

## Syllabus

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

## Chapter Analysis

List of Topics	2016		2017		2018
	D	QD	D	OD	D/OD
Give reason	1Q (3 marks)	–	–	–	–
IUPAC name	1Q (1 mark)	–	–	–	–
Structure of Haloalkanes and Haloarenes	–	–	1Q (1 mark)	1Q (1 mark)	1Q (3 mark)#
S <sub>N</sub> 1 Reaction, S <sub>N</sub> 2 Reaction, Optical Activity and β-elimination Reaction	1Q (1 mark)	1Q (1 mark)	1Q (3 marks)	1Q (3 marks)	1Q (1 mark)
Conversion	–	1Q (3 marks)*	–	–	–
Write the major product(s) or the structure of products formed	–	1Q (3 marks)*	–	–	1Q (3 marks)#

● \* One question of 3 marks with two choices was asked. First choice was to convert compounds. Second choice was to write the major product(s) formed.

● # One question of 3 marks regarding Chirality and Structure of products formed for the given conditions was asked.

On the basis of above analysis, it can be said that from exam point of view, Structure of Haloalkanes and Haloarenes, S<sub>N</sub>1 Reaction, S<sub>N</sub>2 Reaction and Optical Activity are the most important topics of the chapter. Also, Write the major product(s) or the structure of products formed type of question was frequently asked.



## TOPIC-1

## Haloalkanes and their Properties

## Revision Notes

- Hydrogen atom in aliphatic hydrocarbon replaced by halogen are called haloalkanes, while in benzene ring are called haloarenes.
- In haloalkane, halogen is attached with carbon through  $sp^3$  hybridisation while in haloarenes it is attached with  $sp^2$  hybridisation.

## TOPIC - 1

Haloalkanes and their Properties

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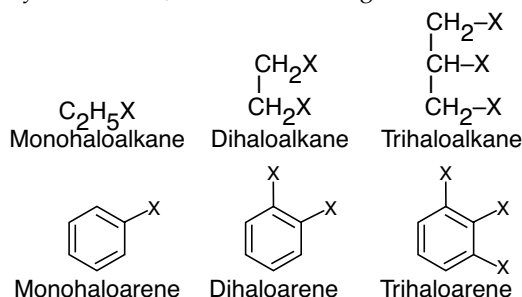
## TOPIC - 2

Haloarenes and Polyhalogen Compounds

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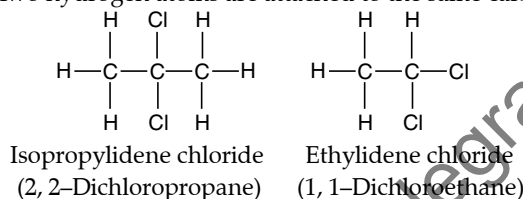
➤ **Classification :**

- **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,



Dihalogen compounds may be further classified as :

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

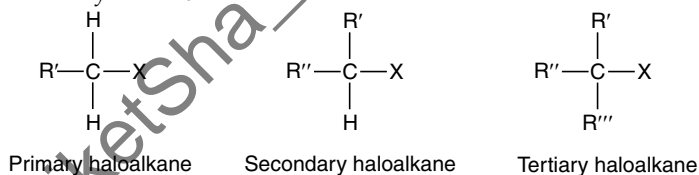


- (ii) **Vicinal dihalides :** Two halogen atoms are attached to adjacent carbon atoms. For example,

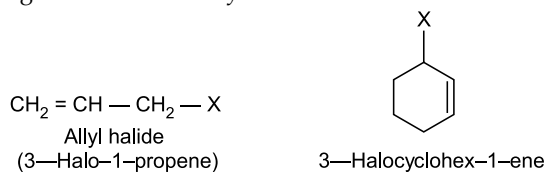


- **On the basis of  $sp^3$  hybridisation :**

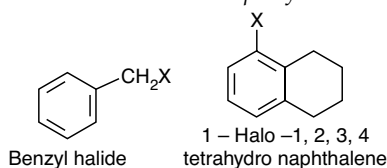
- (i) Haloalkanes or alkyl halides ( $R-X$ ) : General formula is  $C_nH_{2n+1}X$ . They are further classified as primary, secondary and tertiary haloalkanes.



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



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

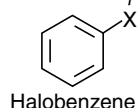


- **On the basis of  $sp^2$  hybridisation :**

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



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



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

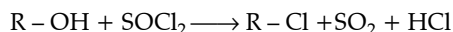
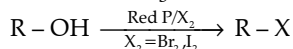
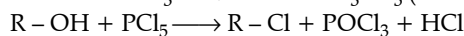
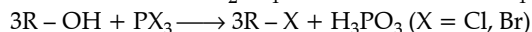
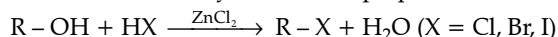
Structure	IUPAC Name	Common names
$\text{CH}_3\text{Cl}$	Chloromethane	Methyl chloride
$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane	Ethyl chloride
$\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Cl}$	1-Chloropropane	<i>n</i> -Propyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\   \\ \text{Cl} \end{array}$	2-Chloropropane	Isopropyl chloride
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{Cl}$	1-Chlorobutane	<i>n</i> -Butyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{Cl} \\   \\ \text{CH}_3 \end{array}$	1-Chloro-2-methyl propane	Isobutyl chloride
$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\   \\ \text{Cl} \end{array}$	2-Chlorobutane	Sec. butyl chloride
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{Cl} \end{array}$	2-Chloro-2-methyl propane	Tertiary butyl chloride
$\text{CH}_3\text{F}$	Fluoromethane	Methyl fluoride
$\text{CH}_3\text{Br}$	Bromomethane	Methyl bromide
$\text{CH}_3\text{I}$	Iodomethane	Methyl iodide
$\text{CH}_2\text{Cl}_2$	Dichloromethane	Methylene dichloride
$\text{CHCl}_3$	Trichloromethane	Chloroform
$\text{CCl}_4$	Tetrachloromethane	Carbon tetrachloride
$\text{CHBr}_3$	Tribromomethane	Bromoform
$\text{CHI}_3$	Triiodomethane	Iodoform
$\text{ClCH}_2-\text{CH}_2\text{Cl}$	1, 2-Dichloroethane	Ethylene dichloride
$\text{CH}_3\text{CHCl}_2$	1, 1-Dichloroethane	Ethylidene chloride
$\text{CH}_2 = \text{CHCl}$	Chloroethene	Vinyl chloride
$\text{CH}_2 = \text{CH}-\text{CH}_2\text{Br}$	3-Bromopropene	Allyl bromide
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	1-Bromo-2, 2-dimethylpropane	neo-pentylbromide
$\text{CF}_3\text{CF}_2\text{CF}_3$	Octafluoropropane	Perfluoropropane
$\text{CCl}_2\text{F}_2$	Dichlorodifluoromethane	Freon
$\text{CHCl}_2-\text{CHCl}_2$	1, 1, 2, 2-Tetrachloroethane	Acetylene tetrachloride
$\text{CHCl} = \text{CCl}_2$	1, 1, 2-Trichloroethene	Acetylene trichloride



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

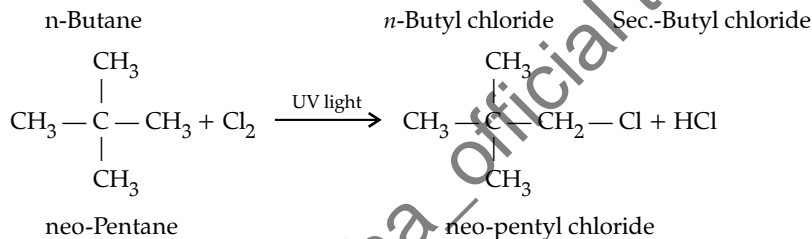
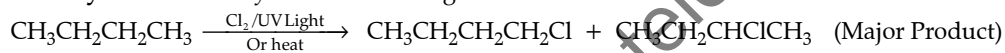
➤ **Methods of preparation of Haloalkanes :**

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

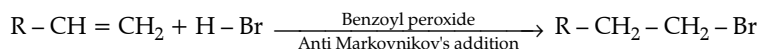
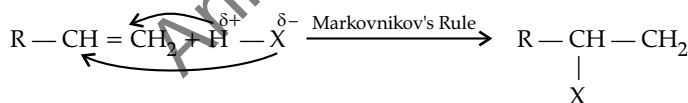


The reaction of primary and secondary alcohols with HX require the presence of the anhydrous catalyst  $ZnCl_2$ .

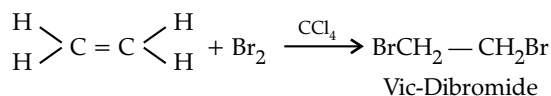
(b) **From hydrocarbons :** By free radical halogenation.



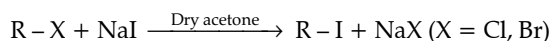
(c) **From alkenes : (i) Addition of hydrogen halide :**



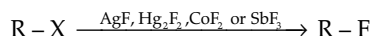
(ii) **Addition of Halogens :**



(d) **Halide Exchange : (i) By Finkelstein Reaction :**



(ii) **By Swarts Reaction :**



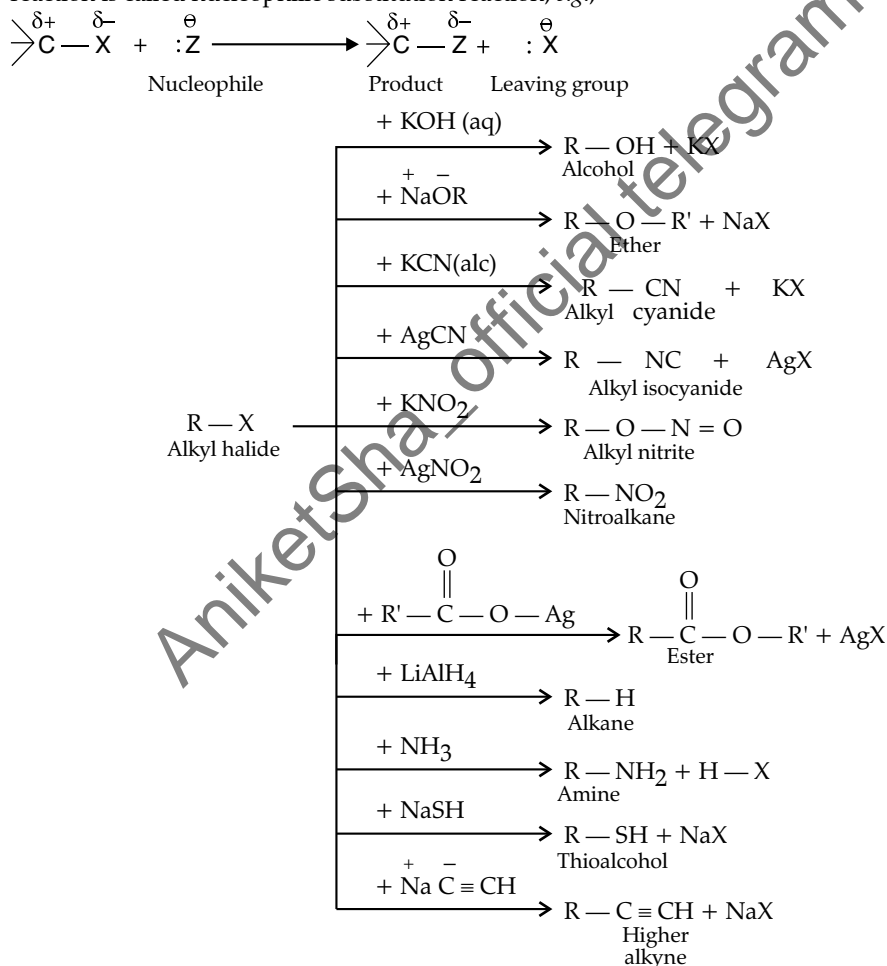
➤ **Nature of C-X bond in haloalkanes :** The carbon halogen bond is polarised. Carbon atom holds partial positive charge and halogen atom holds partial negative charge. This occurs due to difference in electronegativity. Halogens are more electronegative than carbon. Size of the halogen atoms increases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

- **Physical properties of haloalkanes** : Haloalkanes are colourless when pure but compounds of bromine are coloured.
- (i) **Melting and boiling points** : Haloalkanes, due to polar and strong dipole-interactions between their molecules, have high B.P. and M.P. This increase in B.P. and M.P. depends on size and mass of halogens, with weak van der Waals forces of attractions. The increasing order is  $\text{RCl} < \text{RBr} < \text{RI}$ . With respect to isomeric alkyl halides, B.P. decreases with increase in branching due to less surface area and weak inter-particle forces.
- (ii) **Density** : It increases with increase in carbon atoms, halogen atoms and atomic mass of the halogen atoms.
- (iii) **Solubility** : Haloalkanes are insoluble in water but are soluble in organic solvents.
- **Chemical properties of haloalkanes** : Reactivity of haloalkanes, depends on the C-X bond cleavage. Higher the bond dissociation energy of C-X bond, lesser will be the reactivity. Dissociation energy of C-X bond decreases with increase in the halogen size, i.e.,  $\text{C-Cl} > \text{C-Br} > \text{C-I}$ . Reactivity order of haloalkanes would be :

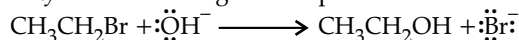
Chlorides < Bromides < Iodides

There are four types of chemical reactions with haloalkanes :

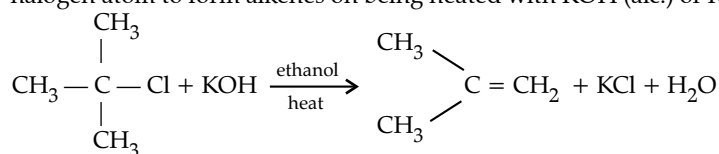
- (a) **Nucleophilic substitution reactions** : When an atom or group of atoms is replaced by a *nucleophile*, the reaction is called nucleophilic substitution reaction, e.g.,



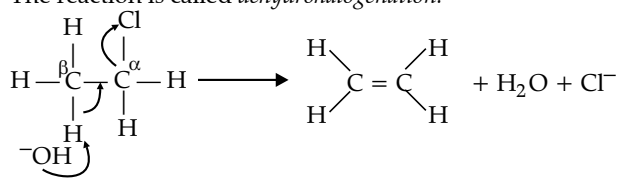
Alkyl halides undergo nucleophilic substitution reactions.



