystyle H}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-X$$

2° (secondary)



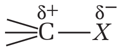
$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-X$$

3° (tertiary)

- **Nomenclature** According to IUPAC system of nomenclature, name of a haloalkane is obtained by adding halo (e.g. chloro, bromo, iodo) as prefix with the corresponding alkane. In dihaloalkane, when both halogen atoms are attached to the same carbon atom, they are said to be in *geminal* (*gem*) position. They are commonly called **alkylidene halides**.
    (i) When the two halogen atoms are on the adjacent carbon atoms, they are said to be in the *vicinal* (*vic*) position. They are commonly called alkylene dihalides.
    (ii) When two halogen atoms are at each of the terminal carbon atoms (α, ω), they are named as polymethylene halides.

Haloalkane	IUPAC Name
CH_3Cl	Chloromethane
CH_3CH_2Cl	Chloroethane
CH_2Cl_2	Dichloromethane
$CHCl_3$	Trichloromethane (chloroform)
CHI_3	Triiodomethane (iodoform)
CCl_4	Tetrachloromethane
CH_3CHCl_2	1,1-dichloroethane (ethylidene chloride)
CH_2BrCH_2Br	1,2,-dibromoethane (ethylene dibromide)
$CH_2BrCH_2CH_2CH_2Br$	1,4-dibromobutane (tetramethylene dibromide)

- **Nature of C—*X* Bond** As halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



$$\overset{\delta+}{C}—\overset{\delta-}{X}$$

Methods of Preparation

The various methods preparation of haloalkanes are given below :

- Haloalkanes can be obtained **from alcohols** by the reaction with halogen acids or phosphorus halides (PX_5 or PX_3) or thionyl chloride.

e.g. $R—OH + HCl \xrightarrow{\text{Anhyd. } ZnCl_2} RCl + H_2O$

$$ROH + HBr \xrightarrow[ZnCl_2]{H_2SO_4(aq)} RBr + H_2O$$

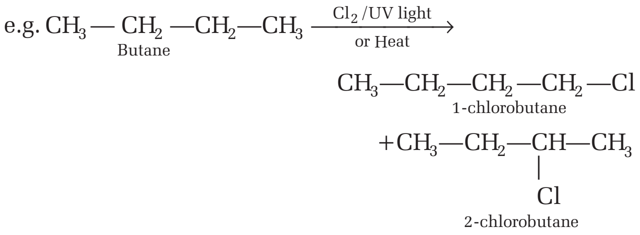
$$3R—OH + PX_3 \longrightarrow 3RX + H_3PO_3$$

$$ROH + PX_5 \longrightarrow RX + POX_3 + HX \; (X = Cl, Br, I)$$

$$R—OH \xrightarrow{P(red)/X_2} RX \; ; (X_2 = Br_2, \; I_2)$$

$$R—OH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + SO_2\uparrow + HCl\uparrow$$

- Haloalkanes are also prepared **from alkanes** which show free radical halogenation in the presence of sunlight.



$$\text{e.g. } \underset{\text{Butane}}{CH_3—CH_2—CH_2—CH_3} \xrightarrow[\text{or Heat}]{Cl_2/\text{UV light}} \underset{\text{1-chlorobutane}}{CH_3—CH_2—CH_2—CH_2—Cl} + \underset{\text{2-chlorobutane}}{CH_3—CH_2—\underset{Cl}{\underset{|}{CH}}—CH_3}$$

- Another method to prepare haloalkane **halide exchange method**. This includes Finkelstein reaction and Swarts reaction.
  - (i) **Finkelstein Reaction** It is used for the conversion of chloroalkane or bromoalkane to iodoalkane.

$$RX + NaI \xrightarrow{\text{Acetone}} RI + NaX \qquad (X = Br, Cl)$$

  - (ii) **Swarts Reaction** (Preparation of alkyl fluorides) Alkyl chloride/bromide when heated with metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3 gives alkyl fluoride.

$$CH_3 — Br + AgF \longrightarrow CH_3F + AgBr$$

Physical Properties of Haloalkanes

The physical properties of alkyl halides or haloalkanes are given below:

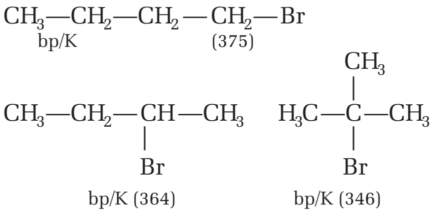
1. Boiling and Melting Point

- Alkyl halides are polar compounds and have higher boiling point due to **dipole-dipole interaction**. Alkyl/aryl halides have higher boiling point than hydrocarbons of comparable molecular mass.
- Decreasing order of boiling point of alkyl halides is as,

$$RI > RBr > RCl > RF$$

This is because with the increase in size and mass of halogen atom, the magnitude of van der Waals' forces increases.

- Straight chain alkyl halides have higher boiling point as compared with branched chain alkyl halide of similar molecular weight, hence boiling points of isomeric haloalkanes decrease with increase in branching due to decrease in surface area, e.g.



$$\underset{\text{bp/K (375)}}{CH_3—CH_2—CH_2—CH_2—Br}$$

$$\underset{\text{bp/K (364)}}{CH_3—CH_2—\underset{Br}{\underset{|}{CH}}—CH_3} \qquad \underset{\text{bp/K (346)}}{H_3C—\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}—CH_3}$$

2. Density and Solubility

- Bromo and iodo derivatives of hydrocarbons are heavier than water.
- Lower haloalkanes are very slightly soluble in water but others are insoluble in water because these do not form hydrogen bond with water.

Chemical Properties of Haloalkanes

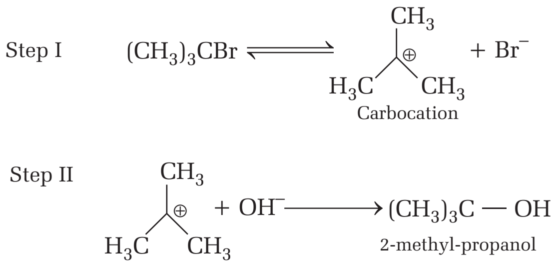
Haloalkanes are highly reactive compounds due to the presence of polar $R—X$ bond. The reactions of haloalkanes may be of two types. These are **nucleophilic substitution reactions** and **elimination reactions**, which are discussed below:

Nucleophilic Substitution Reactions

Nucleophilic substitution reactions proceed either by S_N1 or by S_N2 type of mechanism.

1. Nucleophilic Substitution Unimolecular Reactions (S_N1 Mechanism)

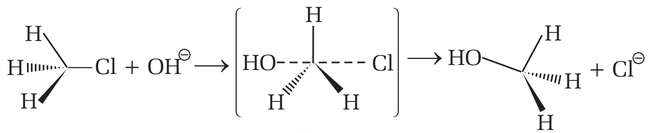
- It follows first order kinetics, rate = k [substrate].
- Reaction is completed in two steps.
- Carbocation is formed and gets rearranged, if possible.
- Nucleophile can attack from front and backside. Therefore, racemic mixture can be formed.
- Tertiary alkyl group and polar solvent favour S_N1 mechanisms e.g.



Reactivity of halides towards S_N1 mechanism is $3° > 2° > 1°$.

2. Nucleophilic Substitution Bimolecular Reactions (S_N2 Mechanism)

- It follows second order kinetics, rate $= k$ [substrate] [nucleophile]
- Reaction is completed in one step.
- Transition state is formed.
- It involves complete inversion in configuration as the attack of the nucleophile occurs from the back side of reactant. e.g.



Transition state

Primary alkyl group and non-polar solvent favour S_N2 :

- Reactivity of halides towards S_N2 mechanism is $1° > 2° > 3° >$ *neo*-pentyl halides.
- In S_N2 mechanism, rate of reaction depend upon the strength of attacking nucleophile.

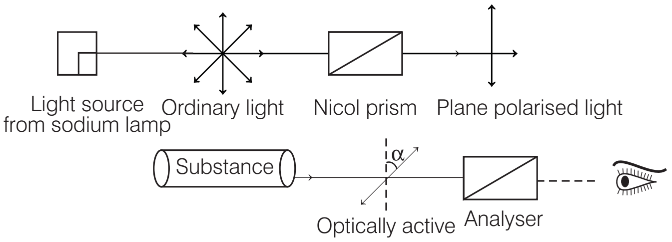
  The strength of different nucleophiles is

  $CN^- > I^- > OR^- > OH^- > CH_3COO^- > H_2O > F^-$.

NOTE 3° halides usually proceed through S_N1 type, 1° halides proceed through S_N2 type and 2° halides may proceed either through S_N1 or S_N2 type depending upon the reaction conditions.

Stereochemical Aspects of Nucleophilic Substitution Reactions

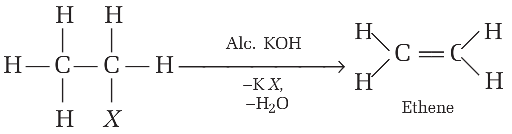
- For S_N1 and S_N2, we need to learn some basic stereochemical principles and notations.



