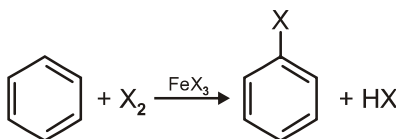


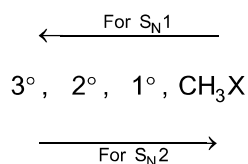
HALOALKANES AND HALOARENES

POINTS TO REMEMBER

1. Haloalkanes are compounds having general formula R-X and haloarenes are denoted by Ar-X.
2. Addition of halogen acids to alkenes takes place via carbocations as intermediates.
3. Halogenation of alkanes takes place via free-radical chain mechanism. Order of reactivity of halogens in $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$.
4. Anti Markownikov's addition takes place only with HBr in presence of a peroxide.
5. Order of reactivity of hydrohalic acids is $\text{HI} > \text{HBr} > \text{HCl}$.
6. Allylic substitution can be carried out using Cl_2 or Br_2 at 800 K or using SO_2Cl_2 at 475 K in presence of light and traces of peroxide.
7. Halogenation of benzene is an electrophilic substitution reaction.



8. Order of reactivity in $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanism are as follows –

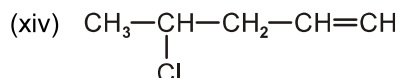
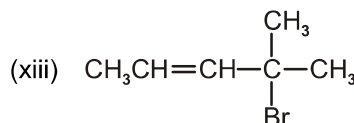
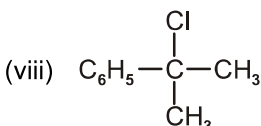
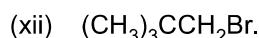
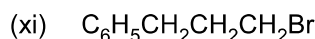
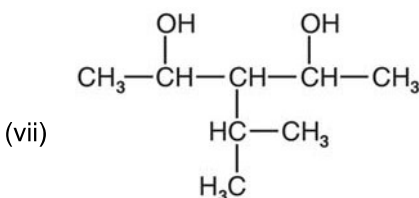
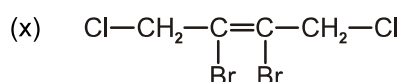
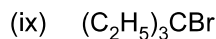
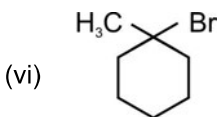
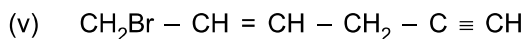
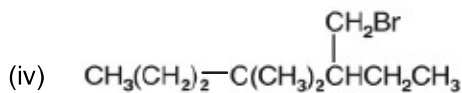
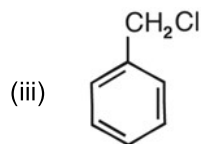
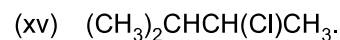
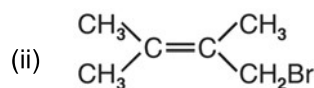
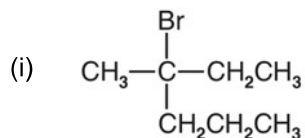


S_{N} reactions are characteristic of haloalkanes.

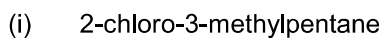
9. In case of optically active alkyl halides, $\text{S}_{\text{N}}2$ mechanism results in the inversion of configuration while $\text{S}_{\text{N}}1$ mechanism results in racemisation.
10. For same alkyl group, boiling points of alkyl halides is in the order –
 $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$.
11. For same halogen, boiling points of halides increases with increase in the size of alkyl group.
12. For isomeric halides, boiling point decreases with increase in the size of alkyl group.
13. C-X bond in aryl halides is shorter, stronger and less polar than in alkyl halides.
14. Aryl halides are much less reactive towards the nucleophilic substitution (S_{N}) reactions. Reactivity towards S_{N} reactions increases if some EWG is present at *o*- and *p*-positions with respect to halogen.
15. D.D.T. is 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane.
16. Freon-12 (CF_2Cl_2) is used as refrigerant.
17. CCl_4 is used as fire extinguisher under the name pyrene.
18. Aryl and vinyl halides do not give precipitate with AgNO_3 solution.