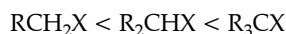
- (b) **Elimination Reaction** : Alkyl halide undergo  $\beta$ -elimination of hydrogen atom from  $\beta$ -carbon atom and halogen atom to form alkenes on being heated with KOH (alc.) or  $\text{KNH}_2$ , e.g.,



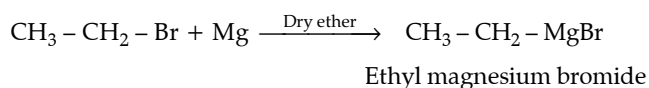
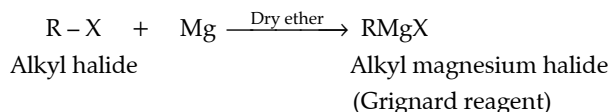
The reaction is called *dehydrohalogenation*.



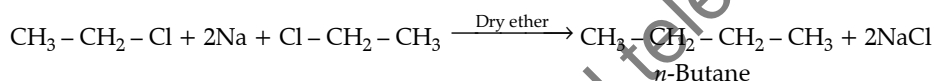
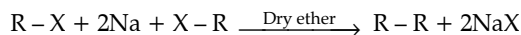
The following is order of reactivity :



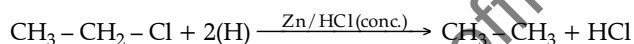
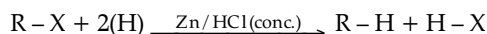
(c) **Reaction with metals : (1) Reaction with magnesium :**



(2) **Reduction with sodium (Wurtz reaction) :**



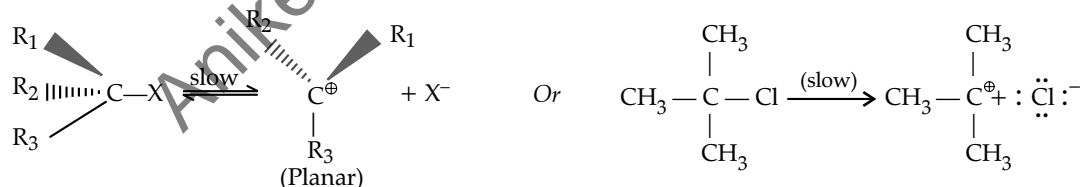
(d) **Reduction :**



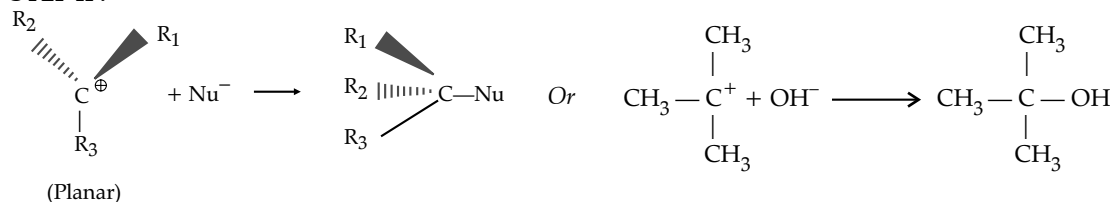
➤ **Mechanism of Nucleophilic substitution reaction :** Alkyl halide undergoes two types of nucleophilic substitution reactions.

(i) **Unimolecular nucleophilic substitution reaction ( $\text{S}_{\text{N}}1$ ) :** Those substitution reactions in which rate of reaction depends upon the concentration of only one of the reactants, *i.e.*, alkyl halides are called  $\text{S}_{\text{N}}1$  reactions, *e.g.*, hydrolysis of tertiary butyl chloride follows  $\text{S}_{\text{N}}1$  reaction. This reaction takes place in two steps.

**STEP I :**

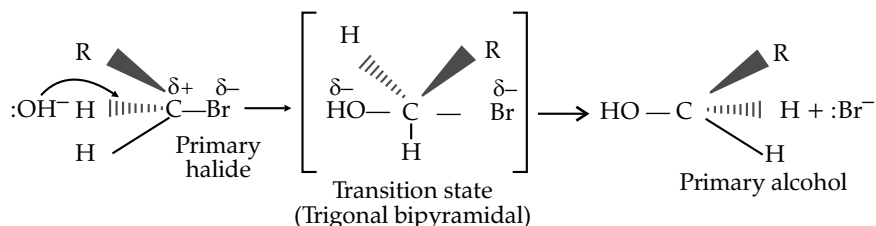


**STEP II :**



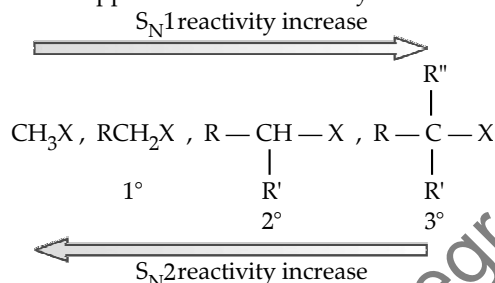
The slowest step is rate determining step which involves one species only. Therefore, rate of reaction depends only on the concentration of tertiary butyl chloride. Tertiary halides follow  $\text{S}_{\text{N}}1$  mechanism. Polar protic solvents like water, alcohol favour  $\text{S}_{\text{N}}1$  because they stabilize carbocation by solvation. Tertiary halides follow  $\text{S}_{\text{N}}1$  mechanism.

(ii) **Bimolecular nucleophilic substitution reaction ( $\text{S}_{\text{N}}2$ ) :** The reaction whose rate depends on the concentration of two species, alkyl halide and nucleophile. They involve one step mechanism: back side attack of nucleophile and departing of leaving group take place simultaneously.



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

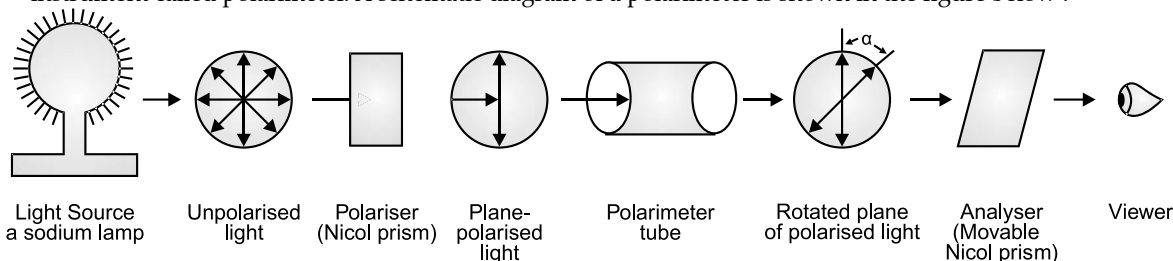
- **Reactivity of  $S_N1$  and  $S_N2$  mechanisms** : S = Substitution, N = Nucleophilic, 2 = Bimolecular, 1 = Unimolecular. Nucleophilic substitution seldom occurs exclusively by one mechanism only. With a given halogen, primary, secondary and tertiary halides show opposite order of reactivity in the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



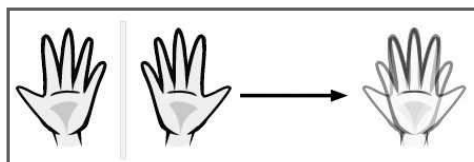
- **Stereoisomerism** : Isomerism exhibited by two or more compounds with the same molecular and structural formula, but different spatial arrangements of atoms or groups in space is called stereoisomerism.
- **Plane-polarised light** : The beam of light whose oscillations or vibrations are confined 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  $\alpha_{\text{obs}}$ ) of a substance depends upon the following factors :
- nature of substance,
  - wavelength of the light used,
  - the number of optically active molecules in the path of light beam (which depends upon concentration of sample),
  - length of polarimeter tube,
  - solvent used.

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

- **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 :

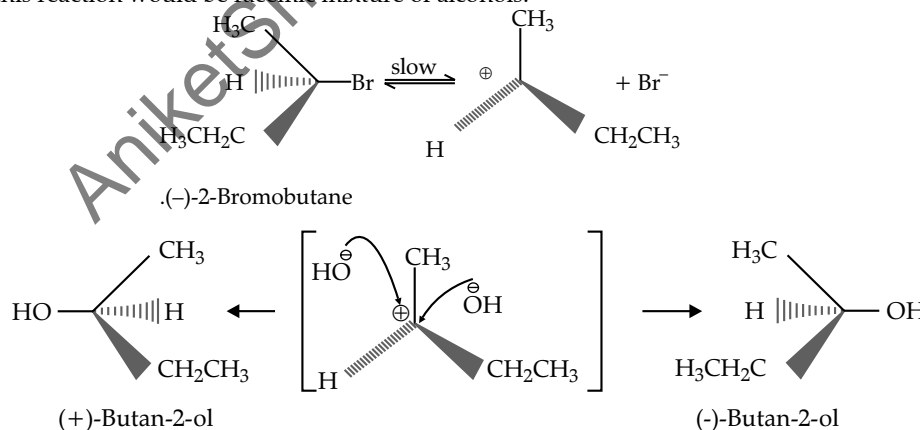


- **Enantiomers** : Those stereoisomers which are mirror images of each other but non-superimposable are called enantiomers, *e.g.*, *d*(+) glucose and *l*(-) glucose are enantiomers.
- **Asymmetric molecule** : If all the four substituents attached to carbon are different, the resulting molecule will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

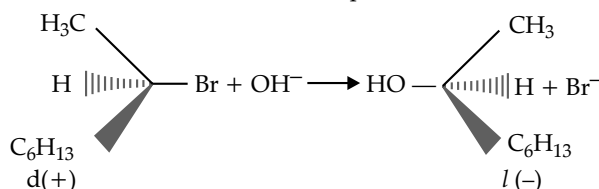


Non-superimposable left hands

- **Achiral** : Achiral objects are those objects which are superimposable on their mirror images.
- **Asymmetric carbon** : The carbon atom which is attached with four different groups of atoms is called asymmetric carbon atom.
- **Racemic mixture** : A mixture containing equal amounts of enantiomers which does not show any optical activity.
- **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 pair of stereo isomers which are not mirror images of each other and are non-superimposable.
  - Diastereoisomers have different physical properties.
  - Diastereoisomers differ in magnitude of specific rotation.
  - A compound with two chiral centres does not always have four stereoisomers.
- **Example of racemisation in  $S_N1$  mechanism** : When optically active alkyl halide undergoes  $S_N1$  mechanism, it is accompanied by racemisation because intermediate carbocation formed is  $sp^2$ -hybridised and polar. Nucleophile ( $OH^-$ ) has equal probability of attacking it from either side leading to formation of equal amount of dextro and laevo-rotatory alcohols. As the products of  $S_N1$  mechanism has both inversion as well as rotation, the products formed by this reaction would be racemic mixture of alcohols.



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

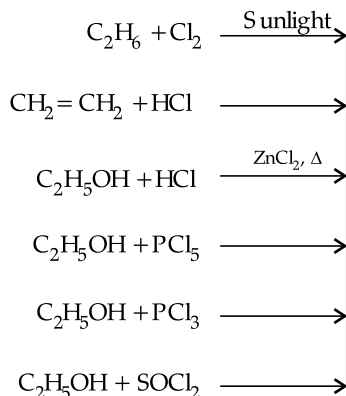


When *d*(+)-2-bromooctane is reacted with NaOH, *l*(-)-2-octanol is formed. Thus,  $S_N2$  mechanism leads to inversion of configuration. This inversion is called Walden's inversion.



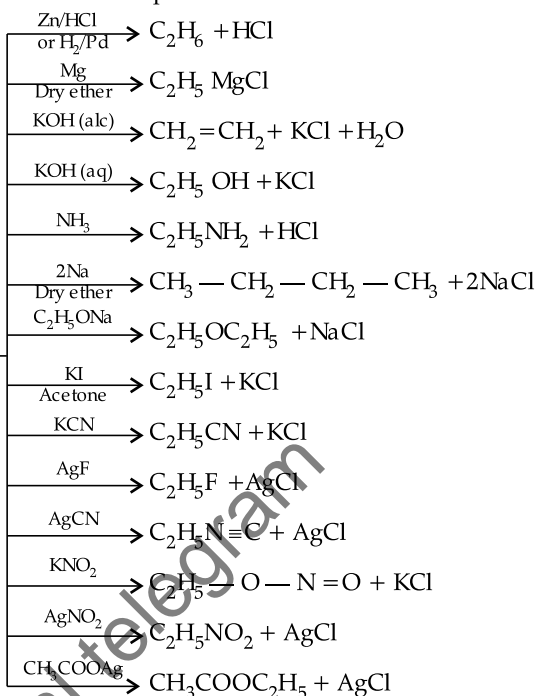
● **Important reactions of chloroethane :**

**Preparation**



**Chloroethane**  
(C<sub>2</sub>H<sub>5</sub>Cl)

**Chemical Properties**



## Know the Terms

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



## Very Short Answer-Objective Type Questions (1 mark each)

### A. Multiple choice Questions:

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

- (i)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$   
 (ii)  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$   
 (iii)  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$

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

[NCERT Exemp. Q. 1, Page 133]

Ans. Correct option : (b)

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

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

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

- (b)  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$

- (c)  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$

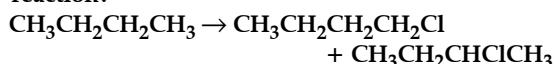
- (d)  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$

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

Ans. Correct option : (d)

**Explanation :** As tertiary carbocation is more stable, so tertiary alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature. While primary and secondary alcohols, require the presence of a catalyst  $\text{ZnCl}_2$ .

Q. 3. Which reagent will you use for the following reaction?



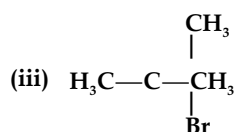
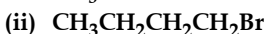
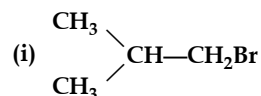
- (a)  $\text{Cl}_2/\text{UV light}$   
 (b)  $\text{NaCl} + \text{H}_2\text{SO}_4$   
 (c)  $\text{Cl}_2$  gas in dark  
 (d)  $\text{Cl}_2$  gas in the presence of iron in dark

[R] [NCERT Exemp. Q. 6, Page 134]

Ans. Correct option : (a)

**Explanation :** The given reaction is a free radical substitution reaction. It occurs in presence of ultraviolet light or at high temperature or peroxides which are free radical generators. Free radical substitution cannot take place in dark.

Q. 4. Arrange the following compounds in increasing order of their boiling points.



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

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

Ans. Correct option : (c)

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

Q. 5. A primary alkyl halide would prefer to undergo

- (a)  $\text{S}_\text{N}^1$  reaction      (b)  $\text{S}_\text{N}^2$  reaction  
 (c)  $\alpha$ -Elimination      (d) Racemisation

[U] [NCERT Exemp. Q. 16, Page 137]

Ans. Correct option : (b)

**Explanation :**  $\text{S}_\text{N}^2$  reaction proceeds, via formation of transition state which is formed easily in primary alkyl halide due to less steric hindrance.

