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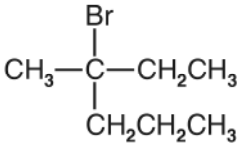
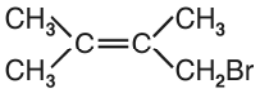
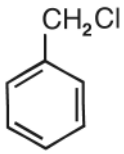
Unit - 10

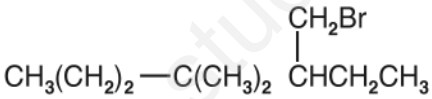
HALOALKANES AND HALOARENES

1. Write the IUPAC names of the following compounds.

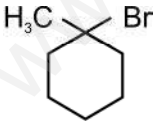
(i) 

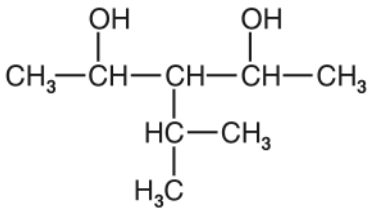
(ii) 

(iii) 

(iv) 

(v) $CH_2Br - CH = CH - CH_2 - C \equiv CH$

(vi) 

(vii) 

(ix) $(CCl_3)_3\ CCl$

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2. Write the structure of following halogen compounds

   (i) 2-chloro-3-methylpentane

   (ii) 2-(2-chlorophenyl)-1-iodooctane

   (iii) 1-bromo-4-sec-butyl-2–methylebenzene.

   (iv) p-bromotoluene.

   (v) chlorophenylmethane

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

   (i) bromomethane, chloromethane, dichloromethane. (Increasing order of boiling points).

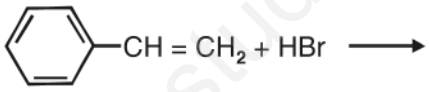
   (ii) 1-chloropropane, isopropyl chloride, 1-chlorobutane (Increasing order of boiling point)

   (iii) dichloromethane, chloroform, carbon terachloride. (Increasing order of dipole moment.

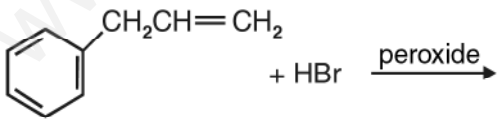
   (iv) CH_3F, CH_3Cl, CH_3Br, CH_3I (Increasing reactivity towards nucleophilic substitution and increasing order of dipole moment)

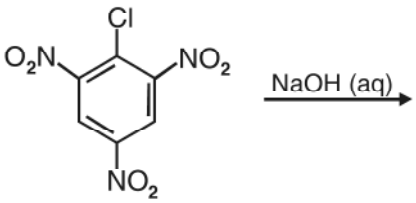
   (v) *o,m.p*-dichlorobenzenes (Increasing order of melting points).

4. Complete the following reactions :

   (i) 

   (ii) $CH_3 - CH_2 - Cl + Ag\ NO_2 \longrightarrow$

   (iii) 

   (iv) 

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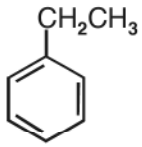
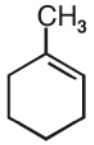
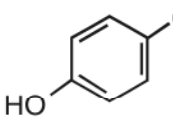
(v)  $\xrightarrow[uv\ \text{light}]{Br_2/\text{heat}}$

(vi)  $+ HI \longrightarrow$

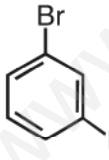
(vii)  $+ SOCl_2 \longrightarrow$

(viii) $CH_3CH_2Br + NaI \xrightarrow{\text{acetone}}$

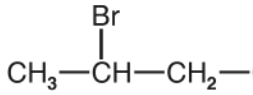
(ix)  $+ Br_2 \xrightarrow{UV\ \text{light}}$

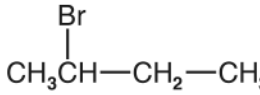
(x) $(CH_3)_3\ CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(xi) $CH_3CH_2Br + KCN \xrightarrow{aq.\ EtOH}$