HALOALKANES AND HALOARENES

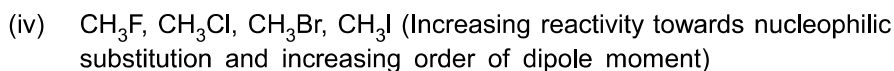
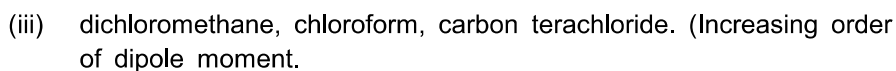
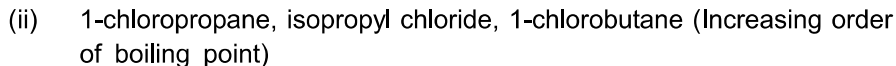
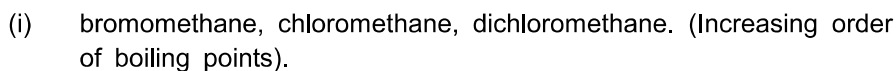
1. Write the IUPAC names of the following compounds.



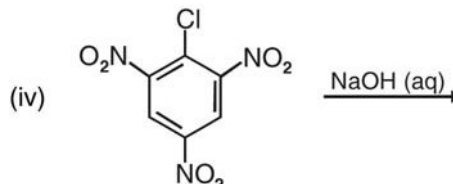
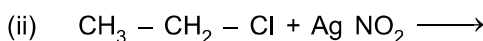
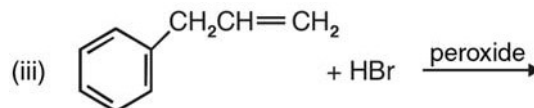
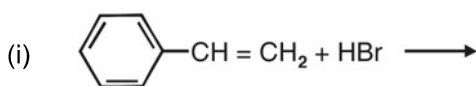
2. Write the structures of following halogen compounds

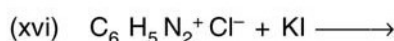
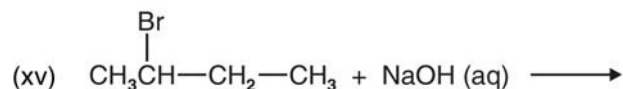
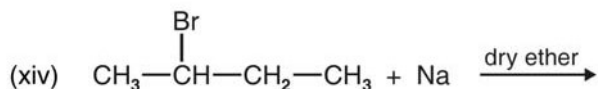
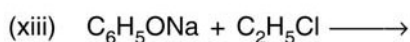
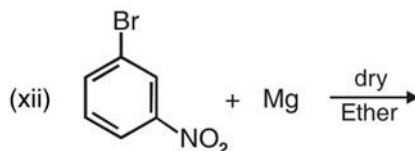
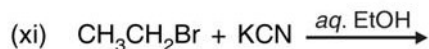
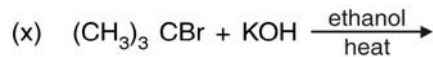
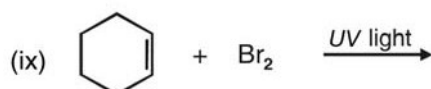
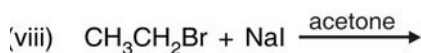
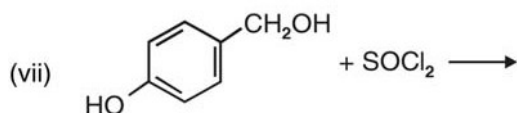
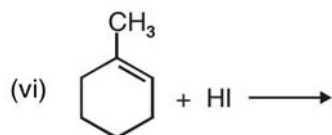
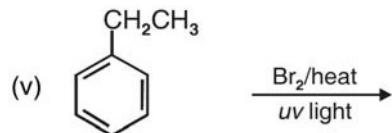