B. Match the following :

Q. 1. Match the species given in Column I with those mentioned in Column II.

Column I		Column II	
(a)	$\text{S}_\text{N}^1$ reaction	(i)	vic-dibromides
(b)	Chemicals in fire extinguisher	(ii)	gem-dihalides
(c)	Bromination of alkenes	(iii)	Racemisation
(d)	Alkylidene halides	(iv)	Saytzeff rule
(e)	Elimination of HX from alkyl halide	(v)	Chlorobromo-carbons

[NCERT Exemp. Q. 39, Page 126]

Ans. (a)  $\rightarrow$  (iii)

(b)  $\rightarrow$  (v)

(c)  $\rightarrow$  (i)

(d)  $\rightarrow$  (ii)

(e)  $\rightarrow$  (iv)

**Explanation :** (i) A mixture containing two enantiomers in equal proportions will have zero optical rotation, such a mixture is known as racemic mixture. The process of conversion of enantiomer into a racemic mixture is known as racemisation. If an alkyl halide follows  $\text{S}_\text{N}^1$  mechanism, then racemisation takes place while if it follows  $\text{S}_\text{N}^2$  mechanism then inversion takes place.

(ii) Chlorobromocarbons are used in fire extinguishers.

(iii) In vicinal dihalides, halogen atoms are present on the adjacent carbon atom. Bromination of alkanes will give vicinal dihalides.

(iv) Alkylidene halides are named as gem-dihalides. In gem-dihalides halogen atoms are present on same carbon atom.

(v) Elimination of HX from alkyl halide follows Saytzeff rule. This rule states that in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.

C. Answer the following:

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



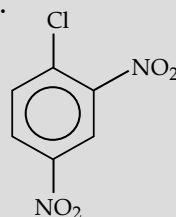
1

[CBSE Marking Scheme 2017]

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

[A] [CBSE Delhi Set-2 2017]

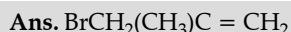
Ans.



1

[CBSE Marking Scheme 2017]

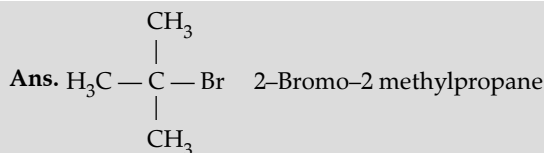
Q. 3. Write the structure of 3-Bromo-2-methylprop-1-ene. [A] [CBSE Delhi Set-3 2017]



1

[CBSE Marking Scheme 2017]

Q. 4. Write the structure of an isomer of compound  $\text{C}_4\text{H}_9\text{Br}$  which is most reactive towards  $\text{S}_\text{N}^1$  reaction. [A] [CBSE OD 2016]



1

[CBSE Marking Scheme 2016]

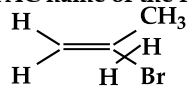
#### Commonly Made Error

- Students often get confused between  $\text{S}_\text{N}^1$  and  $\text{S}_\text{N}^2$  reaction.

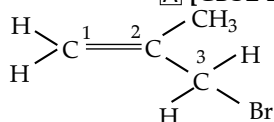
**Answering Tip**

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

Q. 5. Write the IUPAC name of the following :

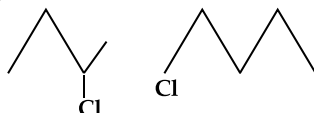


Ans.

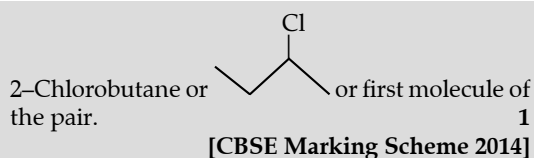


3-bromo-2-methyl prop-1-ene

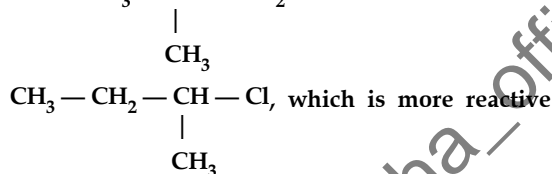
Q. 6. Identify the chiral molecule in the following pair :



Ans.



Q. 7. Out of  $\text{CH}_3 - \text{CH} - \text{CH}_2 - \text{Cl}$  and



towards  $\text{S}_{\text{N}}1$  reaction and why ?

[A&E] [CBSE Delhi 2016]

Ans.  $\text{CH}_3 - \text{CH}_2 - \text{CH} - \text{Cl}$

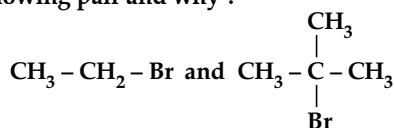
is more reactive as being secondary halide it forms more stable carbocation intermediate than primary halides.

[CBSE Marking Scheme 2016]

**Answering Tip**

- Clearly understand the concept of  $\text{S}_{\text{N}}1$  reaction.

Q. 8. Which would undergo  $\text{S}_{\text{N}}2$  reaction faster in the following pair and why ?



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

Ans.  $\text{CH}_3 - \text{CH}_2 - \text{Br}$  would undergo  $\text{S}_{\text{N}}2$  reaction faster it has less steric hindrance than tert - butyl bromide.

$\text{CH}_3 - \text{CH}_2 - \text{Br}$   $\frac{1}{2} + \frac{1}{2}$

Because it is a primary halide / ( $1^\circ$ ) halide

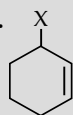
[CBSE Marking Scheme 2015]

**Answering Tip**

- Clearly understand the concept of  $\text{S}_{\text{N}}2$  reaction.

Q. 9. Out of and which is an example of allylic halide? [CBSE OD Set-1 2017]

Ans.



[CBSE Marking Scheme 2017] 1

Q. 10. Out of and , which is an example of vinylic halide? [CBSE OD Set-2 2017]

Ans.



[CBSE Marking Scheme 2017] 1

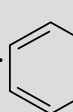
OR

1

[Topper's Answer 2017]

Q. 11. Out of and , which is an example of benzylic halide? [CBSE OD Set-3 2017]

Ans.

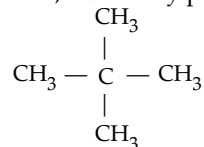


[CBSE Marking Scheme 2017] 1

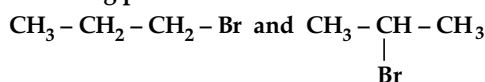
Q. 12. Amongst the isomeric alkanes of molecular formula  $\text{C}_5\text{H}_{12}$ , identify the one that on photochemical chlorination yields a single monochloride.

[CBSE SQP 2016]

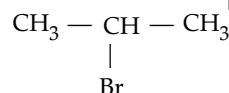
Ans. Neopentane or 2, 2-Dimethylpropane.



Q. 13. Which would undergo  $\text{S}_{\text{N}}1$  reactions faster in the following pair :



Ans.



[CBSE OD 2015]

1

**Answering Tip**

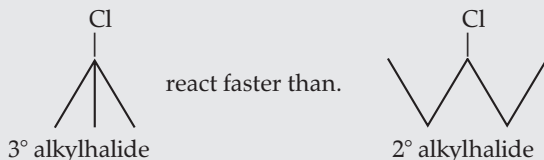
- Clearly understand the concept of  $\text{S}_{\text{N}}1$  reaction.

Q. 14. In the following pair of halogen compounds, which will react faster by  $S_N1$  mechanism?



[U] [CBSE OD 2014]

Ans. The  $3^\circ$  alkyl halides are most reactive, because the intermediate carbonation formed in their case is most stable in  $S_N1$  mechanism. The most stable intermediate is formed at faster rate.



[CBSE Marking Scheme 2014] 1

### Answering Tip

- Remember the fact that tertiary halides are most reactive towards  $S_N1$  reactions

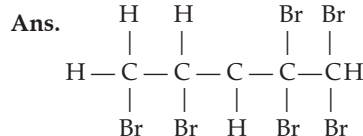
Q. 15. How can methyl bromide be preferentially converted to methyl isocyanide?

[A] [CBSE Comptt. Delhi 2014]

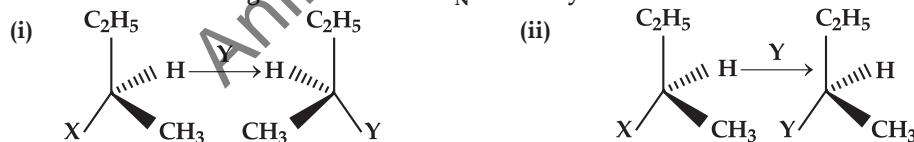
Ans.  $\text{CH}_3\text{Br} + \text{alc. AgCN} \longrightarrow \text{CH}_3\text{NC} + \text{AgBr}$   
Methyl isocyanide 1

[AI] Q. 16. What happens when bromine attacks:

$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{C} \equiv \text{CH}$ ? [A] [CBSE OD 2012]



Q. 20. Which of the following two reactions is  $S_N2$  and why?



[A&E] [CBSE OD Set-2 2016]

Ans.

5. The reaction (i) is  $S_N2$  reaction. This is because it leads to inversion of configuration. In the reaction (ii) the configuration of a chiral carbon has been retained. Retention of configuration is a character of  $S_N1$  reaction.

1

[Topper's Answer 2016]

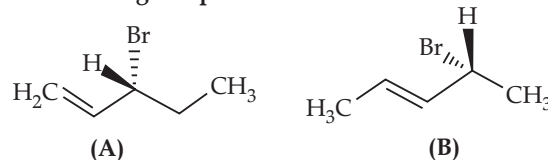
Detailed Answer :

The reaction (i) is  $S_N2$  as it shows inversion of configuration.

1

The reaction of bromine with pent-1-en-4-yne gives 1, 1, 2, 2, 4, 5 hexabromopentane as the main product. 1

Q. 17. Identify the compound that on hydrogenation produces an optically active compound from the following compounds:



[CBSE SQP 2018-19]

Ans. B

1

[CBSE Marking Scheme 2018]

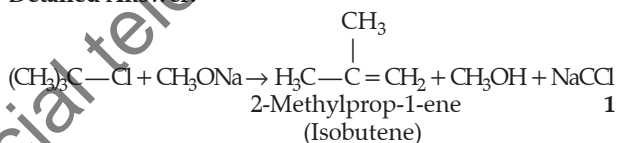
Q. 18. Predict the major product formed when sodium ethoxide reacts with tert-butyl chloride.

[A] [CBSE Comptt. Delhi/O.D. 2018]

Ans. 2-Methylprop-1-ene / isobutene / structure 1

[CBSE Marking Scheme 2018]

Detailed Answer:



Q. 19. Among the isomers of pentane ( $\text{C}_5\text{H}_{12}$ ), write the one which on photochemical chlorination yields a single monochloride.

[A] [CBSE Foreign Set-1 2017]

Ans. Neopentane /  $\text{C}(\text{CH}_3)_4$  1

[CBSE Marking Scheme 2017]

## Short Answer Type Questions

(2 marks each)

**Q. 1.** Answer the following questions :

- (i) What is meant by chirality of a compound ? Give an example.
- (ii) Which one of the following compound is more easily hydrolyzed by KOH and why ?  
 $\text{CH}_3\text{CHClCH}_2\text{CH}_3$  OR  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$

[R + A&E] [CBSE OD 2012]

**Ans. (i)** A carbon atom surrounded by 4 different groups is termed as chiral carbon and the property of being chiral is chirality.

Eg. 2-Butanol (or any other example). 1

- (ii)  $\text{CH}_3\text{CHClCH}_2\text{CH}_3$  will be easily hydrolysed (towards  $\text{S}_\text{N}1$ ) as the cation formed in this case will be secondary, which is more stable. 1

### Answering Tip

- Avoid writing unnecessary information in the answer. Instead be specific about the key word in that statement.

**Q. 2.** Which compound in each of the following pairs will react faster in  $\text{S}_\text{N}2$  reaction with  $\text{OH}^-$  ?

- (i)  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$   
 (ii)  $(\text{CH}_3)_3\text{CCl}$  or  $\text{CH}_3\text{Cl}$

OR

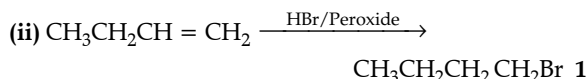
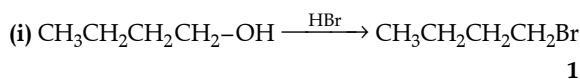
Write the equations for the preparation of 1-bromobutane from :

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

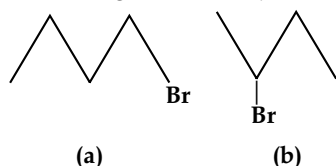
**Ans. (i)**  $\text{CH}_3\text{I}$  as  $\text{I}^-$  ion is better leaving group than  $\text{Br}^-$  ion. 1

- (ii)  $\text{CH}_3\text{Cl}$  as  $1^\circ$  alkyl halides are more reactive than tert-alkyl halides in  $\text{S}_\text{N}2$  reaction with  $\text{OH}^-$ . 1

OR



**Q. 3. (i)** Which alkyl halide from the following pair is chiral and undergoes faster  $\text{S}_\text{N}2$  reaction ?



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

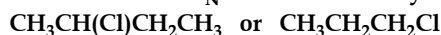
- (ii) Out of  $\text{S}_\text{N}1$  and  $\text{S}_\text{N}2$ , which reaction occurs with

- (a) Inversion of configuration  
 (b) Racemisation [A] [CBSE Delhi 2014]

**Ans. (i)** (b) is chiral ½  
 (a) undergoes faster  $\text{S}_\text{N}2$  ½  
 (ii) (a)  $\text{S}_\text{N}2$  ½  
 (b)  $\text{S}_\text{N}1$  ½

[CBSE Marking Scheme 2014]

**Q. 4.** Which one of the following compounds is more reactive towards  $\text{S}_\text{N}2$  reaction and why?



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

**Ans.**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ , due to primary halide which has less steric hindrance. 1+1

[CBSE Marking Scheme 2018]

**Detailed Answer:**

In  $\text{S}_\text{N}2$  reaction, attack of nucleophile takes place from backward direction. Primary alkyl halide is the least sterically hindered among primary, secondary and tertiary alkyl halides. While in secondary halides presence of bulky  $-\text{CH}_3$  group around causes steric hindrance for nucleophilic attack. Therefore, primary alkyl halides are more reactive towards  $\text{S}_\text{N}2$  reaction. 2

**Q. 5.** Which alkyl halide from the following pair is (i) Chiral and (ii) undergoes  $\text{S}_\text{N}1$  reaction faster?

