IMPORTANT QUESTIONS CLASS – 127<9A =GHFM CHAPTER – 6 HALOALKANES AND HALOARENES

Question 1- Among the following pairs which one undergoes S_N^2 substitution reaction faster. State reasons.

- (i) CH2Cl and C-Cl
- (ii) <u>and</u> (iii)

Answer: (i) It undergoes $S_N 2$ reaction faster as it is a primary halide.

(ii) Due to its large size, Iodine is a better leaving group, therefore, in the presence of an incoming nucleophile, it will be released at a faster rate.

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Question 2- Among the following pairs which one undergoes $S_N 1$ substitution reaction faster. State reasons.

(i)

(ii)



Answer: i) Tertiary halide reacts faster than secondary halide because of the greater stability of tert-carbocation.

(ii) Because of the greater stability of secondary carbocation than primary.

Question 3- How can the following conversions be carried out?

(i) Methyl magnesium bromide to 2-methyl- propan-2-ol

(ii) Benzyl chloride to benzyl alcohol

(iii) 2-Bromopropane to 1-bromopropane

(iv) Benzene to p-chloronitrobenzene



Answer: (i)

Question 4- Although chlorine is an electron-withdrawing group, yet it is ortho-, para- directing in electrophilic aromatic substitution reactions. Why?

Answer: Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilised the intermediate carbocation formed during the electrophilic substitution. Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at the ortho- and parapositions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at the ortho- and para positions and hence makes the deactivation less for ortho- and para attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.



Question 5- State reasons for:

(i) p-dichlorobenzene has a higher melting point than its o- and m-isomers.

(ii) (±)-Butan-2-ol is optically inactive.

(iii) The C–Cl bond length in chlorobenzene is shorter than that in CH₃–Cl.

(iv) Chloroform is stored in closed dark brown bottles.

(v) Alkyl halides, though polar, are immiscible with water.

Answer: (i) p-isomers are comparatively more symmetrical, fits closely in the crystal lattice. Therefore, they require more heat to break the strong forces of attraction. As a result, pisomers have a higher melting point than o- and m-isomers.

(ii) In a racemic mix, one type of rotation is cancelled by another. Therefore, (\pm) -Butan-2-ol is optically inactive.

$$H_3C - CH - H_2C - CH_3$$

OH

(iii) The C–Cl bond length in chlorobenzene is shorter than

that in CH₃–Cl as in haloalkanes, the halogen atom is

attached to sp³ hybridized carbon whereas in haloarenes it is attached to sp² hybridized carbon whose size is smaller than sp³ orbital carbon.

(iv) Chloroform is stored in closed dark brown bottles because chloroform gets slowly oxidised by air in the presence of light and forms an extremely poisonous gas (carbonyl chloride), popularly known as phosgene.

$$\begin{array}{ccc} 2CHCl_3 + O_2 & \xrightarrow{\text{Light}} 2O = C \swarrow + 2HClZ \\ Choloform & Phosgene or \\ Carbonyl chloride \end{array}$$

(v) Alkyl halides are polar molecules that are held together by dipole-dipole interaction. The molecules of H_2O are held together by H- bonds. The forces of attraction between water and alkyl halide molecules are weaker than the existing forces of attraction between alkyl halide-alkyl halide molecules and water-water molecules.

Question 6- Identify chiral and achiral molecules in each of the following pair of compounds:



- (ii) racemic mixture
- (iii) Sandmeyer's reaction

Answer: (i) Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. Cyanide group is a hybrid of two contributing structures and can act as a nucleophile in two different ways $[VC=N \leftrightarrow :C=NV]$, i.e., linking through carbon atoms resulting in alkyl cyanides and through nitrogen atoms leading to isocyanides.

(ii) A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as a racemic mixture or racemic modification. A racemic mixture is represented by prefixing dl or (\pm) before the name, for example (\pm) butan-2-ol. The process of conversion of enantiomer into a racemic mixture is known as racemisation.

(iii) When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of the freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by –Cl or –Br. Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.



Question 8- Write the structures for the following:

(i) 4-tert-Butyl-3-iodoheptane

(ii) 4-Bromo-3-methylpent-2-ene

(iii) p-Bromochlorobenzene

(iv) 1-Chloro-4-ethylcyclohexane

Answer: (i)

(ii)
$$CH_3-CH_2-CH_-CH_-CH_2-CH_3$$

 $H C - C - CH$

CH₃

(111)

(iv)

 $CH_{3} - CH = C - CH - CH_{3}$ $| I = CH_{3} - CH_{3}$ $CH_{3} - Br$

Question 9- Give reasons:

(i) Grignard's reagents should be prepared under anhydrous conditions.

(ii) n-Butyl bromide has a higher boiling point than f-butyl bromide.

Answer: (i) Grignard's reagents react with alcohol, water, amines etc. to form the corresponding hydrocarbon and thus, must be prepared under anhydrous conditions.

 $R-MgX + HOH \rightarrow RH + Mg(OH)X$

(ii) n-Butyl bromide has a higher boiling point than f-butyl bromide as it has a larger surface area. Therefore, it has more Van der Waals' forces.

Question 10- What happens when:

(i) Chlorobenzene is treated with Cl₂/FeCl₃

(ii) Ethyl chloride is treated with AgNO₂

(iii) 2-bromopentane is treated with alcoholic KOH