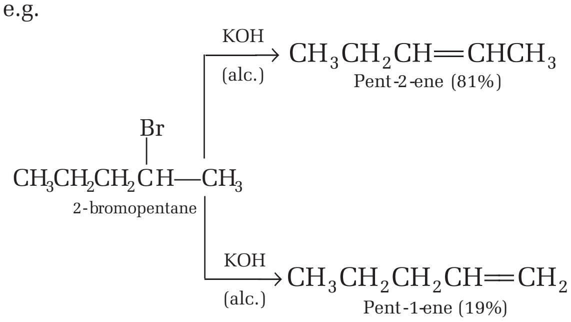
- **Optical Rotation** (Optical activity) The property of a substance to rotate the plane of polarised light is called **optical activity** or **optical rotation**. If plane polarised light rotates in clockwise direction, when passed through a substance, the substance is known as dextrorotatory or (+) or (*d*). If it rotates in anticlockwise, the substance is known as laevorotatory or (–) or (*l*).
- **Chiral Carbon** It has four different groups or atoms attached to it and the molecule which possesses such carbon is called optically active molecules or **chiral molecule**.
- Equimolar mixture of enantiomers (*dextro* and *laevo*) is known as **racemic mixture**. Racemic mixture is optically inactive as the rotation due to one enantiomer will be cancelled by the rotation due to the other enantiomer. This phenomenon is known as racemisation.
- The back side attack by a nucleophile in S_N2 reactions gives rise to a product whose configuration is opposite to the reactant. Therefore, during S_N2 reaction, **inversion of configuration** occurs. This 100% inversion of configuration is known as **Walden inversion**.

Elimination Reactions

In these reactions, haloalkane having β-hydrogen atom is heated with alcoholic KOH, β-elimination takes place. e.g.



- If there is possibility of formation of more than one alkene due to availability of more than one β-H-atoms, the elimination of HX takes place according to Saytzeff rule. It states, "in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms e.g.



$$CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}H-CH_3 \xrightarrow[\text{(alc.)}]{KOH} \underset{\text{Pent-2-ene (81\%)}}{CH_3CH_2CH{=}CHCH_3}$$

$$\underset{\text{2-bromopentane}}{CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}H-CH_3} \xrightarrow[\text{(alc.)}]{KOH} \underset{\text{Pent-1-ene (19\%)}}{CH_3CH_2CH_2CH{=}CH_2}$$

- Some important reactions of haloalkanes are given below

$$R-X \xrightarrow{AgNO_2} \underset{\text{Nitroalkane}}{R-NO_2} + AgX$$

$$RX \xrightarrow{NaNO_2 \text{ or } KNO_2} \underset{\text{Alkyl nitrite}}{R-ONO} + KX \text{ or } NaX$$

$$RX \xrightarrow{KCN \text{ or } NaCN} \underset{\text{Alkyl isocyanide}}{RCN} + KX \text{ or } NaX$$

$$RX \xrightarrow{AgCN} \underset{\text{Alkyl isocyanide}}{RNC} + AgX$$

$$RX + NH_3 \longrightarrow \underset{\text{Alkylamine}}{RNH_2} + R-NH-R$$

$$+ R_3N + [R_4N^+]Cl^-$$

$$RX + KOH(aq.) \longrightarrow \underset{\text{Alcohol}}{R-OH} + KX,$$

(Hofmann ammonolysis reaction)

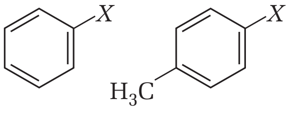
$$RX + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{RMgX}$$

$$2RX + 2Na \longrightarrow R-R + 2NaX$$

(Wurtz reaction)

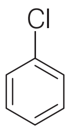
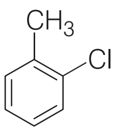
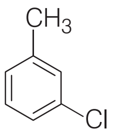
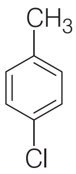
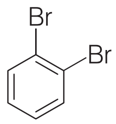
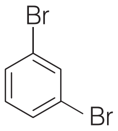
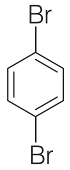
Haloarenes

These are the compounds in which halogen atom is directly attached to sp^2-hybridised C-atom of benzene ring. e.g.

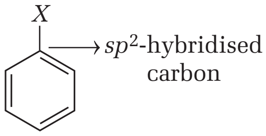


(X = Cl, Br, I)

- **Nomenclature** According to IUPAC system of nomenclature, the numerical prefixes, 1, 2; 1, 3 and 1, 4 are used but in common system prefixes *o*-, *m*- and *p*- are respectively used, e.g.

Haloarene	IUPAC name
	Chlorobenzene
	1-chloro-2-methylbenzene (*o*-chlorotoluene)
	1-chloro-3-methylbenzene (*m*-chlorotoluene)
	1-chloro-4-methyl benzene (*p*-chlorotoluene)
	1, 2-dibromobenzene (*o*-dibromobenzene)
	1, 3-dibromobenzene (*m*-dibromobenzene)
	1, 4-dibromobenzene (*p*-dibromobenzene)

- **Nature of C—X Bond** Haloarenes are the aromatic compound in which carbon atom to which halogen is attaches is sp^2-hybridised.



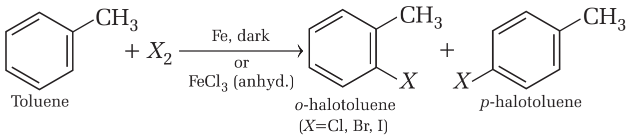
where, (X = Cl, Br, I, F)

Due to high electronegativity of halogen atom, it acquires partial negative charge, while carbon atom acquires partial positive charge.

$$\geqslant \overset{\delta^+}{C} - \overset{\delta^-}{X}$$

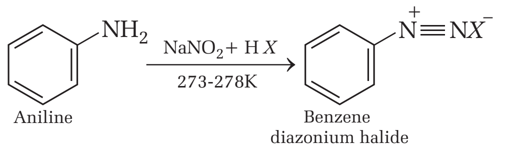
Methods of Preparation

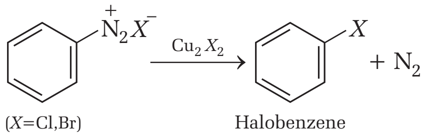
(i) These are carried out in the presence of a halogen carrier (i.e. Lewis acid) like $FeCl_3$, $FeBr_3$ in dark and at low temperature. These reactions are called **electrophilic substitution reactions**.



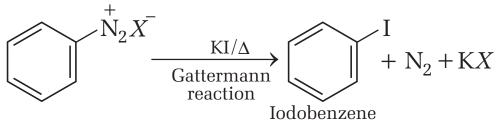
NOTE *m*-bromobenzene trichloride undergoes reduction with Zn in presence of HCl to give *m*-bromotoluene.

(ii) Chloro and bromoarenes are prepared by the reaction in which freshly prepared benzene diazonium halide is warmed with cuprous chloride/bromide in HCl. This reaction is called Sandmeyer's reaction. e.g.

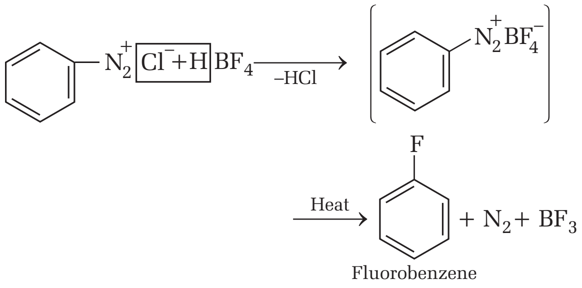




(iii) Iodobenzene is obtained by warming diazonium salt with KI.

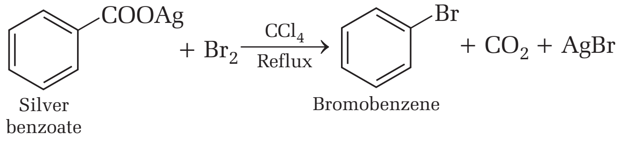


(iv) Fluorobenzene is obtained by using fluoroboric acid, HBF_4. This reaction is known as **Balz-Schiemann reaction**.



(v) Bromoarenes can also be prepared by refluxing the silver salt of aromatic acid with bromine in carbon tetrachloride. This reaction is called **Borodine Hunsdiecker reaction**.

This reaction proceeds through free radical mechanism and is used to reduce the length of carbon chain.

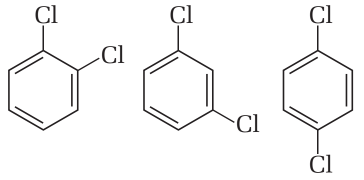


Physical Properties of Haloarenes

Some important physical properties of haloarenes are discussed below :

- **The boiling and melting points of haloarenes** are nearly same as those of haloalkanes with the same number of carbon atoms. For the same aryl group, the melting and boiling points increase as the size of the halogen atom increases.

e.g.



BP/K	453	446	448
MP/K	256	249	323

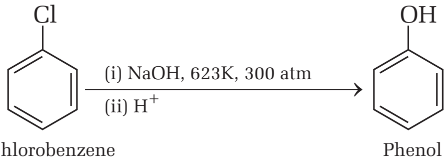
- The *para*-isomers of dihalobenzenes has high melting point as compared to their *ortho* and *meta* isomers. It is due to symmetry of *para* isomers that fits in crystal lattice as compared to *ortho* and *meta* isomers.
- **Density and Solubility** Bromo, iodo and polychloro derivatives of haloarenes are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of halogen atoms.
- Haloarene are insoluble in water due to absence of H-bonding but soluble in organic solvents such a petroleum, ether, benzene, etc.