- (a)  $(\text{CH}_3)_3\text{CBr}$   
 (b)  $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$

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

**Ans. (i)** (b) is chiral. 1  
 (ii) (a) [CBSE Marking Scheme 2017] 1

**Q. 6. (i)** Allyl chloride can be distinguished from Vinyl chloride by NaOH and silver nitrate test. Comment.

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

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

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

- (ii) Hydride ion /  $\text{H}^-$  1

[CBSE Marking Scheme 2017]

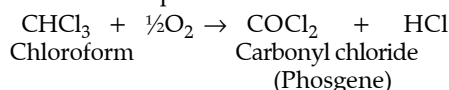
**Q. 7.** Account for the following :

- (i) The C — Cl bond length in chlorobenzene is shorter than that in  $\text{CH}_3\text{—Cl}$ .  
 (ii) Chloroform is stored in closed dark brown bottles.

[A&E] [CBSE Delhi 2013]

**Ans. (i)** Refer to Topic I, LAQ I Q.1 part (i). 1

- (ii) In the presence of air and sunlight, chloroform gets oxidised to phosgene (Carbonyl chloride —  $\text{COCl}_2$ ) a poisonous compound. Thus, to avoid the formation of phosgene, chloroform is stored in dark brown bottles filled up to brim.



1

**AI Q. 8.** Chlorobenzene is extremely less reactive towards a nucleophilic substitution reaction. Give two reasons for the same. [A&E] [CBSE Delhi 2013]

**Ans.** The two reasons are as follows :

(i) **Resonance effect** : The electron pair of chlorine atom is involved in conjugation with the  $\pi$ -electrons of the benzene ring. As a result, electrons of C—Cl bond get delocalized and a partial double bond character develops in the bond and hence, it becomes difficult for the nucleophile to cleave the C—Cl bond. 1

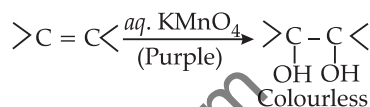
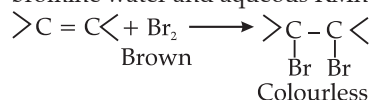
(ii) **Increased electron density** : A repulsion is suffered by the nucleophile due to increased electron density on the benzene ring which prohibits the nucleophile to make a close access for the attack on the molecule. 1

### Answering Tip

- As it is a reason based question carrying 2 marks, mention the two causes followed by the consequence.

**Q. 9.** Write a test to detect the presence of double bond in a molecule. [C] [NCERT Exemp. Q. 68, Page 144]

**Ans.** Presence of a double bond in a molecule can be detected by bromine water test and Baeyer's test. The molecules with a double bond decolourise bromine water and aqueous  $\text{KMnO}_4$ .



2



## Long Answer Type Questions-I

(3 marks each)

**Q. 1.** Give reasons :

- C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in  $\text{CH}_3\text{—Cl}$ .
- The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- $\text{S}_{\text{N}}1$  reactions are accompanied by racemization in optically active alkyl halides.

[A&amp;E] [CBSE Delhi 2016]

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

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

**(iii)** In  $\text{S}_{\text{N}}1$  reaction, carbocation intermediate formed is a planar molecule which will lead to form  $d$ - and  $l$ - products. Hence, racemization occurs. 1

[CBSE Marking Scheme 2016]

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

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

- Write the compound which is most reactive towards  $\text{S}_{\text{N}}2$  reaction.
- Write the compound which is optically active.
- Write the compound which is most reactive towards  $\beta$ -elimination reaction.

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

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

[CBSE Marking Scheme 2017]

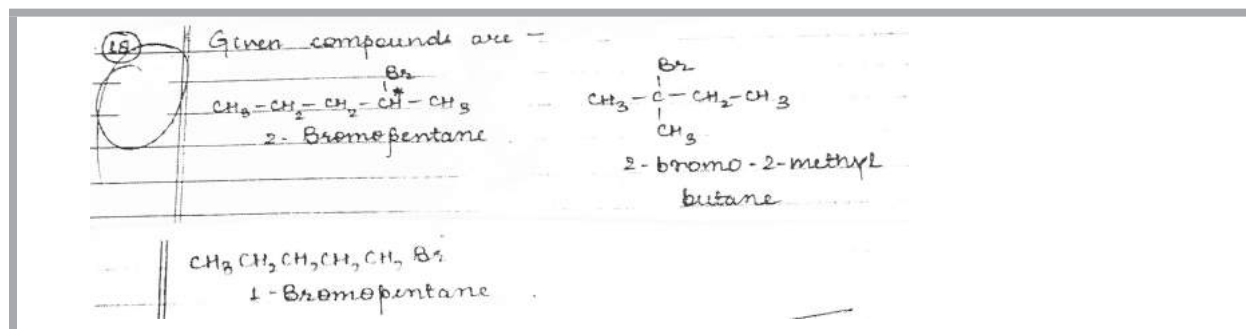
### Commonly Made Error

- There is confusion in the order of reactivity of  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  towards  $\text{S}_{\text{N}}1$ , optical activity and elimination reaction.

### Answering Tip

- Understand the variation in reactivity of  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  haloalkanes.

OR



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

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

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

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

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

3  
[Topper's Answer 2017]

**Detailed Answer:**

- (i) 1-Bromopentane as primary alkyl halides are most reactive for  $S_N2$ . 1
- (ii) 2-Bromopentane as it contains unsymmetrical carbon atom. 1
- (iii) 2-Bromo-2-methylbutane as tertiary alkyl halide is most reactive for elimination. 1

**Q. 3. Explain the following :**

- (i) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- (ii) Alkyl halides, though polar, are immiscible with water.
- (iii) Grignard's reagents should be prepared under anhydrous conditions.

[A&amp;E] [CBSE Comppt. QD Delhi 2012]

Ans. (i) Refer to Ans. of LAQ-I Q. 1 part (ii). 1

- (ii) Alkyl halides though polar are immiscible with water because less energy is released when new attractions are set up between the alkyl halide and the water molecules as they are not as strong as the original hydrogen bonds in the water as a result the solubility of alkyl halides in water is low. 1
- (iii) Grignard reagents should be prepared under anhydrous conditions because Grignard reagents are highly reactive. In the presence of moisture they react to give alkanes.

**[AI] Q. 5. Give the IUPAC name of the product formed when :**

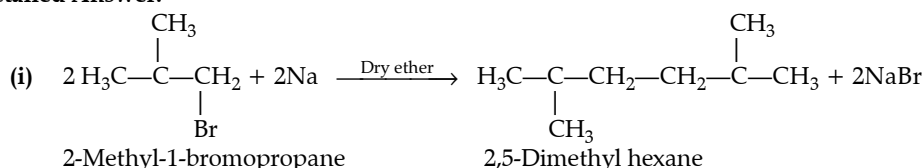
- (i) 2-Methyl-1-bromopropane is treated with sodium in the presence of dry ether.
- (ii) 1-Methyl cyclohexene is treated with HI.
- (iii) Chloroethane is treated with silver nitrite.

[A] [SQP 2017]

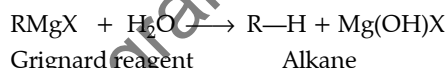
- Ans. (i) 2,5-Dimethyl hexane.
- (ii) 1-Methyl-1-iodocyclohexane
- (iii) Nitroethane

1+1+1

[CBSE Marking Scheme 2017]

**Detailed Answer:**

1



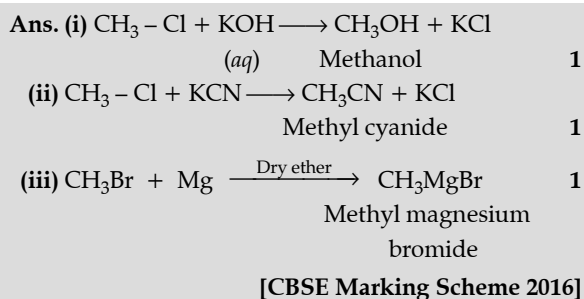
1

**Answering Tip**

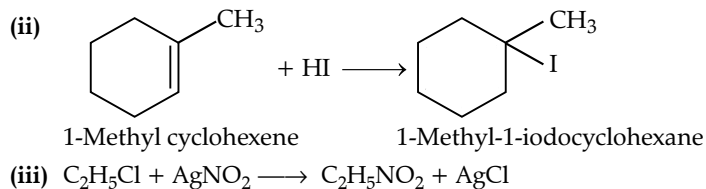
- In reasoning based questions remember to mention the keywords.

**Q. 4. What happens when :**

- (i)  $\text{CH}_3\text{-Cl}$  is treated with aqueous KOH ?
- (ii)  $\text{CH}_3\text{-Cl}$  is treated with KCN ?
- (iii)  $\text{CH}_3\text{-Br}$  is treated with Mg in the presence of dry ether ? [A] [CBSE Delhi 2016]

**Answering Tip**

- Write balanced chemical equations.



1

1



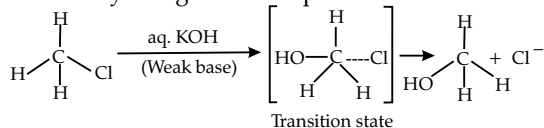
## Long Answer Type Questions-II

(5 marks)

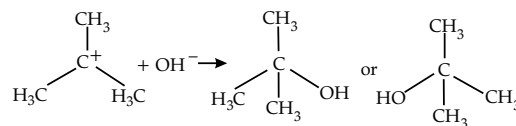
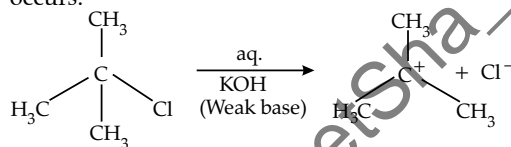
**Q. 1.** Some alkylhalides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.

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

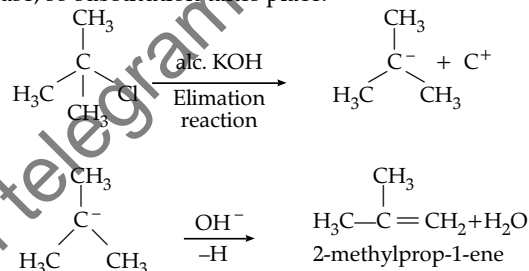
**Ans.** Primary alkyl halides prefer to undergo substitution reactions by  $\text{S}_{\text{N}}2$  mechanism. A transition state is formed in which carbon is bonded to nucleophile and finally halogen atom is pushed out.



In *tert-n*-butyl halides prefer to undergo elimination reactions due to the formation of stable carbocations.  $3^\circ$  alkyl halides follow  $\text{S}_{\text{N}}1$  mechanism by forming tertiary carbocations. Now, if the reagent used is a weak base then substitution occurs while if it is a strong base then instead of substitution elimination occurs.



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



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

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

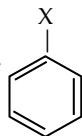
5



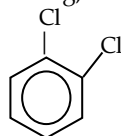
## TOPIC-2

### Haloarenes and Polyhalogen Compounds

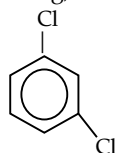
#### Revision Notes

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

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

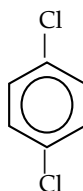


- When two halogens are at 1, 3-positions of benzene ring, it is called meta substituted derivative *e.g.*,

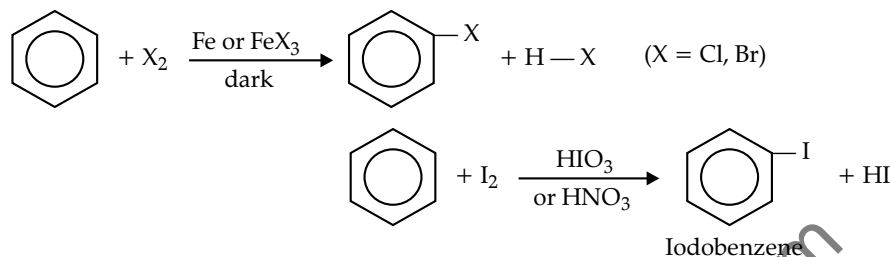




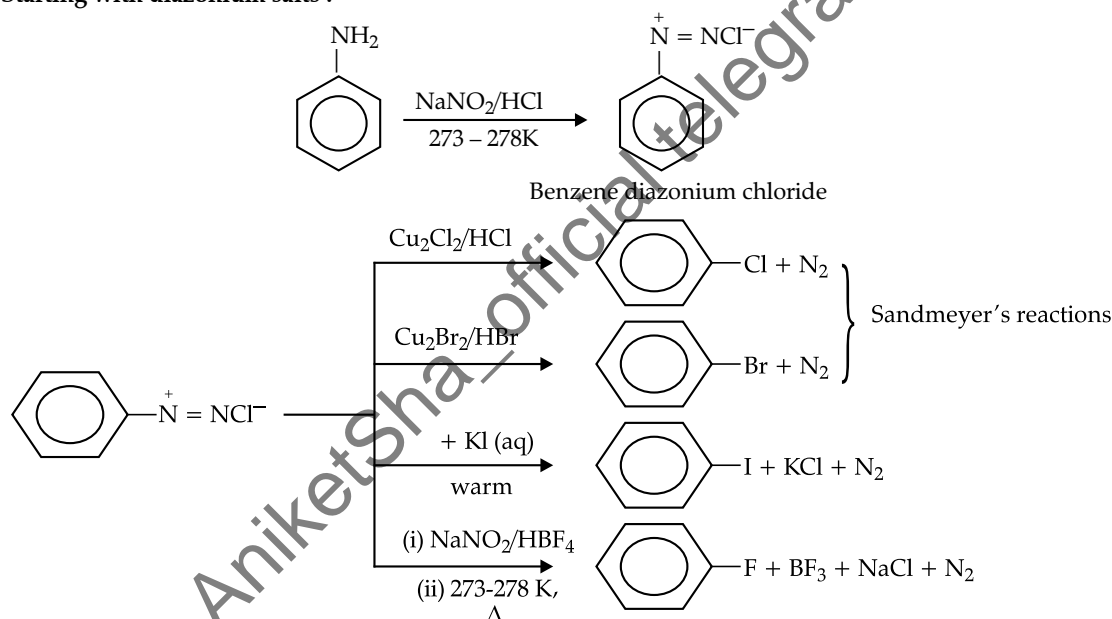
- When two halogens are at 1, 4-positions of benzene ring, it is called para substituted derivative. *e.g.*,



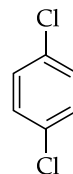
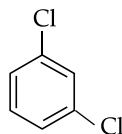
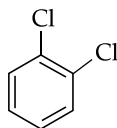
- **Methods of preparation of Haloarenes :** (i) **Reacting benzene directly with halogen :**



- (ii) **Starting with diazonium salts :**



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



b.p. (K) 453  
m.p. (K) 256

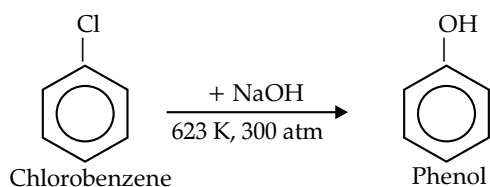
446  
249

448  
323

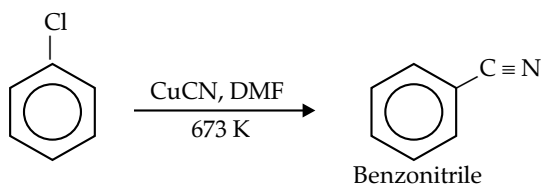
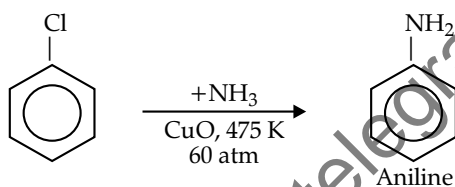
- **Chemical properties of Haloarenes :**

- (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.