(xii)  $+ Mg \xrightarrow[\text{Ether}]{\text{dry}}$

(xiii) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(xiv)  $+ Na \xrightarrow{\text{dry ether}}$

(xv)  $+ NaOH\ (aq) \longrightarrow$

(xvi) $C_6H_5N_2^+Cl^- + KI \longrightarrow$

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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

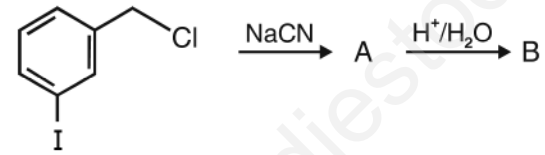
(vii) ethyl chloride to propanoic acid

(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 :

(i) 

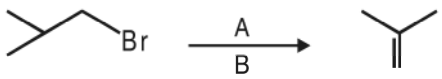
(ii) 

(iii) $C_6H_5CH_2CHBrCH_3 \xrightarrow{\text{alc. KOH}} A \xrightarrow{HBr} B$

(iv) $CH_3CH(Br)-CH_3 \xrightarrow{\text{alc. KOH}} X \xrightarrow[H_2O_2]{HBr} Y$

(v) $CH_3CH_2CH = CH_2 + Br_2 \xrightarrow{CCl_4} A$

(vi) $CH_3CH_2CH = CH_2 + Br_2 \xrightarrow[UV\ light]{heat} B$

(vii) 

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(viii) $CH_3Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} \xrightarrow[ether]{Li\,Al\,H_4}$

7. Explain the following reactions with suitable example :

(i) Finkelstein reaction.

(ii) Swarts reaction.

(iii) Wurtz reaction.

(iv) Wurtz-Fitting reaction

(v) Friedel-Craft's alkylation reaction.

(vi) Friedel-Craft's acylation reaction

(vii) Sandmeyer reaction.

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

(i) $CH_3—CH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3 \xrightarrow[EtOH]{KOH}$

(ii) $CH_3—CH_2—CH = CH_2 + HBr \xrightarrow[organic\ peroxide]{}$

9. Write the difference between

(i) enantiomers and diastereomers

(ii) retention and inversion of configuration.

(iii) electrophilic and nucleophilic substitution reactions.

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

(i) chlorobenzene and cyclohexylchloride.

(ii) vinyl chloride and ethyl chloride.

(iii) n-propyl bromide and isopropyl bromide.

11. Give mechanism of the following reactions :

(i) $(CH_3)_3C - Cl + \bar{O}H \longrightarrow (CH_3)_3\ C - OH$

(ii) $CH_3 - Cl + OH^- \longrightarrow CH_3 - OH$

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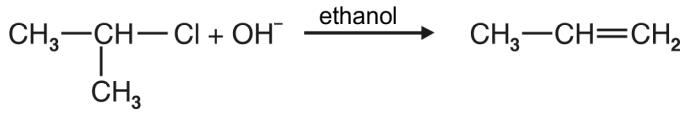
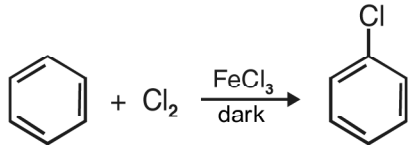
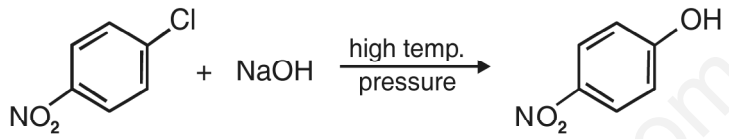
(iii) 

(iv) 

(v) 

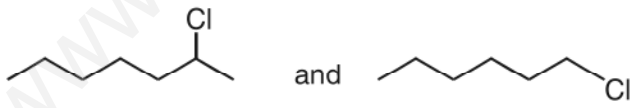
12. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- and why?