3. Arrange the following in the increasing order of property indicated :



4. Complete the following reactions :





5. How will you bring about the following conversions?

(i) benzene to 3-bromonitrobenzene

(ii) ethanol to but-1-yne

(iii) 1-bromopropane to 2-bromopropane

(iv) benzene to 4-bromo-1-nitrobenzene

(v) aniline to chlorobenzene

(vi) 2-methyl-1-propene to 2-chloro-2-methylpropane

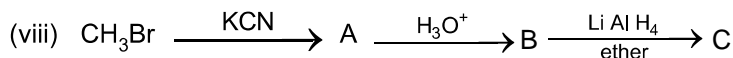
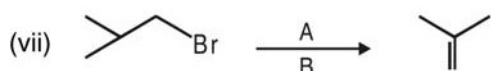
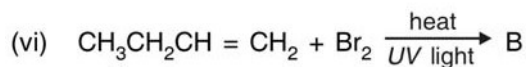
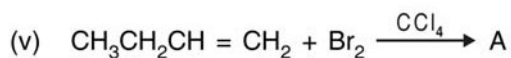
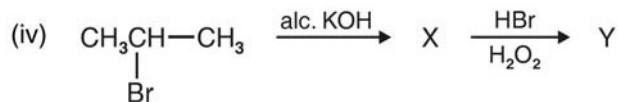
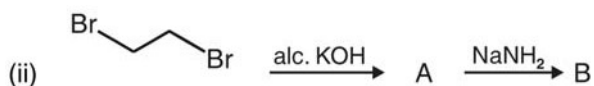
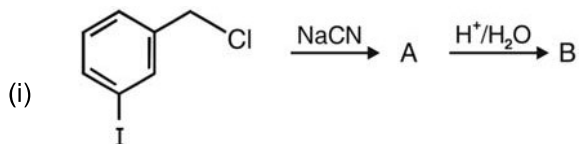
(vii) ethyl chloride to propanoic acid

(viii) but-1-ene to n-butyl iodide

(ix) benzene to phenylchloromethane.

(x) *tert*-butyl bromide to isobutyl bromide.

6. Identify the products formed in the following sequence :



7. Explain the following reactions with suitable example :

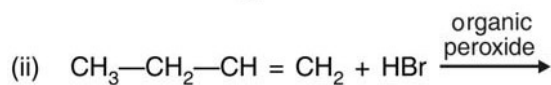
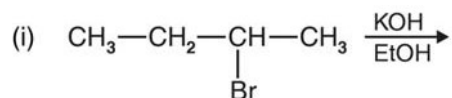
(i) Finkelstein reaction. (iv) Wurtz-Fitting reaction

(vii) Sandmeyer's reaction.

(ii) Swarts reaction. (v) Friedel-Craft's alkylation reaction.

(iii) Wurtz reaction. (vi) Friedel-Craft's acylation reaction

8. Write the major products and name the rule responsible for the formation of the product.



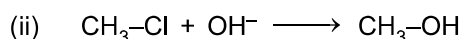
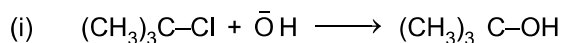
9. Write the difference between

- enantiomers and diastereomers
- retention and inversion of configuration.
- electrophilic and nucleophilic substitution reactions.

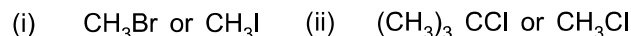
10. Give a chemical test to distinguish between the following pairs of compounds:

- chlorobenzene and cyclohexylchloride.
- vinyl chloride and ethyl chloride.
- n-propyl bromide and isopropyl bromide.

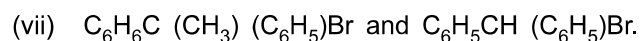
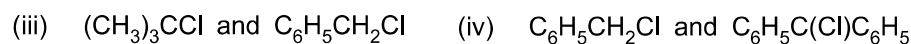
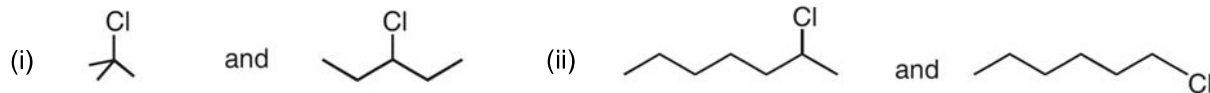
11. Give mechanism of the following reactions :



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



13. In the following pairs, which halogen compound undergoes faster (i) $\text{S}_{\text{N}}1$ and (ii) $\text{S}_{\text{N}}2$ reaction?