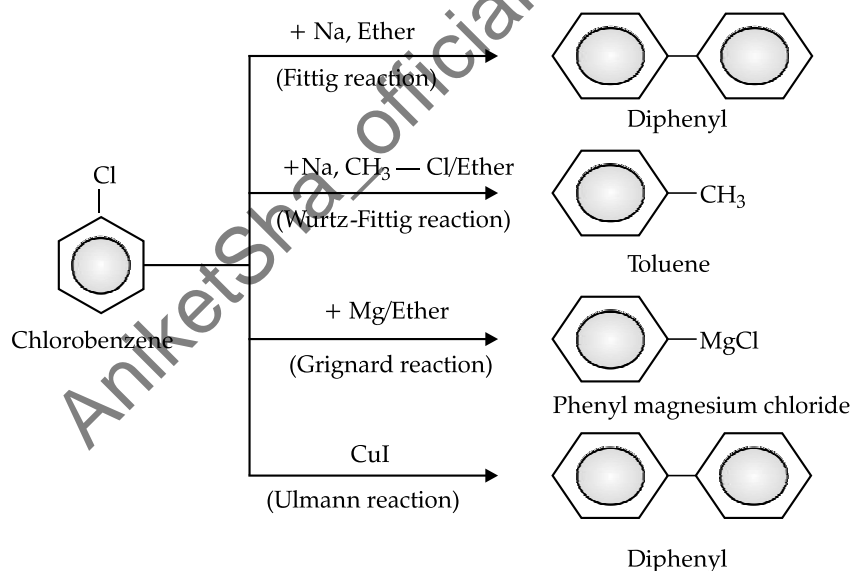
## (i) Substitution by —OH group (Dow's process) :



## (ii) Substitution by —CN group :

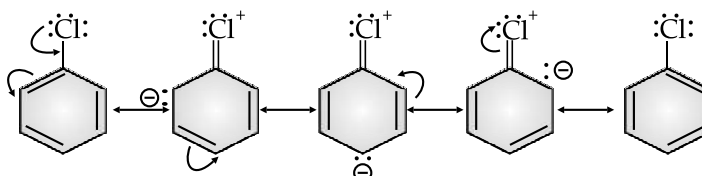
(iii) Substitution by —NH<sub>2</sub> group :

## (iv) Reaction with metals :



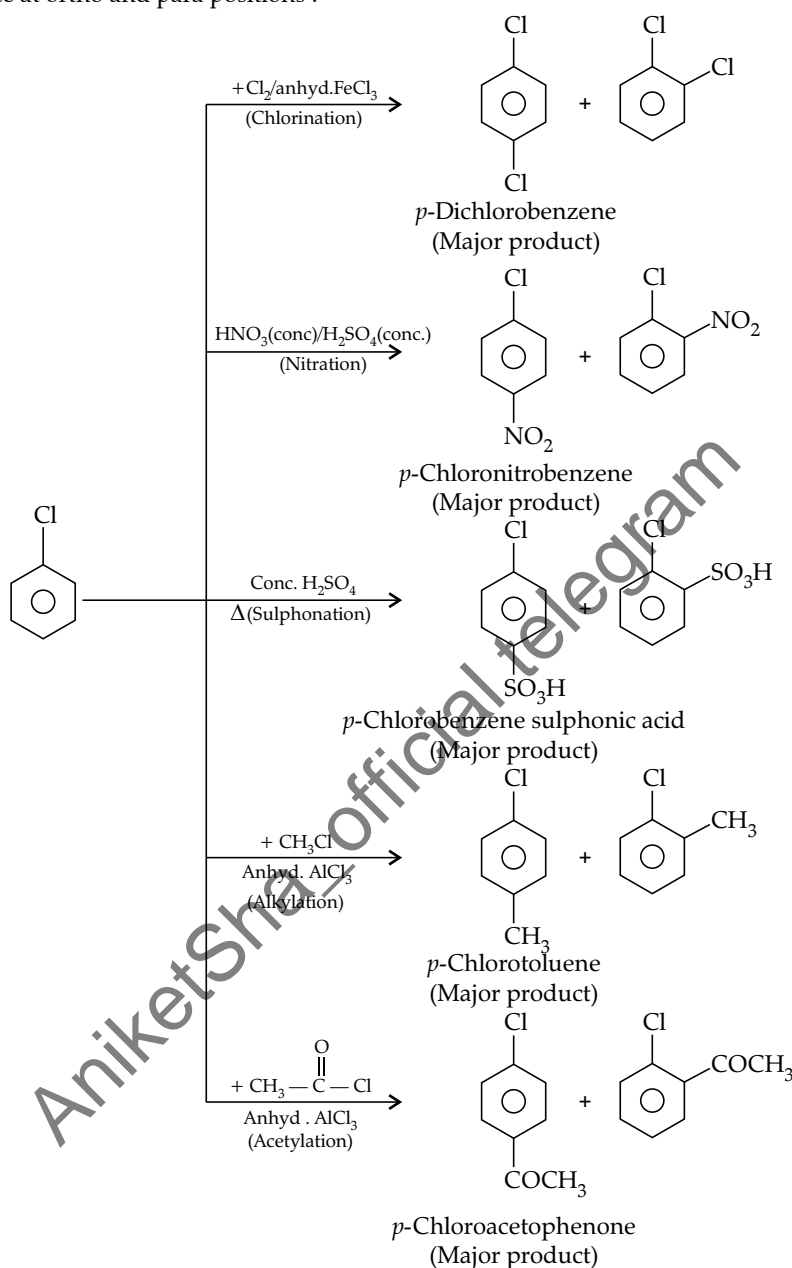
- **Nature of C—X bond in haloarene :** The C—X bond of aryl halide is less reactive than that of haloalkanes. One reason is that in aryl halide, halogen atom is attached to  $sp^2$ -hybrid carbon atom whereas in alkyl halides, it is attached to  $sp^3$ -hybrid carbon atom. Due to more electronegativity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



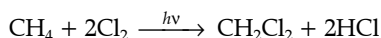
**(v) Electrophilic substitution reactions of haloarenes :**

It take place at ortho and para positions :



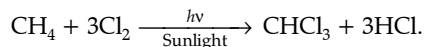
➤ **Polyhalogen compounds :** Carbon compounds containing more than one halogen atoms are usually referred to as polyhalogen compounds. Many of those compounds are useful in industry and agriculture :

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



The mixture so obtained is separated by fractional distillation. It is widely used as solvent in pharmaceuticals and food industry.

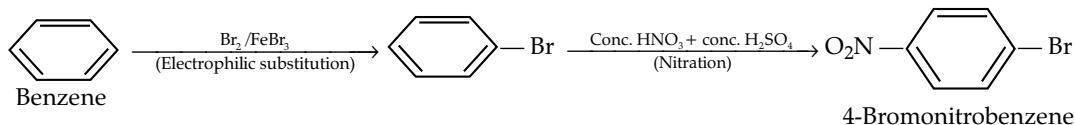
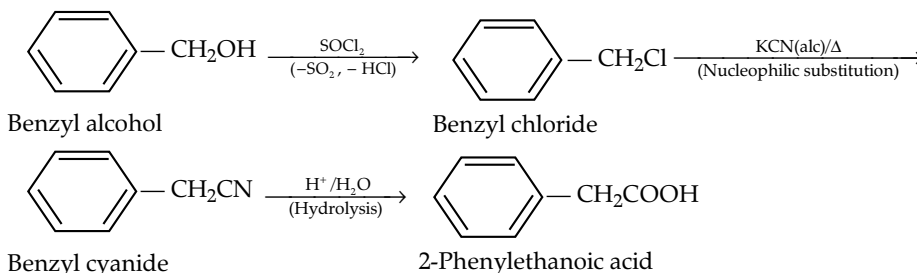
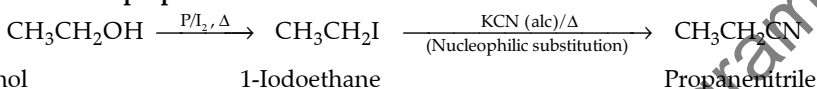
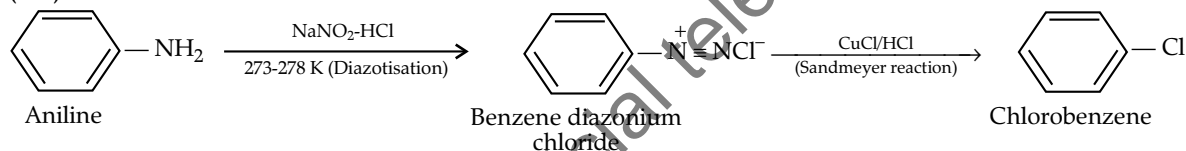
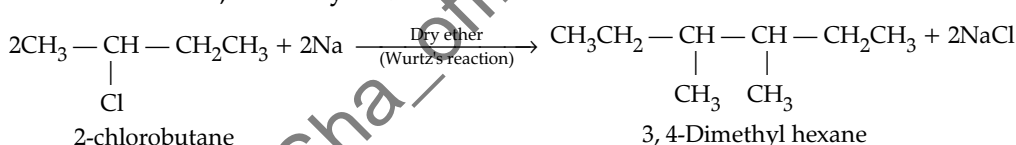
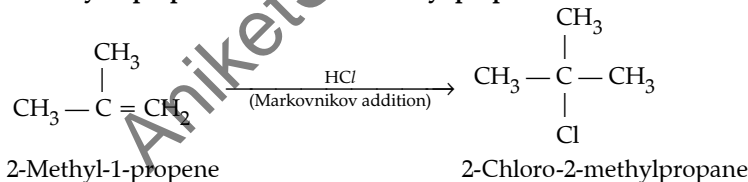
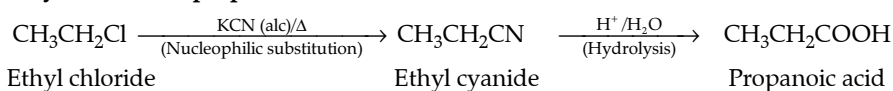
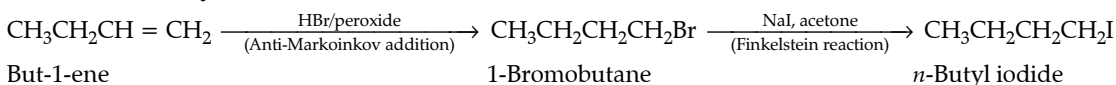
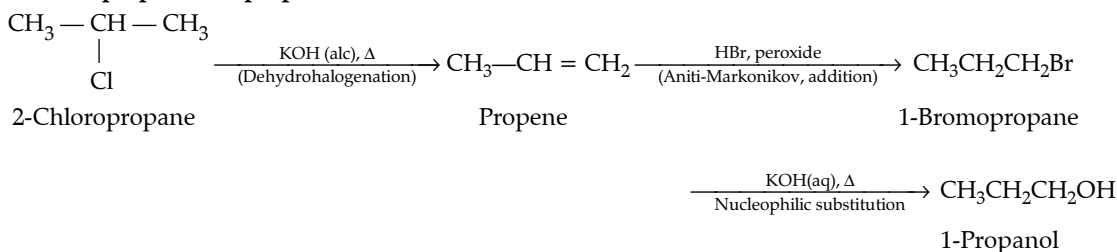
(ii) **Chloroform :** It is manufactured by chlorination of methane followed by separation by fractional distillation.

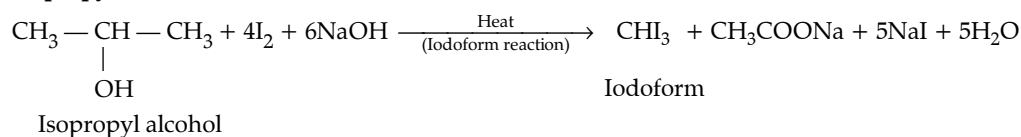
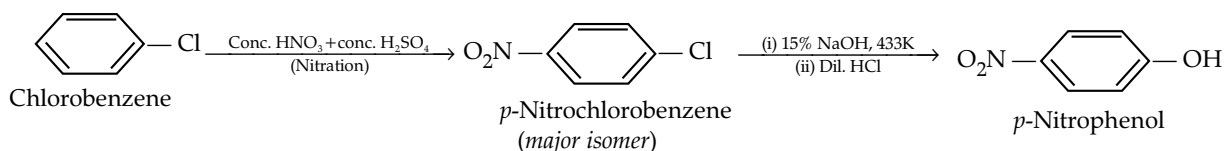
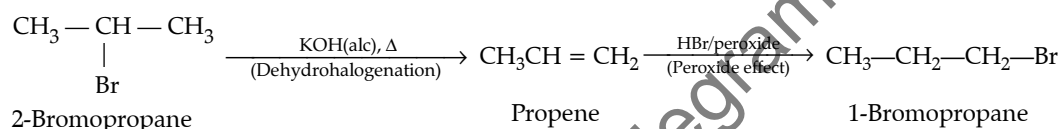
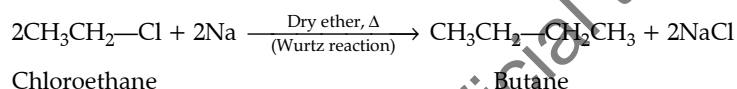
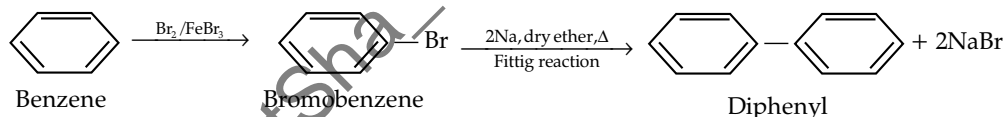
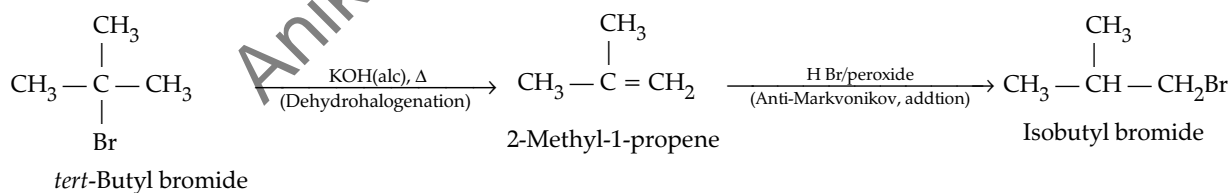
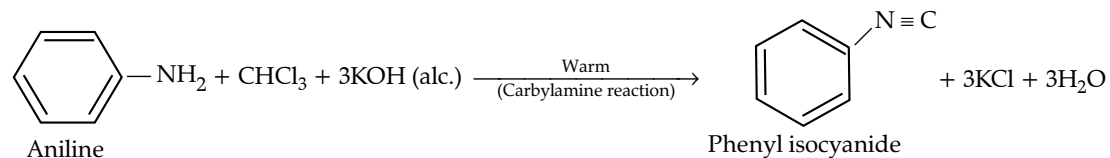


It is extensively used as solvent for waxes, resins, rubber, fats etc. It was earlier used as anaesthetic and swallowing agent, but due to formation of Phosgene gas (poisonous gas), it is not used at present.