Chemical Properties of Haloarenes

Chemical properties of haloarenes give three types of reactions, which are given as follows:

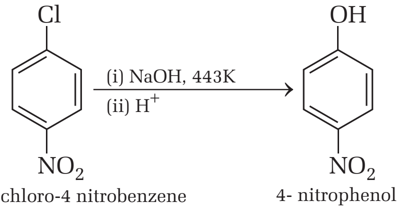
Nucleophilic Substitution Reaction

- Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions. e.g. Chlorobenzene undergoes, this reaction to give phenol at pressure of about 300 atm at 623 K temperature. This is known as **Dow's process**.

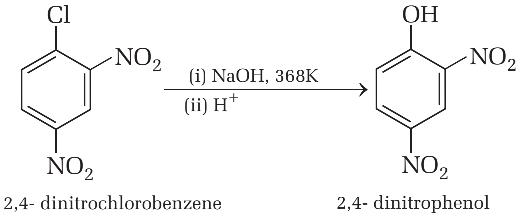


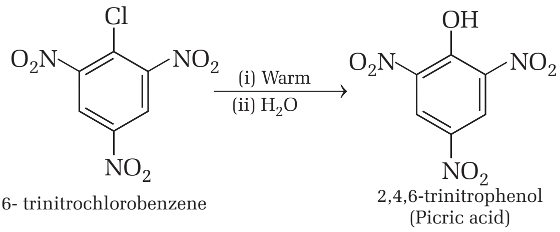
- As the displacement of halogen in haloarenes takes place under drastic conditions. But the presence of electron withdrawing groups such as —NO_2, —CN etc. at *o* and *p*-positions with respect to the halogen greatly activates halogen towards nucleophilic substitution.

(i)



(ii)

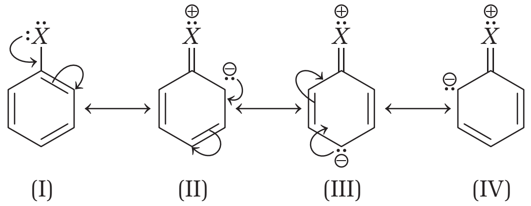


(iii) 

Electrophilic Substitution Reaction

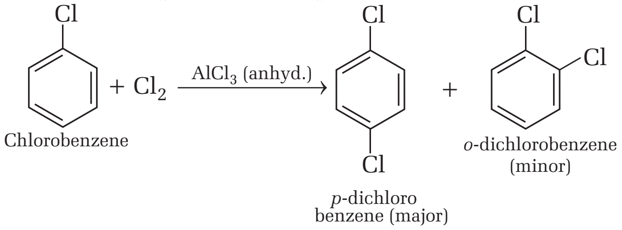
Haloarenes undergo usual **electrophilic substitution reactions** of benzene ring such as halogenation, nitration, sulphation, Friedel-Crafts reactions.

- Halogen atom is slightly deactivating and *o*, *p*-directing. The *o*, *p*-directive influence of halogen atom can be easily understood by following resonating structure.

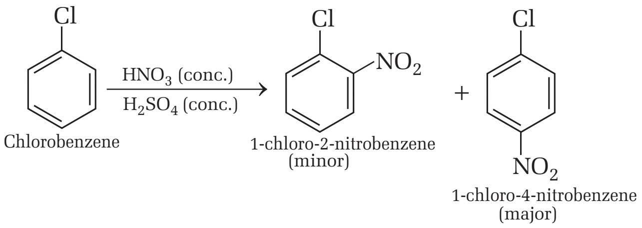


Due to resonance electron density increases more at *o* and *p*-positions than at *m*-positions. Thus, electrophilic substitution reactions in haloarenes occur at *o* and *p*-positions.

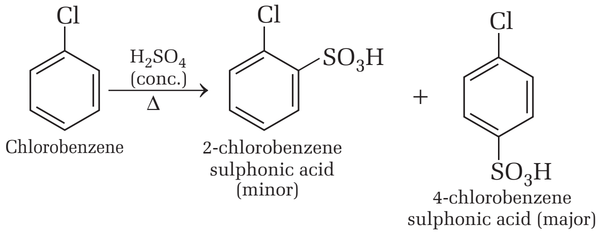
- **Halogenation** In this, chlorobenzene reacts with chlorine to form *o*- and *p*- substituted products.



- **Nitration** In this, chlorobenzene reacts with conc. HNO_3 in the presence of conc. H_2SO_4 to give *o*-and *p*-substituted products.



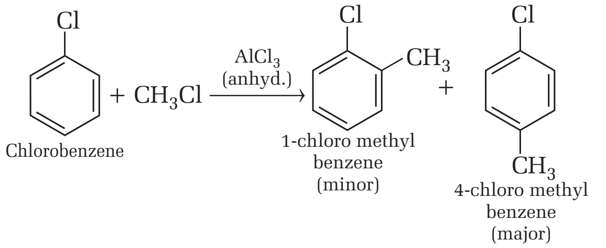
- **Sulphonation** In this, chlorobenzene reacts with conc. H_2SO_4 to form *o*-and *p*- substituted products.



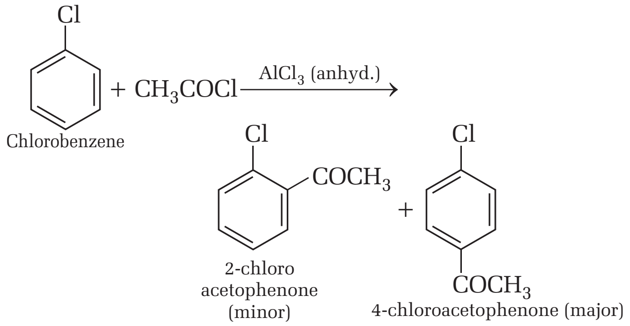
Friedel-Crafts Reactions

These are of following two types:

(i) **Alkylation** In this, chlorobenzene reacts with alkyl halide to give *o*-and *p*- substituted products.



(ii) **Acylation** In this, chlorobenzene reacts with acylchloride to form *o*-and *p*- substituted products.

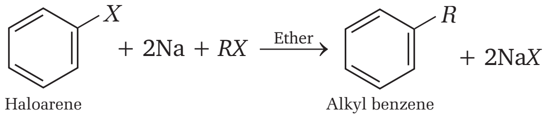


NOTE
- **Nuclear halogenation reaction** takes place by electrophilic substitution mechanism whereas side chain halogenation takes place by free radical mechanism.
- **In case of side chain chlorination** of ethyl benzene, 1-chloro-1-phenyl ethane is the major product while 1-chloro-2-phenyl ethane is the minor product because intermediate, benzylic radical formed in 1st case is resonance stabilised.

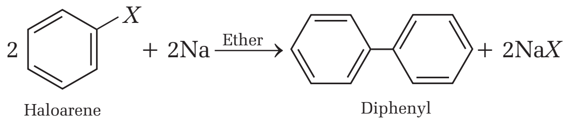
Reaction with Metals

Haloarenes give different kind of products on reaction with metals. These are given below :

- A mixture of haloarene and haloalkane, when treated with Na in dry ether gives alkyl arene. This reaction is known as **Wurtz-Fittig reaction**.



- Haloarenes on treatment with Na in dry ether give analogous compounds, this is called **Fittig reaction**.
e.g.



Used and Environment Effects of Polyhalogen Compounds

The polyhalogenated compounds (PHCs) are any compounds with multiple substitutions of halogens. Some of polyhalogen compounds are given below:

1. Dichloromethane (Methylenechloride; CH_2Cl_2)

- CH_2Cl_2 is widely used as a solvent.
- It isused as a paint remover.
- It is used as a propellant in aerosols.
- It is used as a process solvent in the manufacture of drugs.
- **Effects** It nerms the human central nervous system.

2. Trichloromethane (Chloroform; $CHCl_3$)

- It is employed as a solvent for fats, alkaloids, iodine and other substances.
- It was used as a general anaesthetic but now a days, it is replaced by less toxic and safe anaesthetic, ether.
- The major use of chloroform today is in the production of the refrigerant, freon.
- **Effect** It is stored in closed dark coloured bottles, filled completely so that air is kept out because it is oxidised by air in the presence of light.

$$2CHCl_3 + \underset{\text{(Air)}}{O_2} \xrightarrow{\text{Light}} \underset{\substack{\text{Phosgene} \\ \text{(poisonous gas)}}}{2COCl_2} + 2HCl$$

3. Tri-iodomethane (Iodoform; CHI_3)

- It is prepared by heating ethanol or acetone with sodium hydroxide and iodine or Na_2CO_3 and I_2 in water.

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

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

- This reaction is called **iodoform reaction.** Some of the important characteristic of iodoform are as follows:
  - (i) It is yellow solid having melting point 119°C.
  - (ii) It is insoluble in water but soluble in ethanol and ether.
  - (iii) It is used as antiseptic because it liberates iodine but due to obnoxious (unpleasant) smell, it has been replaced by other medicines.
  - (iv) Its chemical properties are similar to $CHCl_3$.

4. Tetrachloromethane (Carbontetrachloride; CCl_4)

- It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans.
- It is also used as feed stock in the synthesis of chlorofluorocarbons and other chemicals.
- It is widely used as industrial solvent for oils, facts, resins, lacquers, etc.
- It is used as fire extinguusher but after using it to extinguish fire, the room should be ventilated to remove phosgene.
- **Effect** Exposure to CCl_4 causes liver cancer in humans. Exposure of CCl_4 vapours can make heart beat irregular even may stop it.

