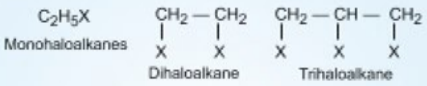
Haloalkanes and Haloarenes

10 Chapter

1 CLASSIFICATION

(a) On the basis of number of halogen atoms



(b) Compounds containing sp^3 C– X bond:

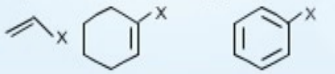
(i) Alkyl halides or haloalkanes (R – X)

Primary (1°) Secondary (2°) Tertiary (3°)

(ii) Allylic halides (iii) Benzylic halides

(c) Compounds containing sp^2 C – X bond:

(i) Vinylic halides : (ii) Aryl halides :



2 METHOD OF PREPARATION

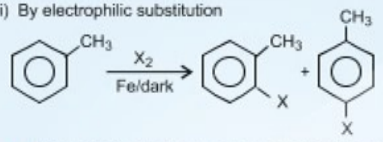
(a) From alcohols

- $R – OH + HCl \xrightarrow{ZnCl_2} R – Cl + H_2O$
- $R – OH + NaBr \xrightarrow{H_2SO_4} R – Br + NaHSO_4 + H_2O$
- $3R – OH + PX_3 \longrightarrow 3R – X + H_3PO_3$ (X = Cl, Br)
- $R – OH + PCl_5 \longrightarrow R – Cl + POCl_3 + HCl$
- $R – OH \xrightarrow[X_2 = Br_2, I_2]{Red\ P/X_2} R – X$
- $R – OH + SOCl_2 \longrightarrow R – Cl + SO_2 + HCl$

(b) From Hydrocarbons

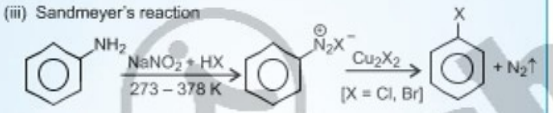
(i) Free radical halogenation

(ii) By electrophilic substitution



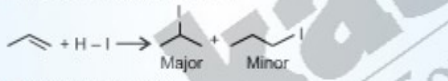
- Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

(iii) Sandmeyer's reaction



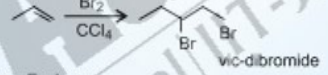
(iv) From alkenes

- Addition of halogen halides :



- Addition of halogen:

Addition of Br_2 in CCl_4 to an alkene results in discharge of reddish brown colour of Br_2



(c) Halogen Exchange

- **Finkelstein reaction :**

$R – X + NaI \longrightarrow R – I + NaX$ [X, Cl, Br]

- **Swarts reaction :**

$CH_3 – Br + AgF \longrightarrow CH_3 – F + AgBr\downarrow$

3 PHYSICAL PROPERTIES

- Boiling point of alkyl halide decrease in the order: RI > RBr > RCl > RCl > RF
- Boiling point of isomeric haloalkanes decrease with increase in branching

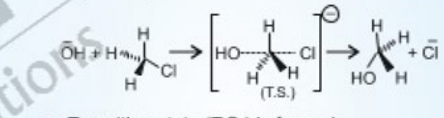
4 CHEMICAL REACTIONS REACTION OF HALOALKANE

(A) Nucleophilic substitution reaction

Mechanism : This reaction has been found to process by two different mechanism.

(i) **Substitution nucleophilic bimolecular (S_N2) :**

- The reaction between CH_3Cl and $\bar{O}H$ ion to yield methanol follows a second order kinetics, *i.e.* the rate depends upon the concentration of both reactants.



- Transition state (T.S.) is formed
- Reaction is generally carried out in acetone or polar aprotic solvents

(ii) **Substitution nucleophilic unimolecular (S_N1) :**

- It occurs in two steps

$HO^- + (CH_3)_3C — Br \longrightarrow (CH_3)_3 C — OH + Br^-$

$(CH_3)_3CBr \underset{Slow}{\overset{Step\text{-}I}{\rightleftharpoons}} (CH_3)_3C^{\oplus} + Br^-$

$(CH_3)_3C^{\oplus} + \bar{O}H \xrightarrow[Fast]{Step\text{-}II} (CH_3)_3COH$

- Greater the stability of carbocation greater is the rate of reaction
- S_N1 and S_N2 order can be generalised as

For S_N2 reaction

Tertiary halide, secondary halide, primary halide, CH_3X

For S_N1 reaction

- For a given alkyl group reactivity of halide follows same order in both the mechanisms
  R – I > R – Br > R — Cl >> R – F

(iii) **Stereochemical aspects of nucleophilic substitution reaction :**

Some important concepts

(a) **Optical activity :**

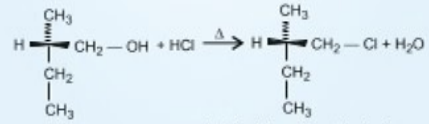
The compounds which rotate plane polarised light are optically active

- If a compound rotates plane polarised light in clockwise direction. It is called **dextrorotatory** and if it rotates in anti clock wise direction it is called **laevorotatory**.