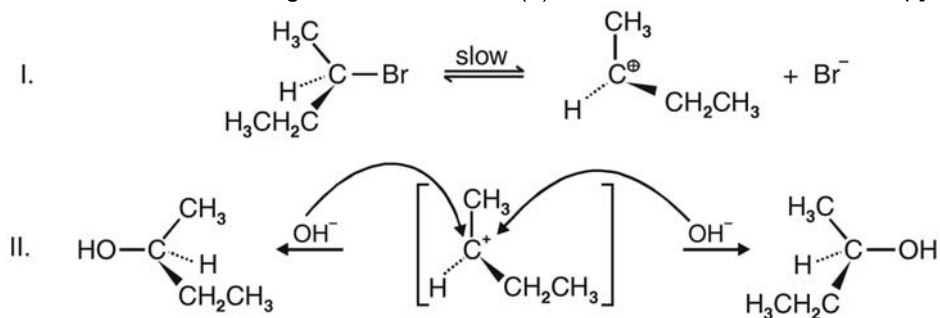


14. Give reasons for the following :

- The bond length of C—Cl bond is larger in haloalkanes than that in haloarenes.
- although alkyl halides are polar in nature but are not soluble in water.
- tert*-butyl bromide has lower boiling point than n-butyl bromide.
- haloalkanes react with KCN to form alkyl cyanide as main product while with AgCN alkyl isocyanide is the main product.
- sulphuric acid is not used in the reaction of alcohol with KI.
- thionyl chloride is the preferred reagent for converting ethanol to chloroethane.
- haloalkanes undergo nucleophilic substitution reaction easily but haloarenes do not undergo nucleophilic substitution under ordinary conditions.
- chlorobenzene on reaction with fuming sulphuric acid gives *ortho* and *para* chlorosulphonic acids.
- 2, 4-dinitro chlorobenzene is much more reactive than chlorobenzene towards hydrolysis reaction with NaOH.
- Grignard reagent should be prepared under anhydrous conditions.
- the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- neopentyl bromide undergoes nucleophilic substitution reactions very slowly
- vinyl chloride is unreactive in nucleophilic substitution reaction.

(xiv) An optically inactive product is obtained after the hydrolysis of optically active 2-bromobutane.

[Hint : The hydrolysis reaction occurs by S_N1 pathway. The carbocation is formed first which gives a mixture of (±) butan-2-ol in the second step].



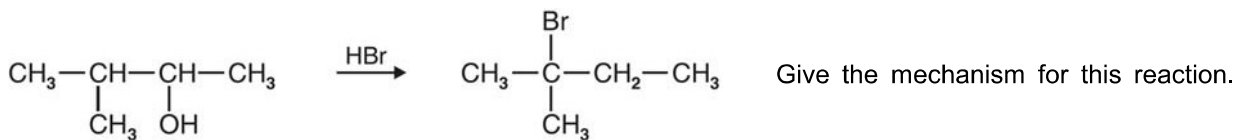
(xv) methyl iodide is hydrolysed at faster rate than methyl chloride.

15. Write the different products and their number formed by the monochlorination of following compounds :

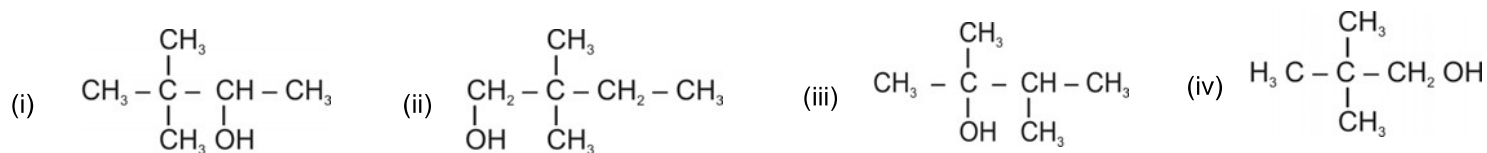
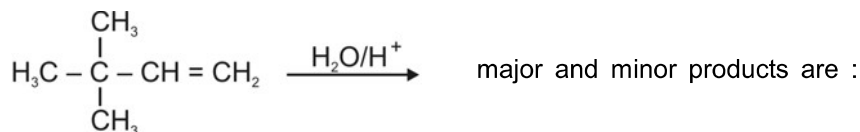
(i) CH₃CH₂CH₂CH₃ (ii) (CH₃)₂CHCH₂CH₃ (iii) (CH₃)₂CHCH(CH₃)₂

[Hint : (i) Two, (ii) four, (iii) three

16. (a) When 3-methylbutan-2-ol is treated with HBr, the following reaction takes places :



(b) In the following reaction :