5. Freons (Chlorofluorocarbon; CCl_2F_2)

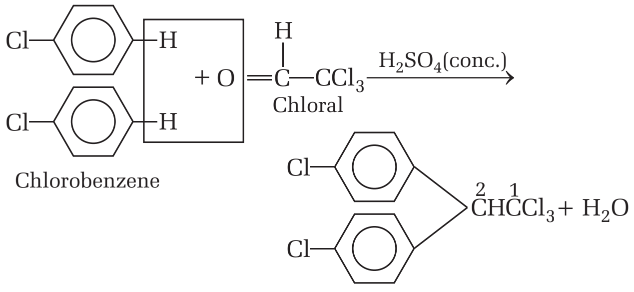
- Freons are extremey stable, unreactive non-toxic, non-corrosive and easily liquefiable gases.
- It is manufactured from tetrachloromethane by Swarts reaction and used for aerosol propellants, refrigeration and air conditioning purposes.
- **Effects** Freons deplete the protective ozone layer surrounding our planet, so their use has been banned in many countries.

6. DDT (Dichlorodiphenyl Trichloroethane)

It is a powerful insecticide but is not easily biodegradable.

Therefore, its long term effects could be potentially dangerous and its use is banned in many countries.

IUPAC name of DDT is 2,2-bis (4-chloro phenyl)– 1, 1, 1-trichloroethane. It is non-biodegradable and slowly changes to another compound DDE by the loss of a molecule of HCl.



(DDT)
p,p′-dichlorodiphenyltrichloroethane

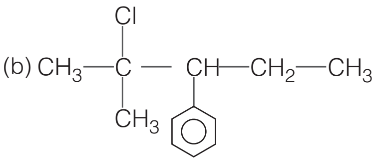
- **Effects** DDT causes pollution due to its extreme stability. It is non-biodegradable.

DAY PRACTICE SESSION 1

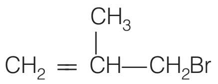
FOUNDATION QUESTIONS EXERCISE

1 Which of the following is correct in accordance with IUPAC system?

(a) $Br—CH_2—CH{=}CH_2$
1-bromoprop-2-ene

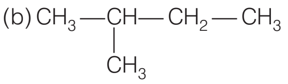
(b)

2 chloro-2 methyl-3 phenylpentane

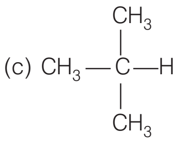
(c) $(CH_3)_3CCl$
1-chloro-1-dimethylpropane

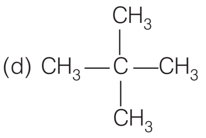
(d)

$CH_2{=}CH(CH_3)—CH_2Br$
1-bromo-2-methylbutene

2 In the following compounds, least number of monochlorination is possible in

(a) $CH_3CH_2CH_2CH_2CH_3$

(b)

$CH_3—CH(CH_3)—CH_2—CH_3$

(c)

$CH_3—CH(CH_3)_2$, i.e. $CH_3—\underset{CH_3}{\overset{CH_3}{C}}—H$

(d)

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

3 Which is the correct increasing order of boiling points of the following compounds?
1-iodobutane, 1-bromobutane, 1-chlorobutane, butane

(a) Butane< 1-chlorobutane < 1- bromobutane < 1-iodobutane
(b) 1-iodobutane < 1- bromobutane < 1-chlorobutane < Butane
(c) Butane < 1-iodobutane < 1- bromobutane < 1-chlorobutane
(d) Butane< 1-chlorobutane < 1-iodobutane < 1- bromobutane

4 The products of alcoholic silver nitrite with ethyl bromide are

(a) ethanol and ethyl nitrite
(b) nitroethane and ethyl nitrite
(c) ethene and nitroethane
(d) ethyl nitrite and nitroethane

5 Isopropyl chloride undergoes hydrolysis by

(a) S_N1 mechanism
(b) S_N2 mechanism
(c) S_N1 or S_N2 mechanism
(d) Neither S_N1 nor S_N2 mechanism

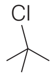
6 In which alkyl halide, S_N2 mechanism is favoured maximum?

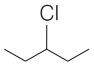
(a) CH_3Cl (b) CH_3CH_2Cl (c) $(CH_3)_2CHCl$ (d) $(CH_3)_3CCl$

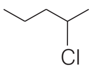
7 The order of reactivities of the following alkyl halides for a S_N2 reaction is

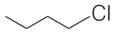
(a) $RF > RCl > RBr > RI$ (b) $RCl > RBr > RF > RI$
(c) $RF > RBr > RCl > RI$ (d) $RI > RBr > RCl > RF$

8. Among the following compounds, which compound undergoes S_N1 reaction faster?

(a)


(b)


(c)


(d)


9 1, 2-dibromoethane reacts with alcoholic KOH to yield a product X. The hybridisation state of the carbons present in X respectively, are

(a) sp, sp (b) sp^3, sp^3 (c) sp^3, sp^2 (d) sp^2, sp^2

10 Identify Z in the following reaction series.

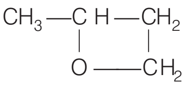
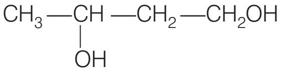
$$C_2H_5I \xrightarrow{\text{Alc. KOH}} X \xrightarrow{Br_2} Y \xrightarrow{KCN} Z$$

(a) $CH_3CH_2\ CN$ (b) $NCCH_2—CH_2CN$
(c) $BrCH_2—CH_2CN$ (d) $BrCH{=}CHCN$

11 The major product formed in the following reaction

$$CH_3CH(Cl)CH_2—CH_2OH \xrightarrow{aq.\ KOH}$$

is

(a) $CH_3CH{=}CH—CH_2OH$
(b) $CH_2{=}CH—CH_2—CH_2OH$
(c)

(d)

$CH_3—\underset{OH}{CH}—CH_2—CH_2OH$

12 Consider the following reaction.

$$C_2H_5Cl + AgCN \xrightarrow{EtOH/H_2O} X \text{ (Major)}$$

Which one of the following statements is true for X?

I. It gives propionic acid on hydrolysis.
II. It has an ester functional group.
III. It has a nitrogen linked to ethyl carbon.
IV. It has a cyanide group.

(a) Statement (IV) (b) Statement (III)
(c) Statement (II) (d) Statement (I)

13 In the following sequence of reactions, **→ CBSE-AIPMT 2012**

$$CH_3—Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[\text{Ether}]{LiAlH_4} C$$

the end product (C) is

(a) acetone (b) methane
(c) acetaldehyde (d) ethyl alcohol

14 Hydrolysis of trichloromethane with aqueous KOH gives

(a) methanol (b) acetic acid
(c) ethanol (d) formic acid

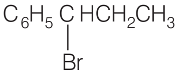
15 An alkyl chloride (A) on reaction with magnesium in dry ether followed by treatment with ethanol gave 2-methylbutane. Give the possible structure of 'A'.

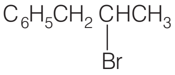
(a) $(CH_3)_2C(Cl)CH_2CH_3$
(b) $(CH_3)_2CHCH_2CH_2Cl$
(c) $CH_3CH_2CH_2CH_2CH_2X$
(d) Both (a) and (b)

16 Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows

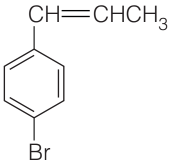
(a) S_N1 mechanism
(b) S_N2 mechanism
(c) Any of the above two depending upon the temperature of reaction
(d) Saytzeff rule

17 The reaction of $C_6H_5CH═CHCH_3$ with HBr produces **→ CBSE-AIPMT 2015**

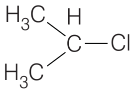
(a) 
$C_6H_5\underset{Br}{\underset{|}{C}}HCH_2CH_3$

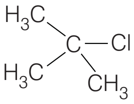
(b) 
$C_6H_5CH_2\underset{Br}{\underset{|}{C}}HCH_3$

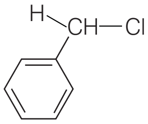
(c) $C_6H_5CH_2CH_2CH_2Br$

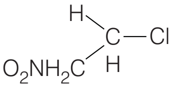
(d) 

18 In which of the following compounds, the C—Cl bond ionisation shall give most stable carbonium ion? **→ CBSE-AIPMT 2015**

(a) 

(b) 

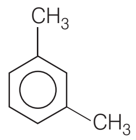
(c) 

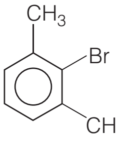
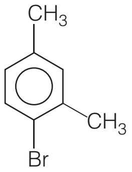
(d) 

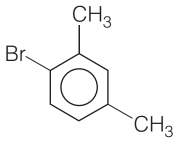
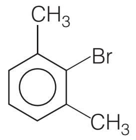
19 p-nitrobromobenzene can be converted to p-nitroaniline by using $NaNH_2$. The reaction proceeds through the intermediate named

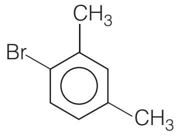
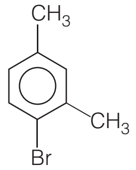
(a) carbocation (b) carbanion
(c) benzyne (d) dianion

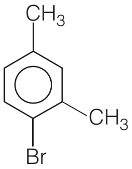
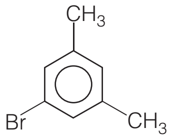
20 What products are formed when the following compound is treated with Br_2 in the presence of $FeBr_3$? **→ CBSE-AIPMT 2014**