    (i) CH_3Br or CH_3I

    (ii) $(CH_3)_3$ CCl or CH_3Cl

13. In the following pairs which halogen compound undergoes faster SN1 reaction?

    (i) 

    (ii) 

    (iii) $(CH_3)_3C$ – Cl and $C_6H_5CH_2Cl$

    (iv) $C_6H_5CH_2Cl$ and $C_6H_5C(Cl)C_6H_5$

    (v) CH_2 = CH – Cl and CH_2 = CH – CH_2Cl

14. Give reasons for the following :

    (i) The bond length of C–Cl bond is larger in haloalkanes than that in haloarenes.

    (ii) Although alkyl halides are polar in nature but are not soluble in water.

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(iii) tert-butyl bromide has lower boiling point than n-Butyl bromide.

(iv) haloalkanes react with KCN to form alkyl cyanide as main product while with AgCN alkyl isocyanide is the main product.

(v) sulphuric acid is not used in the reaction of alcohol with KI.

(vi) thionyl chloride is the preferred reagent for converting ethanol to chloroethane.

(vii) haloalkanes undergo nucleophilic substitution reaction easily but haloarenes do not undergo nucleophilic substitution under ordinary conditions.

(viii) chlorobenzene on reaction with fuming sulphuric acid gives ortho and para chlorosulphonic acids.

(ix) 2, 4-dinitro chlorobenzene is much more reactive than chlorobenzene towards hydrolysis reaction with NaOH.

(x) Grignard reagent should be prepared under anhydrous conditions.

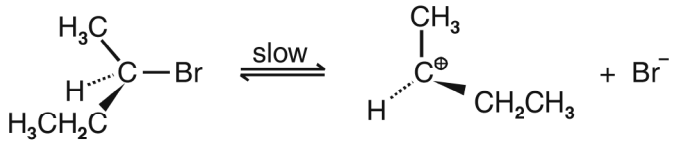
(xi) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

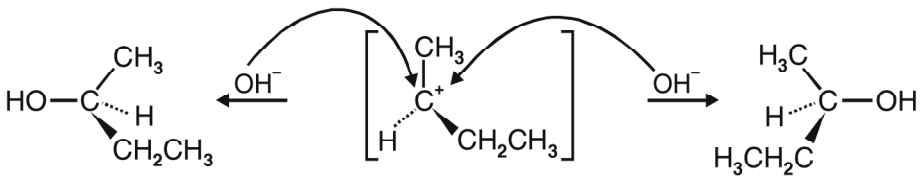
(xii) neopentyl bromide undergoes nucleophilic substitution reactions very slowly

(xiii) 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].

I. 

II. 

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

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

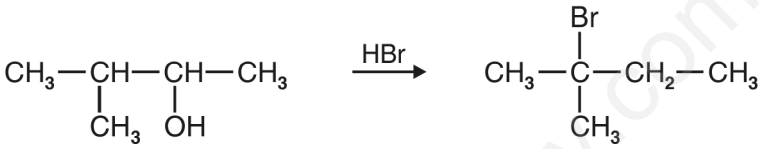
(i) $CH_3CH_2CH_2CH_3$

(ii) $(CH_3)_2CHCH_2CH_3$

(iii) $(CH_3)_2CHCH(CH_3)_2$

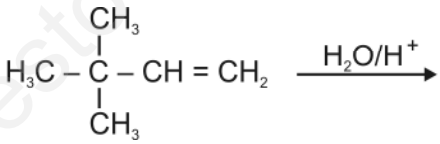
[**Hint :** (i) Two, (ii) four, (iii) three

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

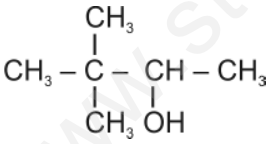


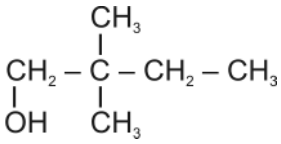
Give the mechanism for this reaction.