(iii) **Iodoform (Triiodomethane) :** It is prepared by heating ethanol or acetone with sodium hydroxide and iodine or  $\text{Na}_2\text{CO}_3$  and  $\text{I}_2$  in water. It is insoluble in water, yellow precipitate of  $\text{CHI}_3$  is formed. This reaction is called iodoform reaction :

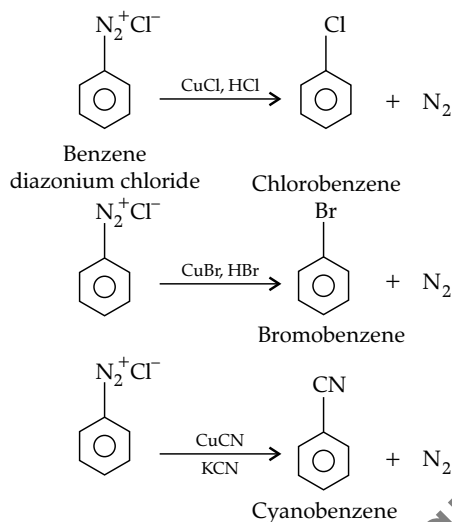


**(v) Benzene to 4-bromonitrobenzene :****(vi) Benzyl alcohol to 2-phenylethanoic acid :****(vii) Ethanol to propanenitrile :****(viii) Aniline to chlorobenzene :****(ix) 2-Chlorobutane to 3, 4-dimethyl hexane :****(x) 2-Methyl-1-propene to 2-chloro-2-methyl propane :****(xi) Ethyl chloride to propanoic acid :****(xii) But-1-ene to n-butyl iodide :****(xiii) 2-Chloropropane to 1-propanol :**

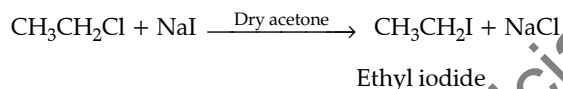
**(xiv) Isopropyl alcohol to iodoform :****(xv) Chlorobenzene to *p*-nitrophenol :****(xvi) 2-Bromopropane to 1-bromopropane :****(xvii) Chloroethane to butane :****(xviii) Benzene to diphenyl :****(xix) *tert*-Butyl bromide to *iso*-butyl bromide :****(xx) Aniline to phenyl isocyanide :**

➤ **Important Name Reactions :**

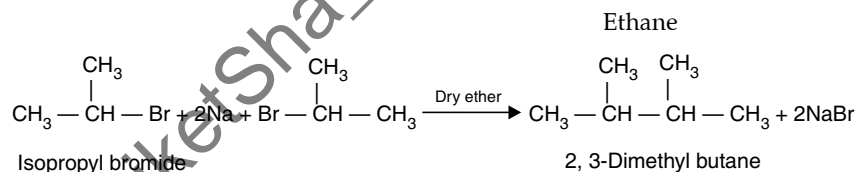
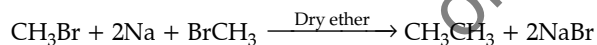
## (i) Sandmeyer's Reaction :



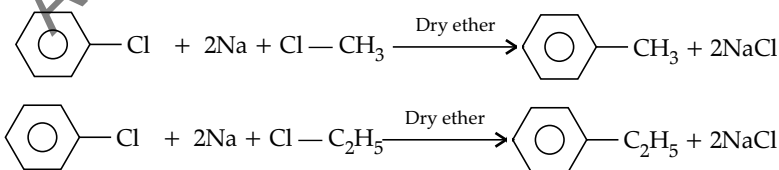
## (ii) Finkelstein Reaction :



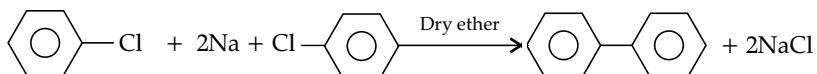
## (iii) Wurtz Reaction :



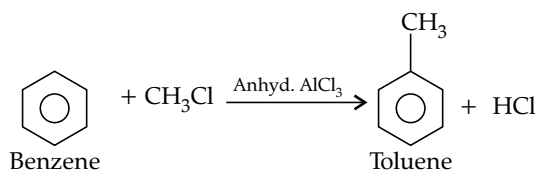
## (iv) Wurtz-Fittig Reaction :

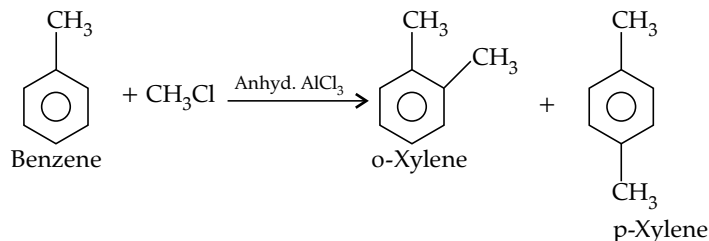


## (v) Fittig's Reaction :

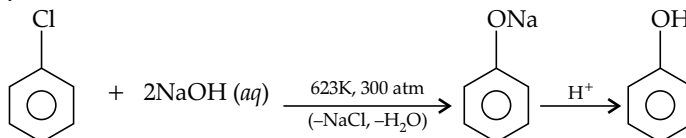


## (vi) Friedel-Crafts Alkylation :

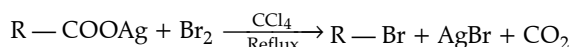




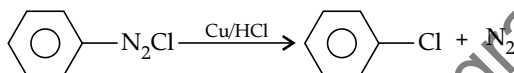
(vii) Dow's Process :



(viii) Hunsdiecker's Reaction :



(ix) Gattermann's Reaction :



## Know the Term

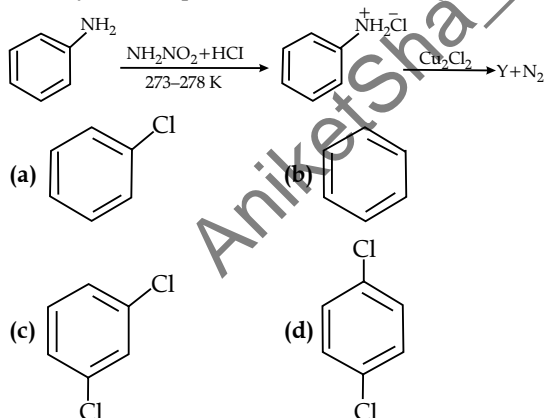
➤ **Phosgene** : A poisonous gas formed on slow oxidation of chloroform in the presence of sunlight.



## Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple choice Questions:

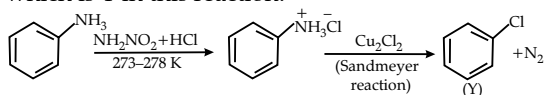
Q. 1. Identify the compound Y in the following reaction.



[NCERT Exemp. Q. 3, Page 134]

Ans. Correct option : (a)

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

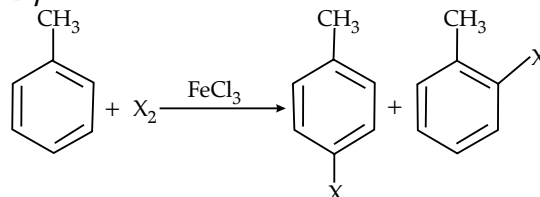


Q. 2. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

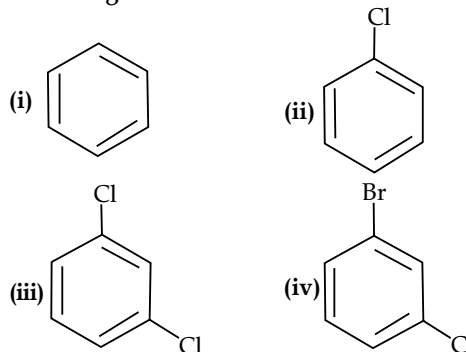
- (a) Electrophilic elimination reaction
- (b) Electrophilic substitution reaction
- (c) Free radical addition reaction
- (d) Nucleophilic substitution reaction

[NCERT Exemp. Q. 4, Page 134]

Ans. Correct option : (b)

**Explanation :**

Q. 3. Arrange the following compounds in the increasing order of their densities.





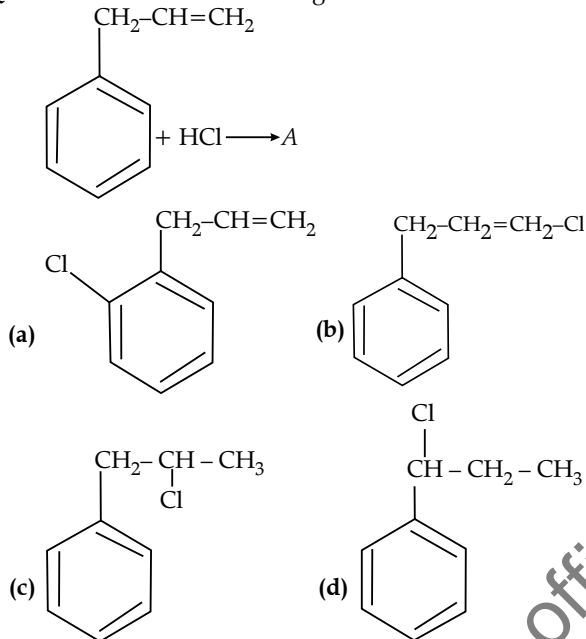
- (a) (i) < (ii) < (iii) < (iv)  
 (b) (i) < (iii) < (iv) < (ii)  
 (c) (iv) < (iii) < (ii) < (i)  
 (d) (ii) < (iv) < (iii) < (i)

[U] [NCERT Exemp. Q. 87, Page 135]

Ans. Correct option : (a)

Explanation : Density increases with increase in molecular mass.

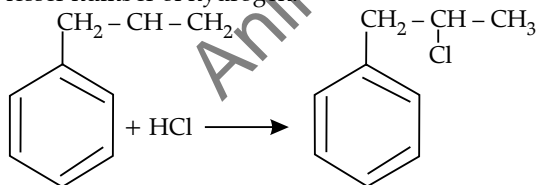
Q. 4. What is 'A' in the following reaction?



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

Ans. Correct option : (c)

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



B. Match the following :

Q. 1. Match the species given in Column I with those mentioned in Column II.

Column I	Column II
(a)	(i) Fittig reaction
(b)	(ii) Wurtz-Fittig reaction
(c)	(iii) Finkelstein reaction
(d) $\text{C}_2\text{H}_5\text{Cl} + \text{NaI} \xrightarrow{\text{Dry acetone}} \text{C}_2\text{H}_5\text{I} + \text{NaCl}$	(iv) Sandmeyer reaction

[NCERT Exemp. Q. 84, Page 147]

Ans. (a) → (ii)

(b) → (i)

(c) → (iv)

(d) → (iii)

Explanation : (a) A mixture of an alkyl halide and aryl halides gives an alkylarene when treated with sodium in dry ether and this is called Wurtz-Fittig reaction.

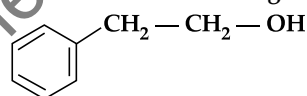
(b) Aryl halides give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.

(c) Diazonium salt when treated with cuprous chloride or cuprous bromide gives chlorobenzene or bromobenzene. The reaction is known as Sandmeyer's reaction.

(d) Alkyl iodides are prepared by the reaction of alkyl chlorides with sodium iodide in dry acetone. The reaction is known as Finkelstein reaction.

C. Answer the following :

[AI] Q. 1. Write the IUPAC name of the given compound :



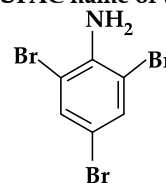
[A] [CBSE OD 2016]

Ans. 2-Phenylethanol.

1

[CBSE Marking Scheme 2016]

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



[A] [CBSE Delhi 2016]

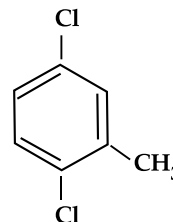
Ans. 2,4,6-Tribromoaniline/2,4,6-Tribromobenzenamine.

1

[CBSE Marking Scheme 2016]

[AI] Q. 3. Write IUPAC name of the following compound ?

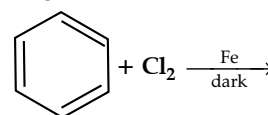
[A] [CBSE OD 2013]



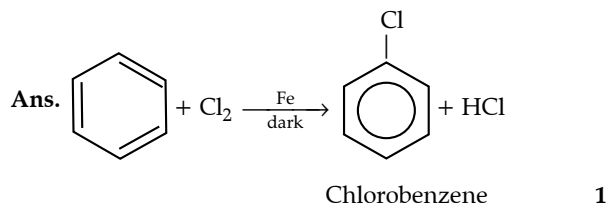
Ans. 1, 4-dichloro-3-methylbenzene.