(a)  and 

(b)  and 

(c)  and 

(d)  and 

21 The compound C_7H_8 undergoes the following reactions:

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

The product 'C' is **→ NEET 2018**

(a) 3-bromo-2, 4, 6-trichlorotoluene
(b) o- bromotoluene
(c) m-bromotoluene
(d) p-bromotoluene

22 o-methoxy bromobenzene is treated with sodamide and then with NH_3. The product formed is

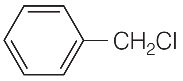
(a) o-methoxy bromobenzene
(b) aniline
(c) methoxy benzene
(d) m-methoxy aniline

23 Replacement of Cl of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced because

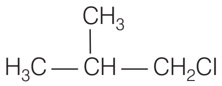
(a) $—NO_2$ makes electron rich ring at o and p-positions
(b) $—NO_2$ donate electrons at m-position
(c) $—NO_2$ withdraws electron at o and p-positions
(d) $—NO_2$ withdraws electron at m-position

24 Which of the following compounds will undergo racemisation with solution of KOH (hydrolysis)?

➞ CBSE-AIPMT 2014

(i) 

(ii) $CH_3CH_2CH_2Cl$

(iii) 
$H_3C{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_2Cl$

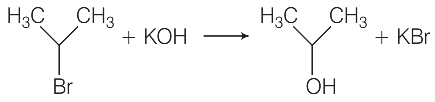
(iv) $(CH_3CH_2)_3CCl$

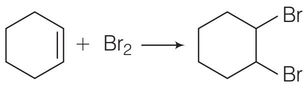
(a) (i) and (ii)
(b) (ii) and (iv)
(c) (iii) and (iv)
(d) (i) and (iv)

25 For the following reactions,

➞ NEET 2016, Phase I

(i) $CH_3CH_2CH_2Br + KOH \rightarrow CH_3CH{=}CH_2 + KBr + H_2O$

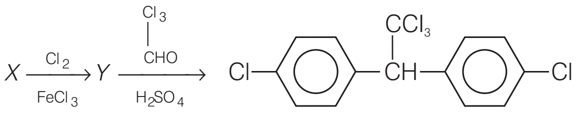
(ii) 

(iii) 

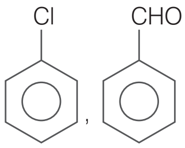
Which of the following statements is correct?

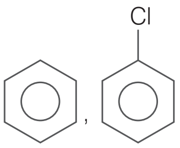
(a) (i) is elimination reaction, (ii) is substitution and (iii) is addition reaction
(b) (i) is elimination, (ii) and (iii) are substitution reactions
(c) (i) is substitution, (ii) and (iii) are addition reactions
(d) (i) and (ii) are elimination reactions and (iii) is addition reaction

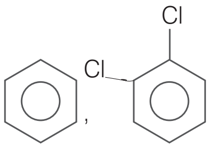
26 In the reaction sequence,

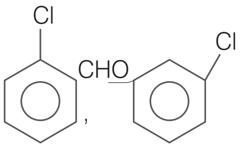


X and Y respectively are

(a) 

(b) 

(c) 

(d) 

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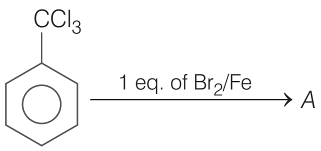
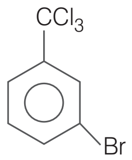
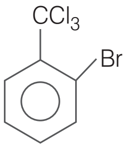
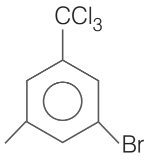


Compound A is

(a) 

(b) 

(c) 

(d) 

28 Freon used as refrigerant is

(a) $CF_2{=}CF_2$
(b) CH_2F_2
(c) CCl_2F_2
(d) CF_4

29 Which one of the following compound reacts with chlorobenzene to produce DDT?

(a) Acetaldehyde
(b) Nitrobenzene
(c) *m*-chloroacetaldehyde
(d) Trichloroacetaldehyde

30 Iodoform can be prepared from all except

(a) ethyl methyl ketone
(b) isopropyl alcohol
(c) 3-methyl-2-butanone
(d) isobutyl alcohol

31 Trichloroacetaldehyde, (CCl_3CHO) reacts with chlorobenzene in the presence of sulphuric acid and produces

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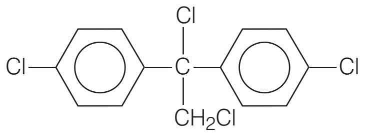
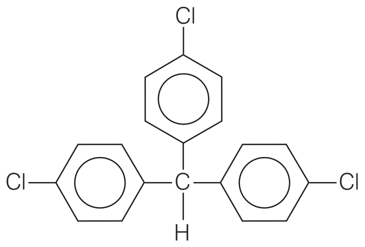
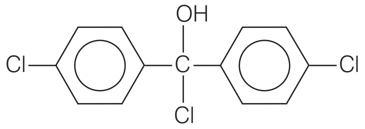
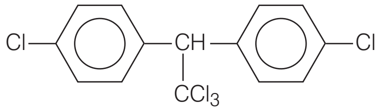
(a) 

(b) 

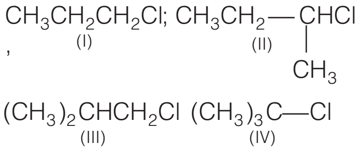
(c) 

(d) 

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

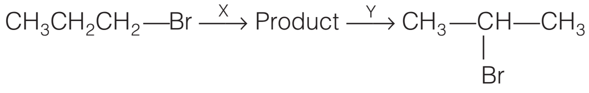
1 Arrange the following in order of increasing tendency towards S_N2 reactions.



$CH_3CH_2CH_2Cl$; $CH_3CH_2—\underset{\underset{CH_3}{|}}{CHCl}$, $(CH_3)_2CHCH_2Cl$ $(CH_3)_3C—Cl$
(I) (II) (III) (IV)

(a) I > III > II > IV
(b) III > IV > II > I
(c) II > I > III > IV
(d) IV > III > II > I

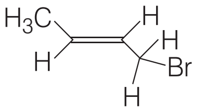
2 Identify the set of reagents/ reaction conditions '*X*' and '*Y*' in the following set of transformation



$$CH_3CH_2CH_2—Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3—\underset{\underset{Br}{|}}{CH}—CH_3$$

(a) X = dilute aqueous solution, 20°C
Y = HBr/acetic acid at 20°C
(b) X = dilute aqueous NaOH, 20°C
Y = HBr/acetic acid at 20°C
(c) X = dilute aqueous NaOH, 20°C
$Y = Br_2 / CHCl_3$, 0°C
(d) X = concentrated alcoholic NaOH, 80°C
$Y = Br_2 / CHCl_3$, 0°C

3 The correct IUPAC name of the following compound is

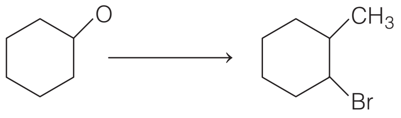


(a) 1-bromobut-2-ene
(b) 2-bromo-2-butane
(c) bromobutane
(d) 1-bromobut-3-ene

4 The incorrect statement with respect to S_N1 and S_N2 mechanisms for alkyl halide is

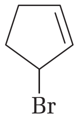
(a) a strong nucleophile in an aprotic solvent increases the rate or favours S_N2 reaction
(b) competing reaction for an S_N2 reaction is rearrangement
(c) S_N1 reactions can be catalysed by some Lewis acids
(d) a weak nucleophile and a protic solvent increases the rate of or favours S_N1 reaction

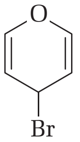
5 Which of the following sequence of reagent is best suited for the reaction shown below?

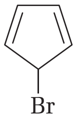


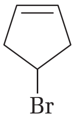
(a) (i) CH_3MgBr, H_3O^+; (ii) H^+/Δ; (iii) HBr/H_2O_2
(b) (i) CH_3MgBr, H_3O^+; (ii) H^+/Δ; (iii) HBr
(c) (i) CH_3MgBr, H_3O^+; (ii) HBr
(d) (i) HBr/*R*OOR; (ii) CH MgBr, H_3O^+

6 The increasing order of reactivity of the following bromides in S_N1 reaction is

I.


II.


III.


IV.


(a) III > I > II > IV
(b) III > II > I > IV
(c) II > III > I > IV
(d) II > I > IV > III

7 Alkaline hydrolysis of which among the following compounds leads to the formation of a racemate?

(a) 1-bromo-1-phenylethane
(b) 1-chloro-3-methylbutane
(c) Bromoethane
(d) 1-chloropropane

8 A solution of (–)-1-chloro-2- phenylethane in toluene racemises slowly in the presence of small of $SbCl_5$ due to the formation of

(a) carbanion
(b) carbene
(c) free radical
(d) carbocation

9 The compound which is not formed when a mixture of bromobutane and bromoethane treated with sodium metal in presence of dry ether is

(a) butane
(b) octane
(c) hexane
(d) ethane

10 When 2-chloro-2-methylbutane is heated with alcoholic KOH, the possible products is/are

(i) $(CH_3)_2 = CHCH_3$
(ii) $CH_2 = C(CH_3)CH_2CH_3$
(iii) $(CH_3)_2CHCH = CH_2$

(a) (i), (ii) and (iii)
(b) (i) and (iii)
(c) (i) and (ii)
(d) Only (i)

11 S_N1 reactivity of the following halides will be in the order of

(i) $(CH_3)_3CBr$
(ii) $(C_6H_5)_2CHBr$
(iii) $(C_6H_5)_2C(CH_3)Br$
(iv) $(CH_3)_2CHBr$
(v) C_2H_5Br

(a) (v) > (iv) > (i) > (ii) > (iii)
(b) (ii) > (i) > (iii) > (v) > (iv)
(c) (iii) > (ii) > (i) > (iv) > (v)
(d) (i) > (iii) > (v) > (ii) > (iv)

12 An alkyl halide with molecular formula $C_6H_{13}Br$ on dehydrohalogenation gave the two isomeric alkenes X and Y with molecular formula C_6H_{12}.