(b) **Molecular asymmetry, Chirality and enantiomers:**

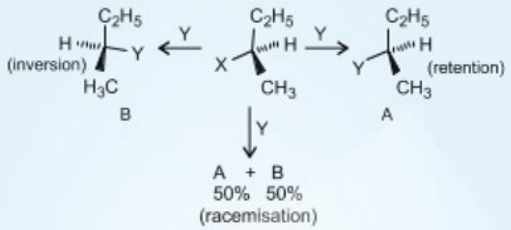
- If the spatial arrangment of four different groups around the central carbon is tetrahedral then the carbon is called **asymmetric carbon**
- The compounds which are non-superimposable on their mirror images are **Chiral** and are called enantiomers
- The stereoisomers having no mirror image relationship are called **diastereomers**.
- A mixture containing two enantiomers in equal proportions will have zero optical rotation. Such mixture is known as **racemic mixture**.

(c) **Retention :** In general, if during a reaction, no bond to the stereocentre is broken, the reaction is said to proceed with retention of configuration

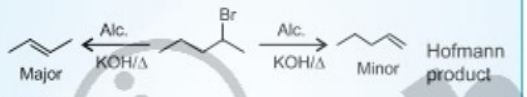


(–)-2-methylbutan-1-ol (+)-1-chloro-2-methylbutane

(d) Inversion, retention and recemisation



(B) Elimination reactions



(C) Reaction with metal

- Preparation

Grignard reagent
(Organometallic compound)

$RMgX + H_2O \longrightarrow \underset{\text{Hydrocarbon}}{RH} + Mg(OH)X$

Reaction of Haloarenes

(A) **Nucleophilic substitution :** Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to following reasons :

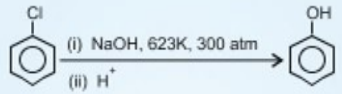
(i) Resonance effect : Lone pair of chlorine is in conjugation with benzene resulting in double bond character of C — Cl bond. As a result bond cleavage in haloarene is difficult.

(ii) Difference in hybridization of carbon atom in C– X bond

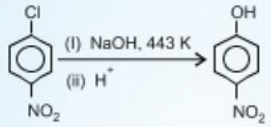
(iii) Instability of phenyl cation

(iv) Repulsion between haloarene and approaching nucleophile

- Replacement by hydroxyl group



Presence of an electron with drawing group at o/p positions increases the reactivity of haloarenes

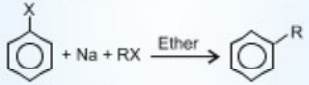


(B) **Electrophilic substitution reactions :**

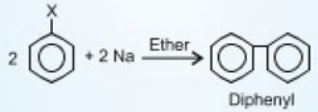
Haloarenes undergo electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and friedel crafts reaction.

Reaction with metals

(i) Wurtz-Fittig reaction



(ii) Fittig reaction



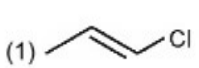
Diphenyl

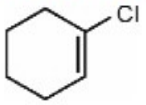
Polyhalogen Compounds

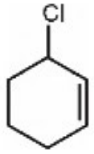
$2CHCl_3 + O_2 \xrightarrow{hv} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$

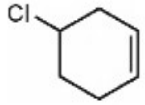
Sharpen Your Understanding

1. Allyl chloride among the following is [NCERT Pg. 290]

(1) 

(2) 

(3) 

(4) 

2. Total number of structural isomers of $C_5H_{11}F$ is [NCERT Pg. 292]

(1) 6 (2) 8

(3) 10 (4) 9

3. Correct order of dipole moment of the given molecules is [NCERT Pg. 294]

$\underset{(I)}{CH_3-I}$ $\underset{(II)}{CH_3-Br}$ $\underset{(III)}{CH_3-Cl}$ $\underset{(IV)}{CH_3F}$

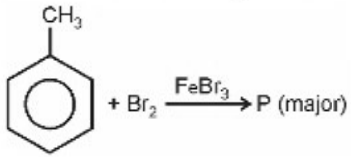
(1) (I) > (III) > (II) > (IV)

(2) (III) > (IV) > (II) > (I)