1

Q. 4. Draw the structure of major monohalo product in the following reaction :



[A] [CBSE Comptt. Delhi 2012]



Q. 5. Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why? [A&E][CBSE Delhi/OD 2018]

Ans. Benzyl chloride; 1/2  
Due to resonance, stable benzyl carbocation is formed. 1/2  
[CBSE Marking Scheme 2018]

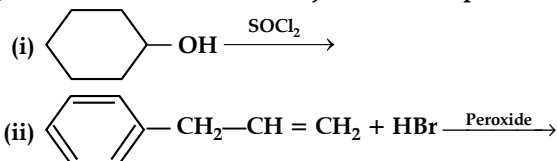
**Detailed Answer:**

Benzyl chloride gets easily hydrolysed by aqueous NaOH as chlorobenzene possesses partial double bond character in the Cl-C bond. The lone pairs delocalised in the ring strengthens Cl-C bond reducing its reactivity. Whereas benzyl chloride undergoes S<sub>N</sub>1 reaction to form stable benzyl carbocation. 1

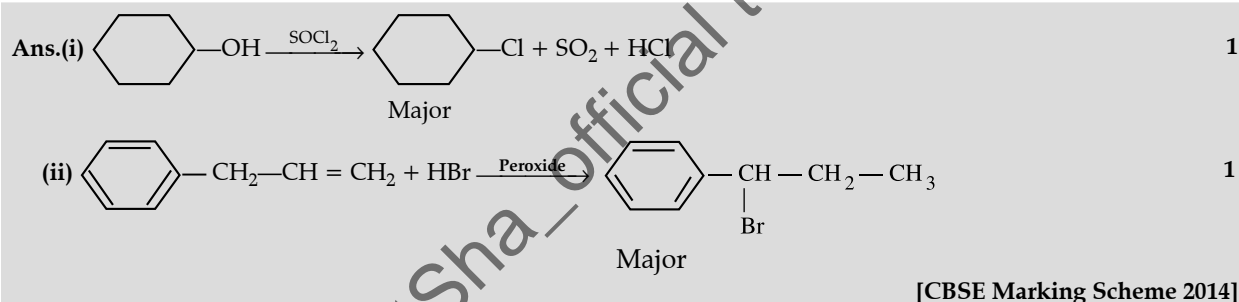
## ? Short Answer Type Questions

(2 marks each)

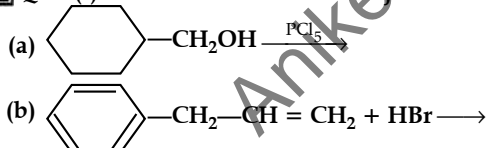
Q. 1. Draw the structure of major monohalo product in each of the following reactions :



[A] [CBSE Delhi 2014]



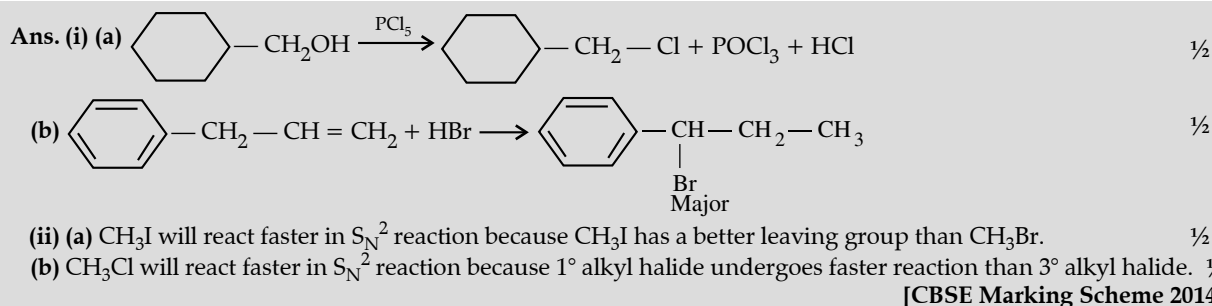
[AI] Q. 2. (i) Draw the structures of major monohalo products in each of the following reactions :



(ii) Which halogen compound in each of the following pairs will react faster in S<sub>N</sub>2 reaction :

- (a) CH<sub>3</sub>Br or CH<sub>3</sub>I  
(b) (CH<sub>3</sub>)<sub>3</sub>C-Cl or CH<sub>3</sub>-Cl

[A] [CBSE Delhi 2014]



### Commonly Made Error

- A number of students write wrong products.

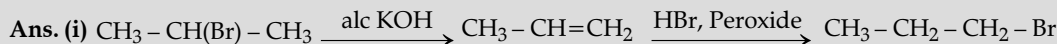
### Answering Tip

- Practice the organic chemical reactions by writing full chemical reactions with reagents and conditions.

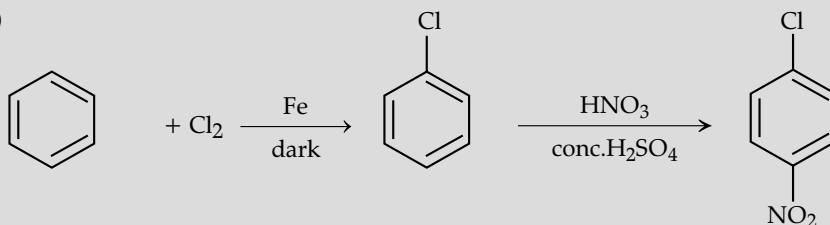
**Q. 3. How will you carry out the following conversion :**

- (i) 2-Bromopropane to 1-bromopropane  
(ii) Benzene to p-chloronitrobenzene

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



(ii)



1+1

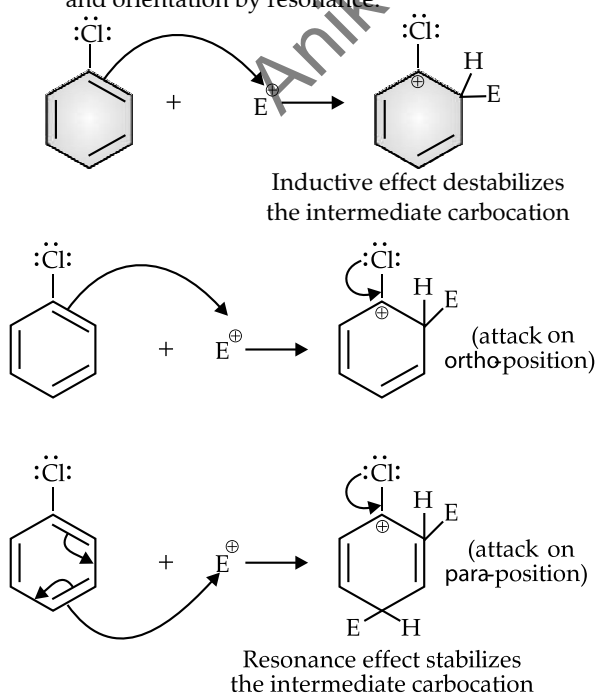
[CBSE Marking Scheme 2017]

### Commonly Made Error

- Reagents involved in each step must be shown.

**Q. 4. Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Explain why it is so ?** [A&E] [CBSE Delhi 2012]

**Ans.** Although chlorine is an electron withdrawing group, yet it is *ortho*-*para* directing in nature in electrophilic aromatic substitution because when chlorine is present in benzene ring, it releases electron by resonance whereas it acts as withdrawing group only through inductive effect. By inductive effect, chlorine atom destabilizes the intermediate carbocation formation but by resonance, chlorine atom stabilises the intermediate carbocation and effect is more at *o*- and *p*-positions. Resonance effect opposes inductive effect. Inductive is stronger than resonance effect due to which reactivity is controlled by inductive effect and orientation by resonance.

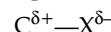


### Answering Tip

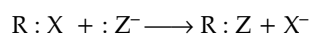
- Give resonance structures in support of answer.

**Q. 5. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain.** [A] [CBSE Comptt. Delhi 2012]

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



Due to presence of partial positive charge on carbon atom, the nucleophiles can attack on electron deficient carbon thereby resulting in the displacement of weaker nucleophile, thus typical reactions of alkyl halides are nucleophilic substitution reactions :



Nucleophile

Halide ion

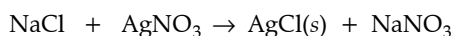
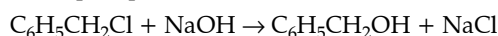
Whereas in haloarenes, as the halogen atom attached to benzene ring releases electron towards benzene ring (+*m* effect) thereby the *ortho* and *para* positions become site of attack for electrophiles more than nucleophiles. 2

**Q. 6. Give chemical tests to distinguish between the following pairs of compounds :**

- (i) Benzyl chloride and chlorobenzene  
(ii) Chloroform and carbon tetrachloride

[A] [CBSE Comptt. OD 2013]

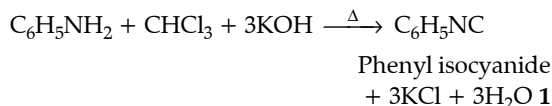
**Ans. (i)** On adding sodium hydroxide and silver nitrate to both the compounds, benzyl chloride forms white precipitate but chlorobenzene does not form white precipitate.



(white ppt.)

1

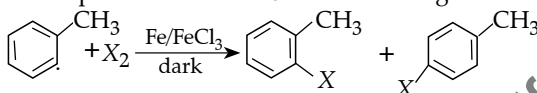
- (ii) On heating chloroform and carbon tetrachloride with aniline and ethanolic potassium hydroxide separately chloroform forms pungent smelling isocyanide but carbon tetrachloride does not form this compound.



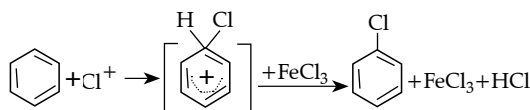
**Q. 7. Discuss the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark.**

[C] [NCERT Exemp. Q. 49, Page 143]

**Ans.** Direct chlorination or bromination of benzene or other aromatic hydrocarbon gives chloroarenes and bromoarenes. These reactions are carried out in the presence of Lewis acids such as ferric or aluminium halides ( $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ) in the dark, at ordinary temperatures (310-320 K). The reaction is electrophilic aromatic substitution. The halogen itself is not a strong electrophile for the attack of benzene ring. The Lewis acid promotes the electrophilic aromatic substitution by polarizing the halogen molecule. Actually, it generates a better electrophile for the attack of benzene ring.



**Mechanism :**  $\text{Cl}-\text{Cl} + \text{FeCl}_3 \rightarrow \text{FeCl}_4 + \text{Cl}^+$



2

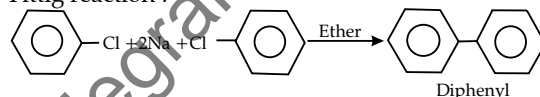
**Q. 8. Diphenyls are potential threat to the environment. How are these produced from arylhalides?**

[C] [NCERT Exemp. Q. 69, Page 144]

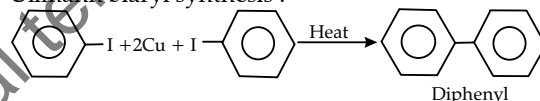
**Ans.** Diphenyls such as p,p-dichlorodiphenyl trichloroethane (DDT) are posing serious environment problems because of its chemical stability and its fat solubility. Its residue accumulates in environment and its long-term effects could be highly dangerous.

Diphenyls can be prepared from aryl halides by the following two methods :

(i) Fittig reaction :



(ii) Ullmann biaryl synthesis :

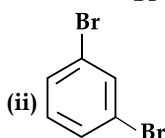
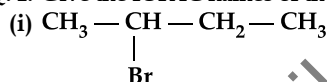


2

## ? Long Answer Type Questions-I

(3 marks each)

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

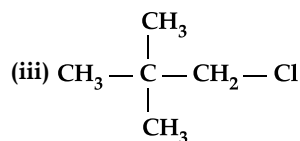
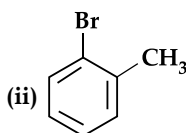
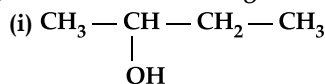


[A] [CBSE Comptt. OD 2015]

<b>Ans. (i)</b> 2-bromobutane	1
<b>(ii)</b> 1, 3-dibromobenzene	1
<b>(iii)</b> 3-chloropropene	1

[CBSE Marking Scheme 2015]

**Q. 2. Name the following according to IUPAC system:**



[A] [CBSE Comptt. Delhi 2015]

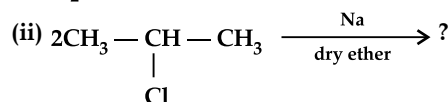
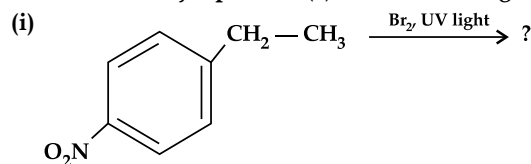
<b>Ans. (i)</b> Butan - 2 - ol	1
<b>(ii)</b> 2 - bromotoluene	1
<b>(iii)</b> 1-chloro-2, 2-dimethylpropane	1

[CBSE Marking Scheme 2015]

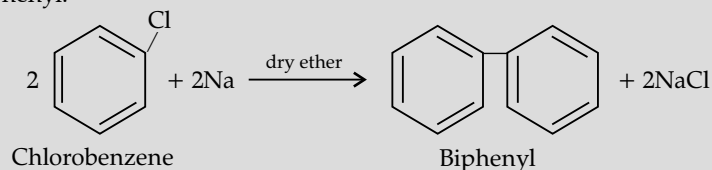
**Q. 3. How do you convert : (i) Chlorobenzene to biphenyl, (ii) Propene to 1-iodopropane, (iii) 2-bromobutane to but-2-ene.**

OR

**Write the major product (s) in the following :**



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



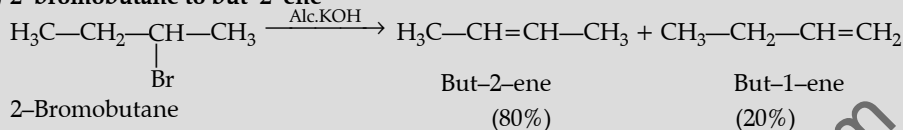
1

**(ii) Propene to 1-iodopropane :**



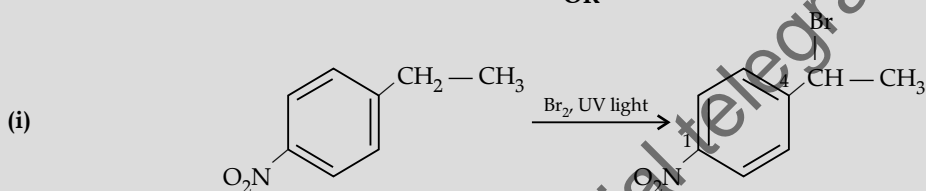
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**(iii) 2-bromobutane to but-2-ene**



1

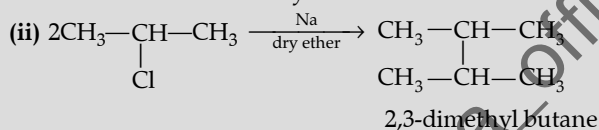
OR



4-Ethyl nitrobenzene

4-(1-Bromomethyl) nitrobenzene

1



1



1

[CBSE Marking Scheme 2016]

### Answering Tip

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

**Q. 4.** How can the following conversion be carried out :

- Aniline to bromobenzene
- Chlorobenzene to 2-chloroacetophenone
- Chloroethane to butane

OR

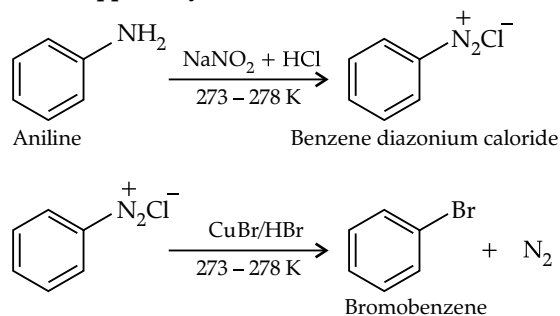
What happens when

- Chlorobenzene is treated with  $\text{Cl}_2/\text{FeCl}_3$
- Ethyl chloride is treated with  $\text{AgNO}_2$
- 2-bromopentane is treated with alcoholic  $\text{KOH}$  ?