On reductive ozonolysis, X and Y gave four compounds CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2CHCHO$. The alkyl halide is

(a) 3-bromo-2-methylpentane
(b) 2-bromohexane

(c) 4-bromo-2-methylpentane
(d) 2-bromo-2, 3-dimethylbutane

13 In alkaline hydrolysis of a tertiary alkyl halide by aqueous alkali, if concentration of alkali is doubled, then the reaction rate constant temperature

(a) will be doubled
(b) will be halved
(c) will become four times greater
(d) will remain constant

14 Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original lables. They were labelled *A* and *B* for testing. *A* and *B* were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance *B* gave a yellow precipitate. Which one of the following statements is true for this experiment ?

(a) *A* was C_6H_5I
(b) *A* was $C_6H_5CH_2I$
(c) *B* was C_6H_5I
(d) Addition of HNO_3 was unnecessary

15 The compound which is formed on heating chlorobenzene with chloral in the presence of conc. H_2SO_4 is

(a) freon
(b) gammaxene
(c) DDT
(d) hexachloroethane

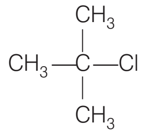
ANSWERS

SESSION 2	1 (b) 11 (d) 21 (c) 31 (d)	2 (d) 12 (b) 22 (d)	3 (a) 13 (d) 23 (c)	4 (d) 14 (d) 24 (c)	5 (c) 15 (d) 25 (a)	6 (a) 16 (a) 26 (b)	7 (d) 17 (a) 27 (a)	8 (a) 18 (c) 28 (c)	9 (a) 19 (c) 29 (d)	10 (b) 20 (c) 30 (d)
SESSION 1	1 (a) 11 (c)	2 (b) 12 (a)	3 (a) 13 (d)	4 (b) 14 (a)	5 (a) 15 (c)	6 (d)	7 (a)	8 (d)	9 (d)	10 (c)

Hints and Explanations

1 $\mathrm{Br—\overset{3}{C}H_2—\overset{2}{C}H=\overset{1}{C}H_2}$

3-bromoprop-1-ene

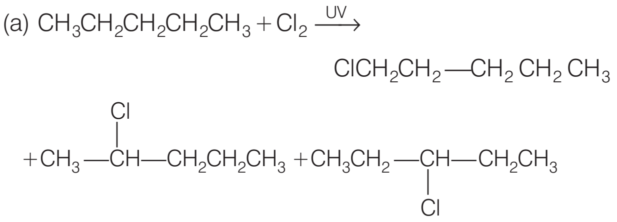

$\mathrm{CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—Cl}$

2-chloro-2-methylpropane

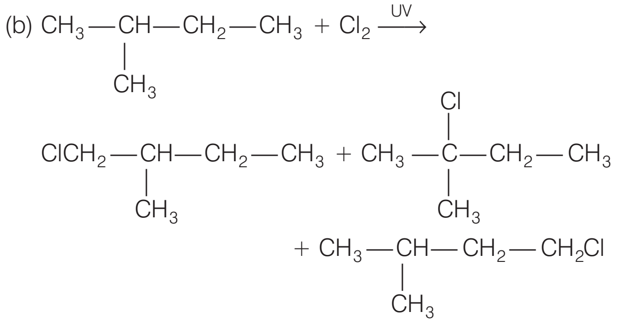
$\mathrm{CH_2=CH—CH—CH_2—Br}$

4-bromo-3-methyl butane

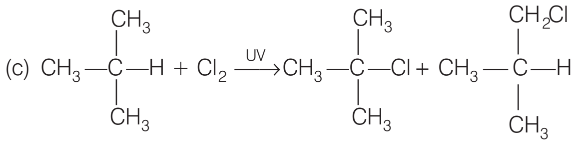
2 On writing chlorination reaction for all of them to find which gives the maximum number of monochlorination products.


(a) $\mathrm{CH_3CH_2CH_2CH_2CH_3+Cl_2 \xrightarrow{UV} ClCH_2CH_2—CH_2CH_2CH_3 + CH_3—\overset{\overset{Cl}{|}}{C}H—CH_2CH_2CH_3 + CH_3CH_2—\underset{\underset{Cl}{|}}{C}H—CH_2CH_3}$

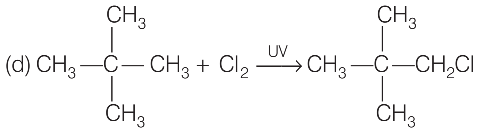
∴ Total 3 monochlorinated products are formed.


(b) $\mathrm{CH_3—\underset{\underset{CH_3}{|}}{C}H—CH_2—CH_3 + Cl_2 \xrightarrow{UV} ClCH_2—\underset{\underset{CH_3}{|}}{C}H—CH_2—CH_3 + CH_3—\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2—CH_3 + CH_3—\underset{\underset{CH_3}{|}}{C}H—CH_2—CH_2Cl}$

∴ Total 3 monochlorinated products are formed.


(c) $\mathrm{CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—H + Cl_2 \xrightarrow{UV} CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—Cl + CH_3—\overset{\overset{CH_2Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}—H}$

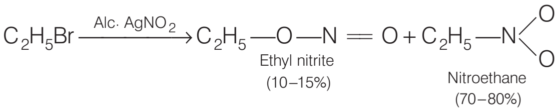
∴ Total 2 monochlorinated products are formed.


(d) $\mathrm{CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3 + Cl_2 \xrightarrow{UV} CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2Cl}$

∴ Only one monochlorinated product is formed.

3 Boiling point increases with increase in the size and mass of the halogen atom.
Hence, increasing order of boiling point is
butane < 1-chlorobutane < 1-bromobutane < 1-iodobutane

4 Ethyl bromide react with alcoholic $AgNO_2$ gives ethyl nitrite as well as nitroethane.



$$C_2H_5Br \xrightarrow{\text{Alc. }AgNO_2} \underset{\substack{\text{Ethyl nitrite}\\(10\text{–}15\%)}}{C_2H_5-O-N=O} + \underset{\substack{\text{Nitroethane}\\(70\text{–}80\%)}}{C_2H_5-NO_2}$$

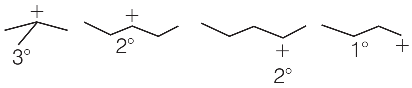
5 Isopropyl chloride is 2° alkyl halide. It undergoes hydrolysis by any one of S_N1 or S_N2 reaction.

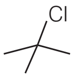
6 For S_N2 substitution nucleophilic bimolecular reaction, order of different alkyl halides is $1° > 2° > 3°$ (due to less steric hinderance).

7 $RI > RBr > RCl > RF$
As the bond strength decreases, reactivity increases.

8 In S_N1 mechanism, carbocation intermediate is involved, so the alkyl halide that gives more stable carbocation readily undergoes S_N1 reaction faster.

The order of stability of carbocations is $3° > 2° > 1°$



Thus,  readily undergoes S_N1 reaction.

9 Alkyl halides give elimination reaction with alcoholic KOH and yield an alkyne (from dihalides) e.g.

$$\underset{\text{1, 2-dibromoethane}}{Br-CH_2-CH_2-Br} \xrightarrow[\Delta]{\text{Alc. KOH}} \underset{\text{Acetylene}}{\overset{sp}{CH} \equiv \overset{sp}{CH}}$$

Hence, product has both *sp*-hybridised carbon.