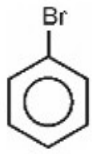
(3) (IV) > (III) > (II) > (I)

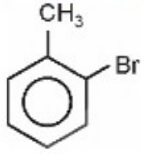
(4) (III) > (II) > (I) > (IV)

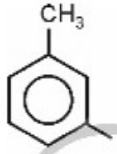
4. Consider the following reaction



Major product P is [NCERT Pg. 296]

(1) 

(2) 

(3) 

(4) 

5. Which among the following is liquid at room temperature? [NCERT Pg. 298]

(1) Methyl chloride

(2) Methyl bromide

(3) Ethyl chloride

(4) Dichloromethane

6. Correct order of S_N2 reactivity of the given compounds will be [NCERT Pg. 305]

$\underset{(I)}{(CH_3)_3CBr}$ $\underset{(II)}{(CH_3)_2CHCH_2Br}$

$\underset{(III)}{CH_3CH_2CH(Br)CH_3}$

(1) (III) > (II) > (I)

(2) (II) > (I) > (III)

(3) (II) > (III) > (I)

(4) (I) > (III) > (II)

NCERT Based MCQs

7. Consider the following statements

(a) If a compound rotates plane polarized light in clockwise direction then it is called dextrorotatory

(b) A molecule which is non-superimposable on its mirror image is chiral and optically active

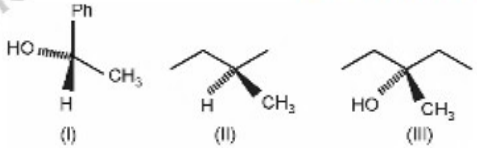
(c) Propan-2-ol is an achiral molecule

The correct statements are [NCERT Pg. 305]

(1) (a) and (b) only (2) (b) and (c) only

(3) (a), (b) and (c) (4) (a) and (c) only

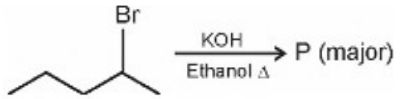
8. Chiral molecule(s) among the following is/are [NCERT Pg. 307]



(1) (I) only (2) (I) and (II) only

(3) (I) and (III) only (4) (I), (II) and (III)

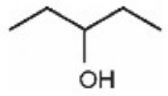
9. Consider the following reaction

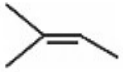


Major product P is [NCERT Pg. 310]

(1) 

(2) 

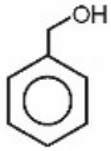
(3) 

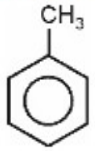
(4) 

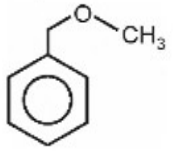
10. Consider the following reaction sequence

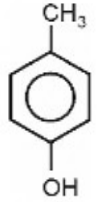
$PhCH_2Br + Mg \xrightarrow[ether]{dry} A \xrightarrow{CH_3OH} B$

Product B is [NCERT Pg. 310]

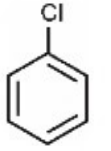
(1) 

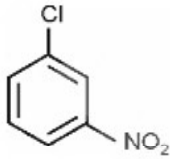
(2) 

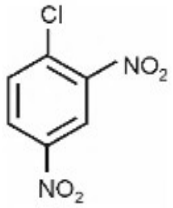
(3) 

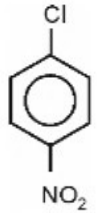
(4) 

11. The compound which will react at a slowest rate with $\bar{O}H$ ion is [NCERT Pg. 312]

(1) 

(2) 

(3) 

(4) 

12. Consider the following statement [NCERT Pg. 310-311]

(a) CH_3MgBr is an organometallic compound

(b) CH_3MgBr does not react with diethyl ether

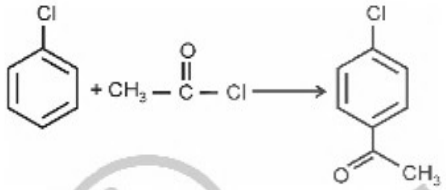
(c) CH_3MgBr evolves ethane when treated with water

The correct statement is/are

(1) (a) and (b) only (2) (b) and (c) only

(3) (a), (b) and (c) (4) (a) and (c) only

13. In the given reaction, catalyst used is



[NCERT Pg. 315]

(1) Cu_2Cl_2 (2) Anhyd. $AlCl_3$

(3) HCl (4) AgF

14. The given reaction is called

[NCERT Pg. 316]