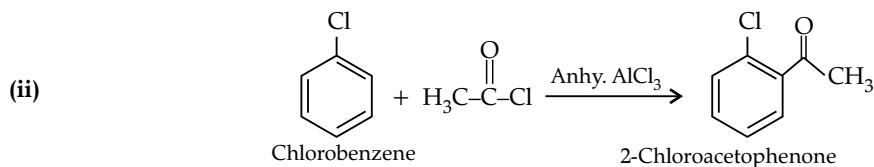
Write the chemical equations in support of your answer.

[A] [CBSE OD 2015]

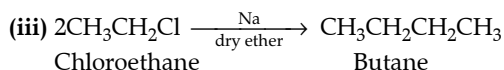
**Ans. (i)**



1

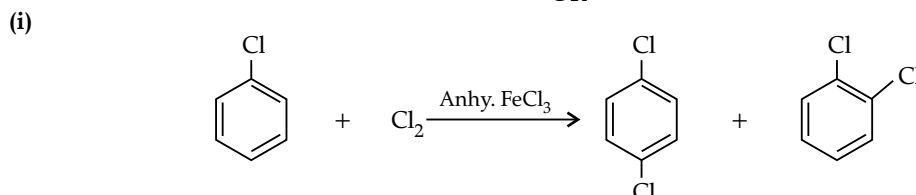


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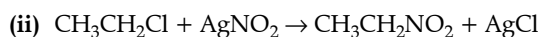


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OR



1

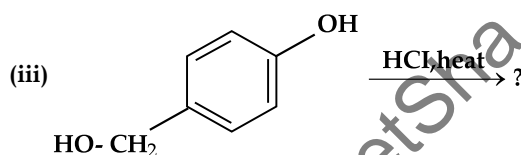
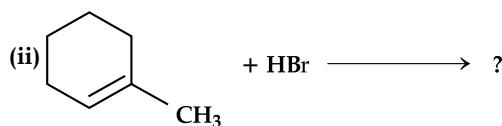
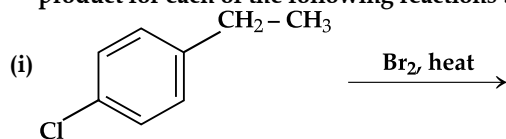


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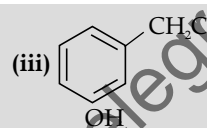
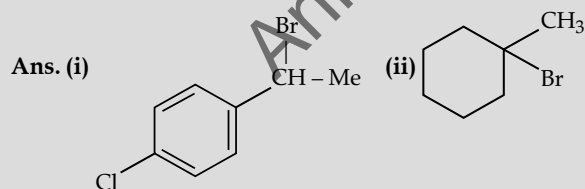


1

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



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



1+1+1

[CBSE Marking Scheme 2017]

Q. 6. (i) Account for the following :

(a) Electrophilic substitution reactions in haloarenes occur slowly.

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

(ii) Arrange the following compounds in increasing order of reactivity towards  $\text{S}_{\text{N}}2$  displacement :

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

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

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

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

1

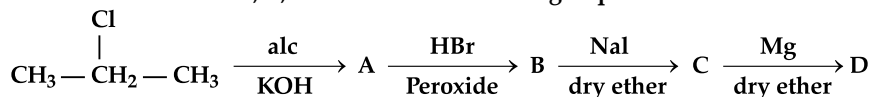
(ii) 2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane [CBSE Marking Scheme 2017] 1

Detailed Answer :

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

1

[A] Q. 7. (i) Write the structural formula of A, B, C and D in the following sequence of reaction :

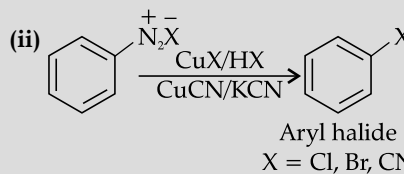


(ii) Illustrate Sandmeyer's reaction with the help of a suitable example.

[A + R] [CBSE Comptt. Delhi Set-1, 2, 3 2017]

Ans. (i) A:  $\text{CH}_3-\text{CH}=\text{CH}_2\text{I}$   
 B:  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$   
 C:  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{I}$   
 D:  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{MgI}$

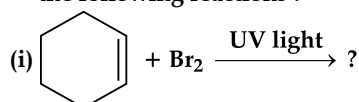
$\frac{1}{2} \times 4$



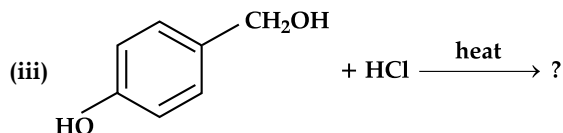
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[CBSE Marking Scheme 2017]

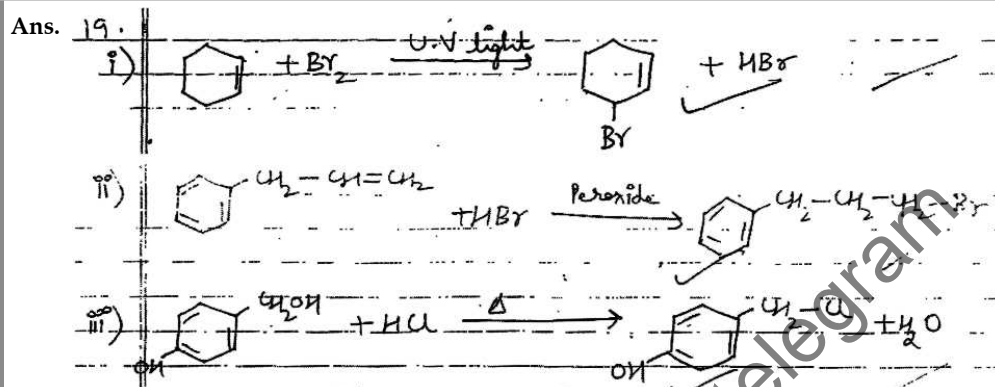
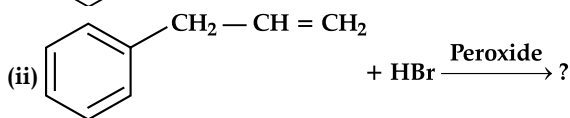
Q. 8. Write the major monohalo product(s) in each of the following reactions :



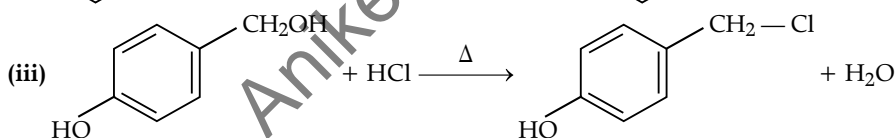
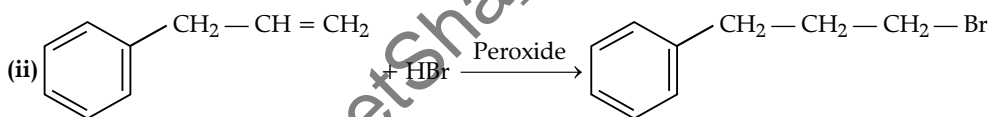
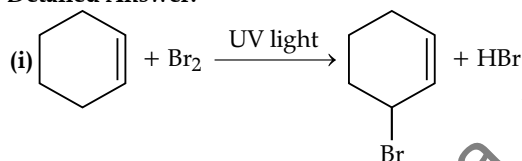
[DDE]



[A] [CBSE OD Set-2 2016]

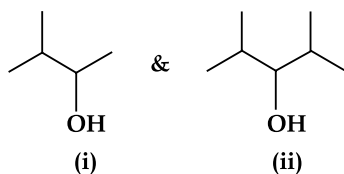
3  
[Topper's Answer 2016]

Detailed Answer:



3

Q. 9. (a) Identify the chiral molecule in the following pair :

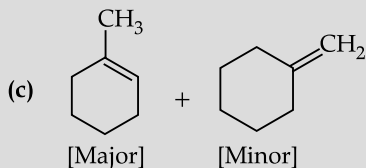
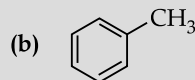


(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

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

[A] [CBSE Delhi/OD 2018]

Ans. (a) (i)

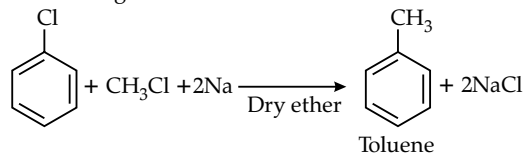


1+1+1

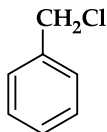
[CBSE Marking Scheme 2018]

Detailed Answer:

(b) Wurtz-Fittig reaction



Q. 10. Which one of the following compounds will undergo faster hydrolysis reaction by  $S_N1$  mechanism? Justify your answer.

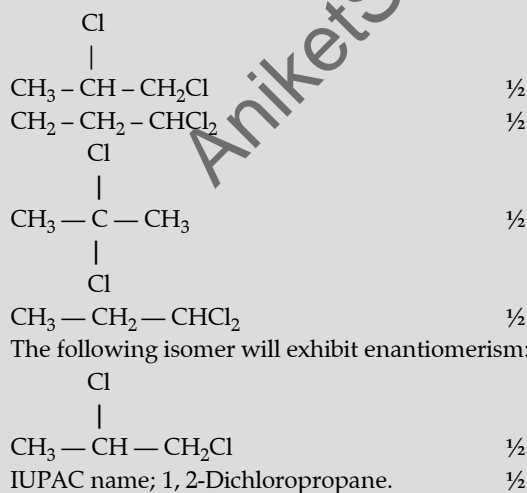
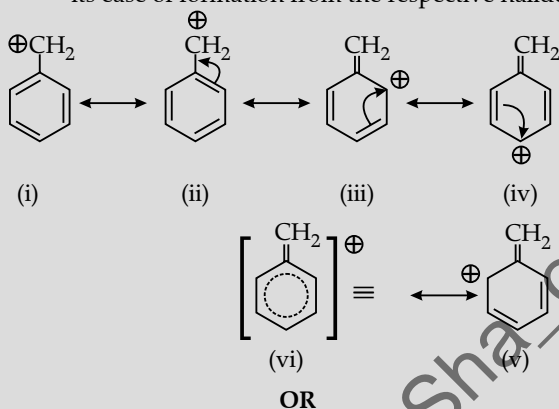


or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  [A&E]

OR

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

Ans.  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  will undergo  $S_N1$  reaction faster.  $\frac{1}{2}$   
The carbocation formed by  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  gets stabilized through resonance.  $\frac{1}{2}$   
Greater the stability of carbocation, greater will be its ease of formation from the respective halide. 1



[CBSE Marking Scheme 2018]

Q. 11. Give reasons :

- $n$ -Butyl bromide has higher boiling point than  $t$ -butyl bromide.
- Racemic mixture is optically active.
- The presence of nitro group ( $-\text{NO}_2$ ) at O/P positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

[A&E] [CBSE Delhi 2015]

- Ans. (i) Larger surface area, higher van der Waals' forces, higher the boiling point. 1  
(ii) Rotation due to one enantiomer is cancelled by another enantiomer. 1  
(iii)  $-\text{NO}_2$  acts as Electron withdrawing group or  $-I$  effect. 1

[CBSE Marking Scheme 2015]

#### Answering Tip

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

#### Detailed Answer:

- (i)  $n$ -Butyl bromide is a straight chain molecule with strong intermolecular forces whereas  $t$ -butyl bromide is a branched chain molecule with weak intermolecular forces due to smaller surface area. Hence,  $n$ -Butyl bromide has higher boiling point than  $t$ -butyl bromide. 1

[A] Q. 12. Write the product(s) formed when

- 2-Bromopropane undergoes dehydrohalogenation reaction.
- Chlorobenzene undergoes nitration reaction.
- Methylbromide is treated with KCN.

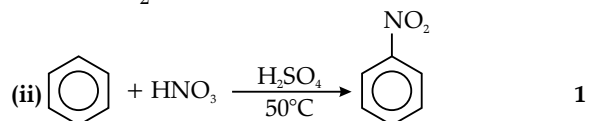
[A] [CBSE Comptt. Delhi/OD 2018]

- Ans. (i) Propene 1  
(ii) 4-nitrochlorobenzene and 2-nitrochlorobenzene / structures  $\frac{1}{2} + \frac{1}{2}$   
(iii) Methylcyanide / Ethanenitrile / structure 1

[CBSE Marking Scheme 2018]

Detailed Answer:

- (i)  $\text{CH}_3 - \text{CHBr} - \text{CH}_3 + \text{KOH} \rightarrow \text{CH}_3 - \text{CH} = \text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$  1



- (iii)  $\text{CH}_3\text{Br} + \text{KCN} \rightarrow \text{CH}_3\text{CN} + \text{KBr}$  1





## Long Answer Type Question-II

(5 marks)

**Q. 1.** Some halogen containing compounds are useful in daily life. Some compounds of this class are responsible for exposure of flora and fauna to more and more of UV light which causes destruction to a great extent. Name the class of these halocompounds. In your opinion, what should be done to minimise harmful effects of these compounds.

© [NCERT Exemp. Q. 96, Page 149]

**Ans.** There are a number of halogen containing compounds such as chloroform, iodoform, carbon tetrachloride, DDT, benzene hexachloride, freons, etc, which are useful in our daily life. But these compounds have adverse effects on health of humans, animals and other living beings. Compounds like freons containing chlorofluorocarbons cause the depletion of ozone layer. Consequently, UV rays reach the earth which harm flora and fauna.

(i) Tetrachloromethane: In contact with air, carbon tetrachloride rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer

increases human exposure to UV rays leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system. These UV rays cause damages to plants, and reduction of plankton populations in the ocean's euphotic zone.

(ii) Freons: Freon-113 remains in the air long enough to reach the upper atmosphere. It provides chlorine atoms which damage the ozone layer. Because of this depletion, UV rays enter in our atmosphere and become responsible for the damage to great extent.

(iii) p-p'-dichlorodiphenyltrichloroethane (DDT): It is non-biodegradable so gets deposited in fatty tissues. If ingestion continues for a long time, DDT builds up within the animal and affect the reproductive system.

To minimize the harmful effect of these compounds the use of equipments like, air-conditioner, refrigerator, aerosol that produce such compounds should be discouraged. Government has tightened laws on use of DDT. Such rules should be strictly followed.

5

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