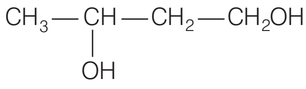
10 $C_2H_5I \xrightarrow[-HI]{\text{Alc.KOH}} CH_2=CH_2 \xrightarrow{Br_2}$

$BrCH_2-CH_2Br \xrightarrow{KCN} NCCH_2-CH_2CN$

11 It is an example of nucleophilic substitution reaction.

$R-X + KOH \longrightarrow R-OH + KX$

So, $CH_3CH(Cl)CH_2-CH_2OH \xrightarrow{aq.KOH}$



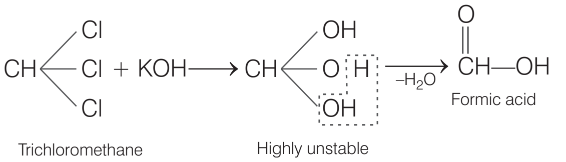
$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_2OH$$

12 $C_2H_5Cl + AgCN \xrightarrow[H_2O]{EtOH} C_2H_5-NC + AgCl$

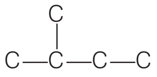
⇒N-Linked to ethyl carbon

13 $$\underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow[-KBr]{KCN} \underset{\substack{\text{Ethane}\\\text{nitrile}\\A}}{CH_3CN} \xrightarrow{H_3O^+} \underset{\substack{\text{Ethanoic}\\\text{acid}\\B}}{CH_3COOH} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\substack{\text{Ethanol}\\C}}{CH_3CH_2OH}$$

14



15 Since, the compound gives 2-methyl butane, it must contain the following carbon skeleton.



$$C-\overset{\displaystyle C}{\overset{|}{C}}-C-C$$

Thus, the structure of chloride may be

$(CH_3)_2C(Cl)CH_2CH_3$ or $(CH_3)_2CHCH_2CH_2Cl$

and the reactions are as follows:

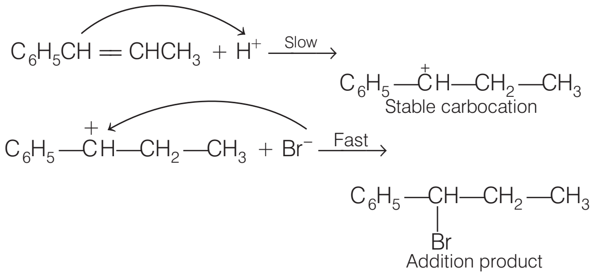
(a) $(CH_3)_2C(Cl)CH_2CH_3 + Mg \xrightarrow[+C_2H_5OH]{\text{Dry ether}} (CH_3)_2CHCH_2CH_3$

(b) $(CH_3)_2CHCH_2CH_2Cl + Mg \xrightarrow{\text{Dry ether}} (CH_3)_2CHCH_2CH_2MgCl$

$(CH_3)_2CHCH_2CH_2MgCl \xrightarrow{C_2H_5OH} (CH_3)_2CHCH_2CH_3$

16 $C_6H_5\overset{+}{C}H_2$ is a stable cation, so favours the progress of reaction by S_N1 mechanism.

17

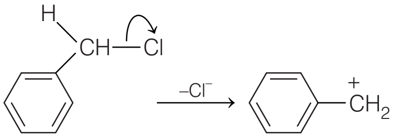


$$C_6H_5CH=CHCH_3 + H^+ \xrightarrow{\text{Slow}} \underset{\text{Stable carbocation}}{C_6H_5-\overset{+}{C}H-CH_2-CH_3}$$

$$C_6H_5-\overset{+}{C}H-CH_2-CH_3 + Br^- \xrightarrow{\text{Fast}} \underset{\text{Addition product}}{C_6H_5-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-CH_3}$$

Electrophilic addition reaction takes place *via* more stable carbocation.

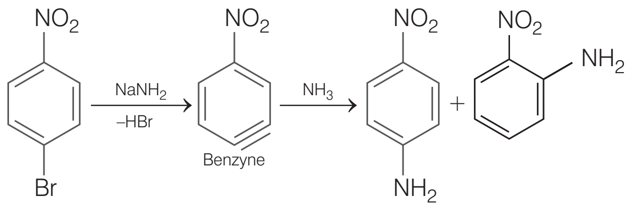
18 The stability of carbocation follow the order $3° > 2° > 1° >$ methyl. More the number of alkyl group attached with the carbon atom carrying the positive charge greater would be the tendency to stabilise positive charge *via* inductive effect and hence more stable is that carbocation.



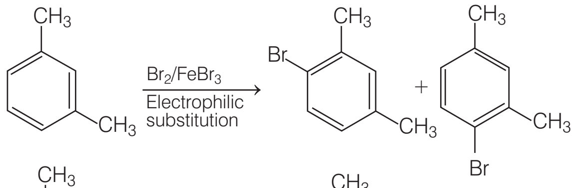
Benzyl carbocation

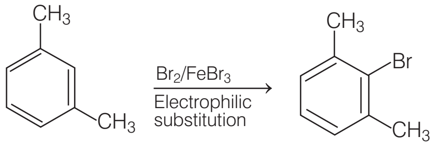
It has slightly lesser stability as compared to 3°-alkyl carbocation due to presence of three electron donating alkyl group in 3°-alkyl carbocation. Although the stabilities of 3° and benzyl carbonium ion are almost same and cannot be compared in solution but whenever a comparison is made between **resonance** (the cause of stability in benzyl carbonium ion) and **no bond resonance** (the cause of stability in 3° carbonium ion) then the former is always preferred hence here in this question benzyl carbonium ion is more stable than 3° carbonium ion.

19 Aryl halides, in presence of strong base like $NaNH_2$, gives nucleophilic substitution reaction through benzyne intermediate.



20 (c) CH_3 is a *o*/*p*-directing group, thus electrophilic substitution reaction of toluene



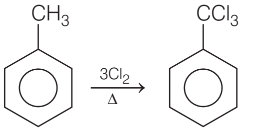


Not possible due to steric hinderance

21 Given, $C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$

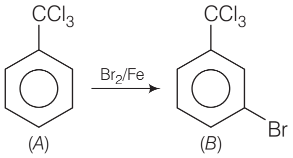
The reaction in the above road map can be explained by the following steps :

Step I Toluene (*A*) undergoes side chain halogenation with excess of chlorine to give benzotrichloride (*A*).



C_7H_8 (Toluene) (*A*) (Benzotrichloride)

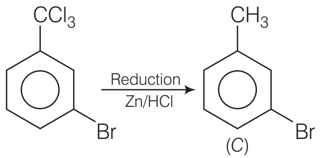
Step II In compound (A), the substituent CCl_3 is an electron withdrawing group, so the electrophile will attack at *m*-position. Thus, benzotrichloride reacts with bromine in presence of Fe-catalyst to give *m*-bromobenzotrichloride (*B*)



(*A*) (*B*)

m-bromobenzotrichloride

Step III *m*- bromobenzene chloride undergoes reduction with Zn in presence of HCl to give *m*-bromotoluene

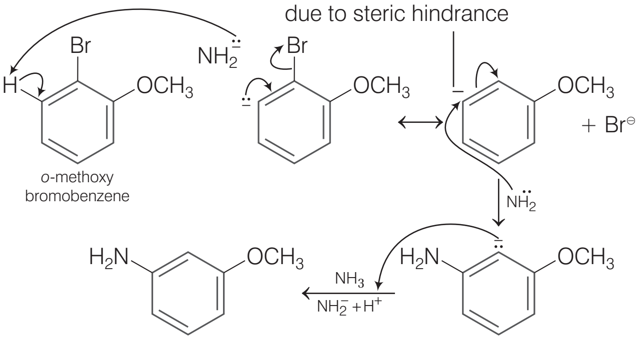


(*C*)

m-bromotoluene

22

NH$_2$ attacks here not at *o*-position due to steric hindrance

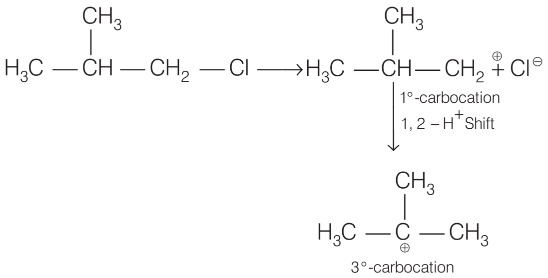


o-methoxy bromobenzene

m-methoxy aniline

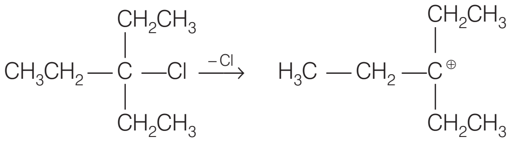
23 $-NO_2$ group deactivates the benzene ring and it withdraws electron from *o*-and *p*-positions. It is *m*-directing in nature.

24



$$H_3C-\overset{\overset{\large CH_3}{|}}{CH}-CH_2-Cl \longrightarrow H_3C-\overset{\overset{\large CH_3}{|}}{CH}-\overset{\oplus}{CH_2}+Cl^{\ominus}\ \xrightarrow[\text{1, 2 }-H^+\text{ Shift}]{1°\text{-carbocation}}\ H_3C-\underset{\oplus}{\overset{\overset{\large CH_3}{|}}{C}}-CH_3$$

3°-carbocation



$$CH_3CH_2-\underset{\underset{\large CH_2CH_3}{|}}{\overset{\overset{\large CH_2CH_3}{|}}{C}}-Cl \xrightarrow{-Cl} H_3C-CH_2-\underset{\underset{\large CH_2CH_3}{|}}{\overset{\overset{\large CH_2CH_3}{|}}{C^{\oplus}}}$$

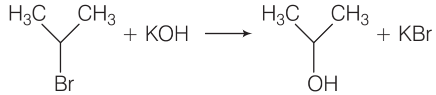
3°-carbocation

Since, 3°-carbocation will give racemisation product because it undergoes S_N1 reaction.