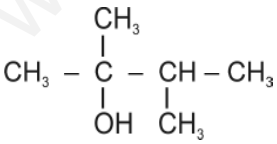
(b) In the following reaction :

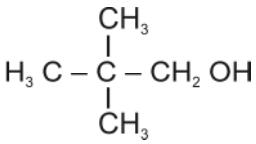


major and minor products are :

(i) 

(ii) 

(iii) 

(iv) 

Ans. Major (iii) minor (i)

17. Give one use of each of following :

(i) Freon-12 (ii) DDT

(iii) Carbon tetrachloride (iv) Iodoform

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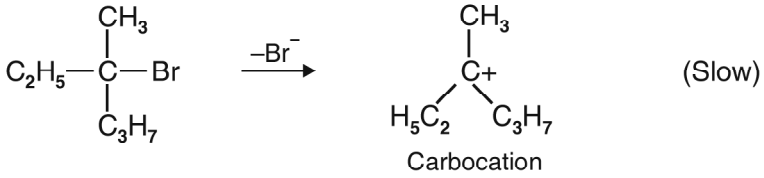
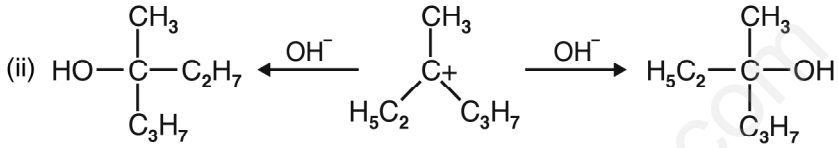
18. An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give $C_7H_{15}OH$, which is optically inactive. Give mechanism for the reaction.

[**Ans. :** (i) 

(Slow)

Carbocation

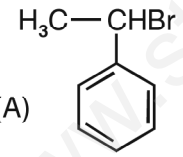
(ii) 

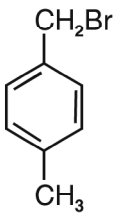
product with inversion of configuration

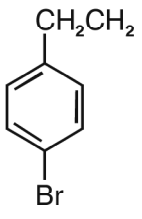
product having retention of configuration

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.

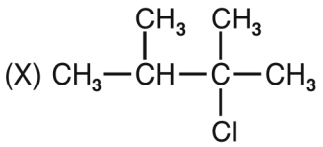
[**Ans. :** (A) 

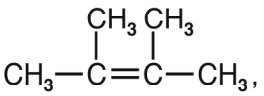
(B) 

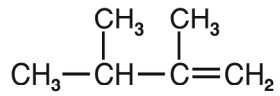
(C) 

*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 symetrical. Both alkenes on hydrogenation give 2, 3-dimethylbutane. Identify X, Y and Z.

[**Ans.**

(X) 

, (Y) 

, (Z) 

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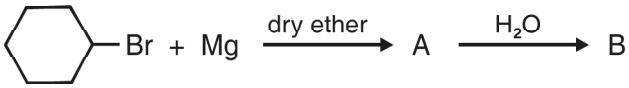
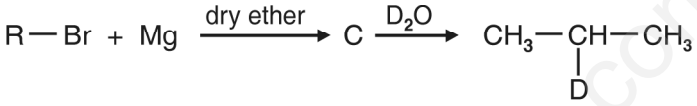
*21. An organic compound (A) having molecular formula C_3H_7Cl on reaction with alcoholic solution of KCN gives compound B. The compound B on hydrolysis with dilute HCl gives compound C. C on reduction with H_2/ Ni gives 1-aminobutane. Identify A, B and C.

[**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 :

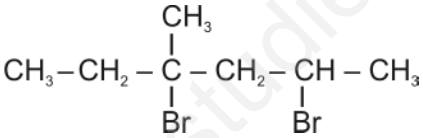
(a) 

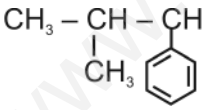
(b) 

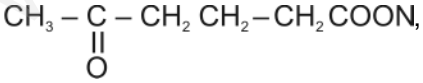
(c) 

23. Which nomenclature is not according to IUPAC system.

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

(ii)  4–bromo-2, 4-dimethylhexane

(iii)  2–methyl–3–phenylpentane

(iv)  5–oxohexanoic acid

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