(1) Fittig reaction

(2) Wurtz reaction

(3) Swarts reaction

(4) Wurtz-Fittig reaction

15. Consider the following statement [NCERT Pg. 317-318]

(a) Chloroform is oxidized by air in presence of light to phosgene gas

(b) Chloroform is used in the production of freon refrigerant R-22

(c) One molecule of DDT contains six chlorine atoms

The incorrect statement(s) is/are

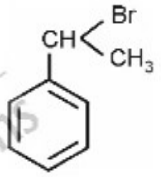
(1) (b) and (c) only

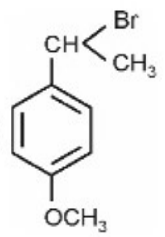
(2) (b) only

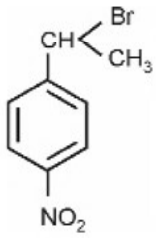
(3) (c) only

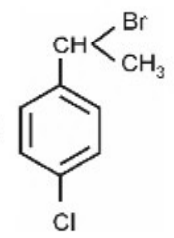
(4) (a), (b) and (c)

16. The compound which will react fastest by S_N1 mechanism is [NCERT Pg. 304]

(1) 

(2) 

(3) 

(4) 

17. Which among the following is not a polar protic solvent? [NCERT Pg. 303]

(1) Acetic acid

(2) Acetone

(3) Water

(4) Ethanol

18. Incorrect statement among the following is [NCERT Pg. 301, 305, 306, 307]

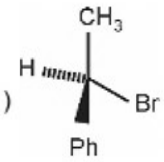
(1) S_N2 reaction takes place in single step and no intermediate is formed

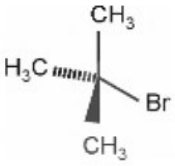
(2) 2-Bromopropane is an achiral molecule

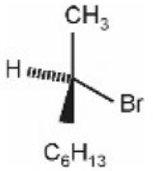
(3) Enantiomers are non-superimposable mirror images of each other

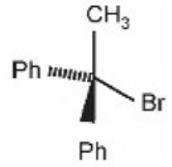
(4) Enantiomers have different melting point

19. Which compound on reaction with aqueous alkali gives maximum racemised product? [NCERT Pg. 309

(1) 

(2) 

(3) 

(4) 

20. Which among the following is an ambident nucleophile? [NCERT Pg. 300]

(1) NO_2^- (2) N_3^-

(3) CH_3O^- (4) $\bar{S}H$

Thinking in Context

1. In vinyl chloride, the chlorine atom is bonded to _____ hybridized carbon. [NCERT Pg. 291]
2. Iodobenzene is prepared by shaking the diazonium salt with ____. [NCERT Pg. 296]
3. Propene on reaction with HBr yield two products, however only one predominates as per _____ rule. [NCERT Pg. 295]
4. Addition of _____ in CCl_4 to an alkene results in discharge of reddish brown colour. [NCERT Pg. 295]
5. Alkyl iodides are prepared by reaction of alkyl chlorides/ bromides with NaI in dry ____. [NCERT Pg. 295]
6. Ethyl chloride reacts with AgCN to form _____ as major product [NCERT Pg. 301]
7. S_N1 reactions are generally carried out in ____ solvents. [NCERT Pg. 303]
8. The reaction between tert-butyl bromide and hydroxide ion yields tert-butyl alcohol and follows _____ kinetics [NCERT Pg. 303]
9. In S_N1 reactions, step-I is ____ and ____. [NCERT Pg. 304]
10. The angle by which that plane polarized light is rotated is measured by an instrument called _____. [NCERT Pg. 303]
11. (+) and (–) isomers of a compound are called _____ isomers. [NCERT Pg. 303]
12. The object which are ____ on their mirror image are said to be chiral. [NCERT Pg. 306]
13. If one of the enantiomer is dextrorotatory, the other will be ____. [NCERT Pg. 307]
14. A mixture containing two enantiomers in equal proportions will have ____ optical rotation. [NCERT Pg. 307]
15. In case of optically active alkyl halide, S_N1 reaction is accompanied by ____. [NCERT Pg. 309]
16. Alkyl halides react with ____ in dry ether to give hydrocarbon containing double the number of carbon atoms. [NCERT Pg. 311]
17. 4-chloroacetophenone is obtained when ____ is treated with acetylchloride in presence of ____. [NCERT Pg. 315]
18. When chlorobenzene is treated with sodium in presence of dry ether then the product formed is _____. [NCERT Pg. 316]
19. Swarts reaction is useful in the synthesis of _____. [NCERT Pg. 295]
20. When a haloalkane with β-hydrogen atom is heated with alcoholic solution of KOH, ____ is formed as major product. [NCERT Pg. 309]

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