25 (i) $CH_3CH_2CH_2Br + KOH \rightarrow CH_3CH{=}CH_2 + KBr + H_2O$

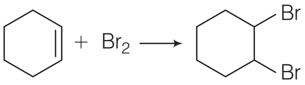
Elimination reaction

(ii)



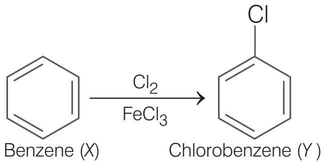
Substitution reaction

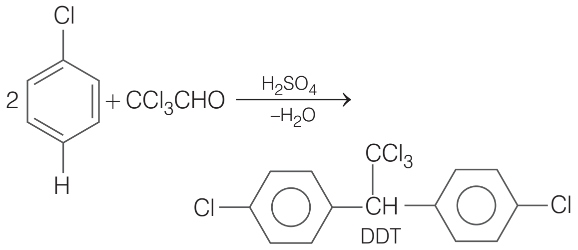
(iii)



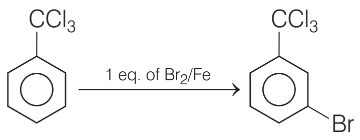
Addition reaction

26 This is the preparation method of DDT (dichlorodiphenyl trichloroethane).



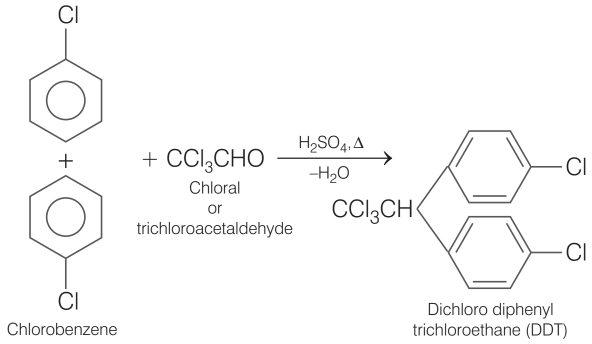


27 Due to presence of electron withdrawing group —Cl, benzene ring deactivates and becomes *meta*-directing.



28 Freon used as refrigerant is CCl_2F_2.

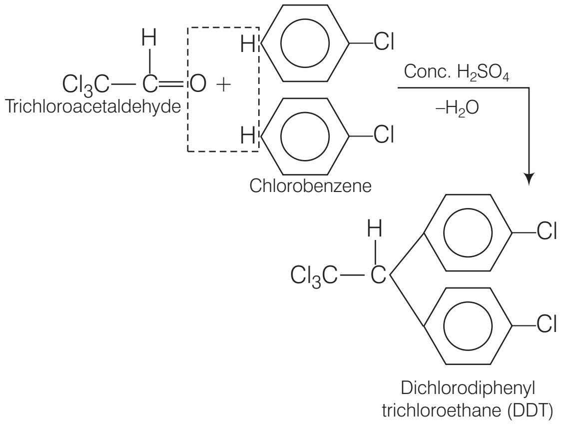
29



30 Iodoform reaction is given by alcohols and ketones containing $CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}$ and $CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}$ group, respectively. Thus, among the given compounds, isobutyl alcohol does not contain $CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}$ group.

Hence, it does not give iodoform reaction on treatment with I_2/NaOH.

31

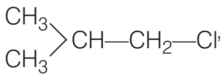


SESSION 2

1 For S_N2 reactions, lesser be the steric hinderance, faster is the S_N2 reaction, thus increasing order for S_N2 reaction will be

(i) $CH_3CH_2CH_2{-}Cl$, then

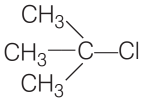
(ii)



then

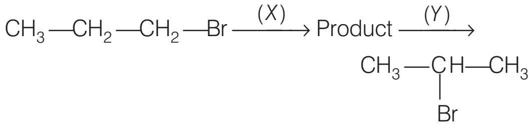
(iii) $CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}Cl$, then

(iv)



i.e. (i) > (iii) > (ii) > (iv)

2 For the given reaction,


$$CH_3{-}CH_2{-}CH_2{-}Br \xrightarrow{(X)} \text{Product} \xrightarrow{(Y)} CH_3{-}\underset{\displaystyle Br}{\underset{|}{C}}H{-}CH_3$$

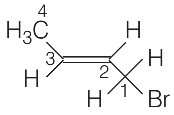
Initially, $CH_3 \cdot CH_2 \cdot CH_2Br$ changes to 1° carbocation in the presence of reagent dilute aqueous NaOH.

In step (ii), the produced carbocation go for rearrangement and produce 2° alkyl bromide using the reagents HBr/acetic acid.

Thus, (X) is dilute NaOH and (Y) is HBr/acetic acid.

Hence, (b) is the correct option.

3 The correct IUPAC name of



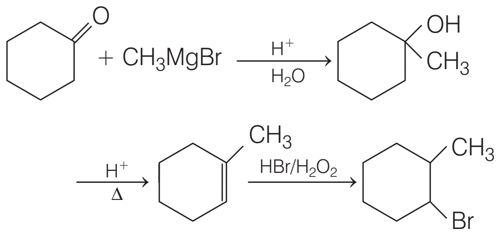
is

1-bromobut-2-ene

4 Elimination reaction (E_1, E_2 etc.) are competing reaction for an S_N2 reactions.

$\therefore$ Statement (b) is the incorrect statement.

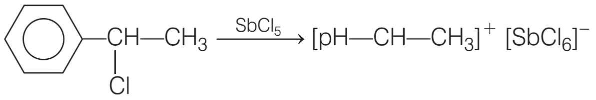
5



6 II is most reactive as it produces an aromatic carbocation while IV is less reactive as it produces a non-resonance stabilised carbocation.III is least reactive than I as former involve an anti-aromatic carbocation.

7 Organic-halides contain aromatic ring go for alkaline hydrolysis and form corresponding resonating carbocation which ultimately give the racemic mixture. Hence, (a) is the correct answer.

8 A solution of (–) 1 chloro-1 phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to formation of carbocation. The reaction occurs is as follows



Hence, (d) is the correct option.

9 The given reaction is an example of Wurtz reaction, in which alkyl halide when treated with Na-metal in the presence of dry ether, it gives alkanes by elimination of halogen atoms and combining the C—C atoms of the two alkyl halide molecules. Thus, mixture of bromobutane and bromoethane can given the alkanes are

$C_2 + C_4 \longrightarrow$ hexane (C_6)

$C_2 + C_2 \longrightarrow$ butane (C_4)

$C_6 + C_2 \longrightarrow$ octane (C_8)

but it will not give C_2 (ethane).

Hence, (d) is the correct option.

10 When 2-chloro-2 methyl butane is heated with KOH (alcoholic), it will go for elimination and give possible alkenes.

The possible alkenes are

(i) $(CH_3)_2—C = CH—CH_3$ (using Saytzeff rule)

(ii) $CH_2 = C(CH_3)CH_2CH_3$
(using Hofmann elimination rule)

Hence, (c) is the correct option.

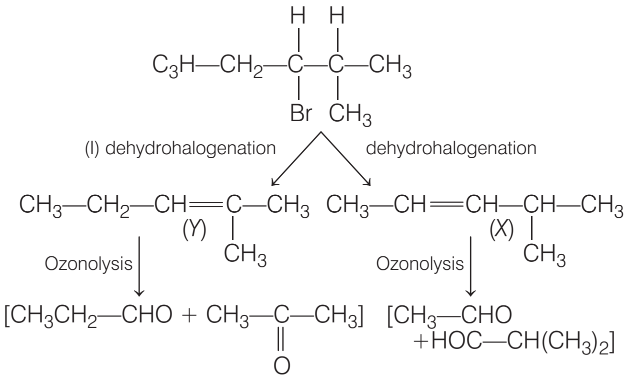
11 More be the resonance shown by the conjugate and hyperconjugation by the given species, more is its reactivity towards S_N1 reaction.

$\because$ In (iii) we have two benzene rings along with alkyl groups, thus it will show maximum S_N1 reactivity (ii), is next reactive species due to presence of two benzene rings.

(iv) is the next species having three alkyl groups and (iv) is there after due to presence of two alkyl groups while (v) is least reactive due to presence of one alkyl group. Hence, correct order is

(iii) > (ii) > (i) > (iv) > (v)

12 The given alkyl halide ($C_6H_{13}Br$) is 3-bromo 2-methyl-pentane as its dehydrohalogenation can give



Hence, (a) is the correct option.

13 Alkaline hydrolysis of tertiary alkyl halide by aqueous alkali show substitution reaction. The given organic molecule show S_N1 reaction as halide is attached with the 3° C-atom, which will form stable carbocation.

$\because$ S_N1 reaction only depends on the concentration of alkyl halide and not on the concentration of base used, i.e.

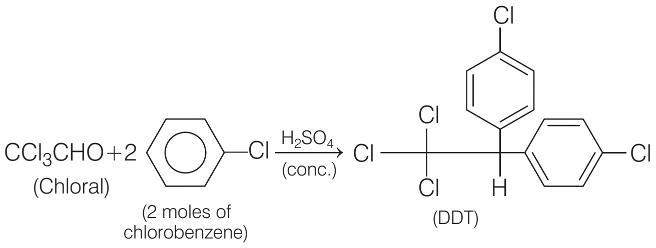
Rate (S_N1) $\propto$ conc. of alkyl halide.

Hence, at constant pressure, the rate of reaction remain as such on doubling the concentration of alkali.

14 In $C_6H_5CH_2—I$, C—I bond is reactive, so it gives yellow precipitate of AgI. On the other hand, C — I bond in C_6H_5I is stable, so it does not give yellow precipitate with $AgNO_3$.

$\therefore$ (A) was $C_6H_5—I$

15 When 2 moles of chlorobenzene is heated with chloral in the presence of H_2SO_4 (conc.) we get DDT, as follows :



(p, p dichloro diphenyl chloroethane)