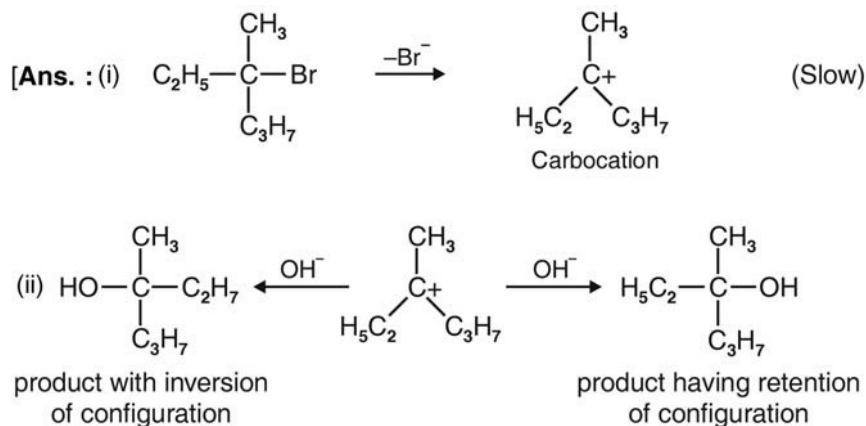


Ans. Major (iii) minor (i)

17. Give one use of each of following :

(i) Freon-12 (ii) DDT (iii) Carbon tetrachloride (iv) Iodoform

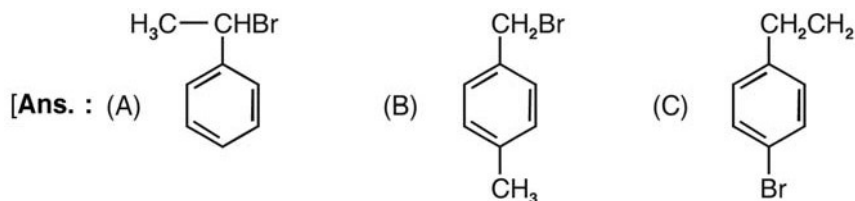
18. An optically active compound having molecular formula C₇H₁₅Br reacts with aqueous KOH to give C₇H₁₅OH, which is optically inactive. Give mechanism for the reaction.



A *racemic* mixture is obtained which is optically inactive.]

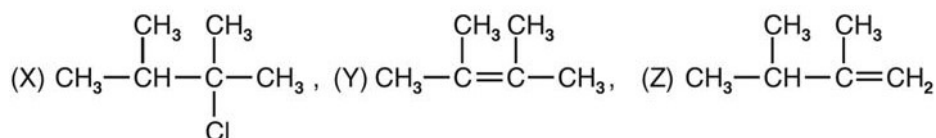
19. An organic compound C_8H_9Br has three isomers A, B and C. A is optically active. Both A and B gave the white precipitate when warmed with alcoholic $AgNO_3$ solution in alkaline medium. Benzoic acid, terephthalic and p-bromobenzoic acid were obtained on oxidation of A, B and C respectively.

Identify A, B and C.



- *20. An alkyl halide X having molecular formula $C_6H_{13}Cl$ on treatment with potassium tert-butoxide gives two isomeric alkenes Y and Z but alkene Y is symmetrical. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Identify X, Y and Z.

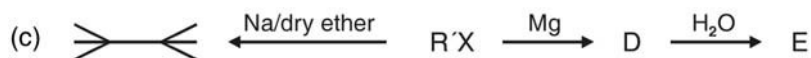
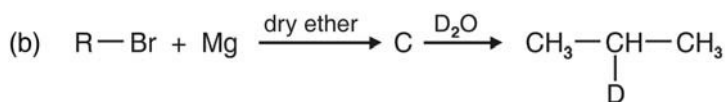
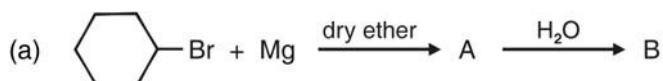
[Ans.



- *21. An organic compound (A) having molecular formula C_3H_7Cl on reaction with alcoholic solution of KCN gives compound B. The compound B on hydrolysis with dilute HCl gives compound C. C on reduction with H_2/Ni gives 1-aminobutane. Identify A, B and C.

[Ans. : (A) $CH_3CH_2CH_2Cl$, (B) $CH_3CH_2CH_2CN$, (C) $CH_3CH_2CH_2CONH_2$

- *22. Identify A, B, C, D, E, R and R' in the following sequence of reactions :



23. Which nomenclature is not according to IUPAC system.

(i) $Br-CH_2-CH=CH_2$; 1-bromoprop-2-ene
