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Haloalkanes and their Properties

Definition and Classification

Haloalkanes are aliphatic hydrocarbons in which one or more hydrogen atoms are replaced by halogen atoms (fluorine, chlorine, bromine, iodine). Haloarenes are aromatic hydrocarbons where hydrogen atoms in the benzene ring are replaced by halogen atoms.

Types of Haloalkanes

Based on the number of halogen atoms, haloalkanes are classified as monohaloalkanes, dihaloalkanes, and polyhaloalkanes. Dihaloalkanes can be geminal (two halogens on the same carbon) or vicinal (halogens on adjacent carbons).

Hybridisation and Subtypes

In haloalkanes, the halogen is attached to an sp^3 hybridised carbon. Subtypes include primary, secondary, and tertiary haloalkanes depending on the number of alkyl groups attached to the carbon bonded to the halogen. Allylic halides have halogen attached to

an allylic carbon (adjacent to a double bond), and benzylic halides have halogen attached to a carbon adjacent to an aromatic ring.

Physical Properties

Haloalkanes generally have higher boiling and melting points than their parent hydrocarbons due to polar C–X bonds and dipole–dipole interactions. Boiling points increase with the size of the halogen (RF < RCl < RBr < RI). They are insoluble in water but soluble in organic solvents and have densities greater than water.

Chemical Properties

Reactivity depends on the bond dissociation energy of the C–X bond, which decreases down the group (C–Cl > C–Br > C–I). Haloalkanes undergo nucleophilic substitution, elimination, reactions with metals (forming Grignard reagents or Wurtz coupling), and reduction.

Mechanisms of Nucleophilic Substitution

Two main mechanisms are SN1 and SN2. SN1 involves a carbocation intermediate and is unimolecular, favored by tertiary haloalkanes and polar protic solvents. SN2 is bimolecular, involves a backside attack, and is favored by primary haloalkanes and polar aprotic solvents.

Stereochemistry

Haloalkanes can exhibit stereoisomerism. Optical activity arises from chiral carbons bonded to four different groups. SN2 reactions cause inversion of configuration (Walden inversion), while SN1 reactions can lead to racemisation.

Solved Examples

Example 1: Write the IUPAC names of the following compounds: (i) 4-Bromopent-2-ene, (ii) 3-Bromo-2-methylbut-1-ene.

Solution: Identify the longest chain containing the double bond, number it to give the double bond the lowest number, locate substituents, and name accordingly. The names are as given.

Example 2: Identify all possible monochloro isomers formed on free radical chlorination of $(CH_3)_2CHCH_2CH_3$.

Solution: Four types of hydrogens can be replaced, leading to four isomers: $(CH_3)_2CHCH_2CH_2Cl$, $(CH_3)_2CHCH(Cl)CH_3$, $(CH_3)_2C(Cl)CH_2CH_3$, and $CH_3CH(CH_2Cl)CH_2CH_3$.

Example 3: Write the products of addition of HBr to propene with and without peroxide.

Solution: Without peroxide, Markovnikov addition gives 2-bromopropane. With peroxide, anti-Markovnikov addition gives 1-bromopropane.

Practice Set

- **Level 1 (Easy):** Define primary, secondary, and tertiary haloalkanes with examples.
- **Level 2 (Moderate):** Explain the difference between SN1 and SN2 mechanisms with suitable examples.
- **Level 3 (Challenging):** Predict the major product and mechanism when 2-bromopropane reacts with aqueous KOH.

Answer Key

- **Level 1:** Primary haloalkane: halogen attached to carbon bonded to one other carbon (e.g., chloromethane). Secondary: halogen attached to carbon bonded to two

carbons (e.g., 2-chloropropane). Tertiary: halogen attached to carbon bonded to three carbons (e.g., tert-butyl chloride).

- **Level 2:** SN1 is unimolecular, involves carbocation intermediate, favored by tertiary haloalkanes and polar protic solvents. SN2 is bimolecular, one-step backside attack, favored by primary haloalkanes and polar aprotic solvents.
- **Level 3:** 2-bromopropane reacts with aqueous KOH mainly via SN1 mechanism forming 2-propanol as the major product due to carbocation intermediate formation.

Haloarenes and Polyhalogen Compounds

Definition and Substitution Patterns

Haloarenes are aromatic compounds where one or more hydrogen atoms on the benzene ring are replaced by halogen atoms. Substitution patterns include ortho (1,2-), meta (1,3-), and para (1,4-) positions.

Preparation Methods

Haloarenes are prepared by direct halogenation of benzene using halogens and catalysts (Fe, FeX_3), Sandmeyer reactions from diazonium salts, and other substitution reactions.

Physical Properties

Isomeric haloarenes have similar boiling points, but para isomers have higher melting points due to better crystal packing.

Chemical Properties

Haloarenes are less reactive in nucleophilic substitution due to partial double bond character of C–X bond from resonance. Electrophilic substitution occurs mainly at ortho and para positions.

Important Reactions

Reactions include Sandmeyer, Finkelstein, Wurtz, Friedel-Crafts alkylation, Dow’s process, Hunsdiecker, and Gattermann reactions.

Polyhalogen Compounds

Compounds with multiple halogen atoms, such as dichloromethane, chloroform, carbon tetrachloride, iodoform, and DDT, have industrial and agricultural uses but may pose environmental hazards.

Solved Examples

Example 4: Explain why KCN reacts with haloalkanes to form alkyl cyanides, while AgCN forms isocyanides.

Solution: KCN is ionic and attacks via carbon, forming alkyl cyanides. AgCN is covalent, and nitrogen attacks, forming isocyanides.

Example 5: Which compound undergoes SN2 reaction faster: cyclohexylmethyl chloride or cyclohexyl chloride?

Solution: Cyclohexylmethyl chloride reacts faster due to less steric hindrance.

Example 6: Predict the order of reactivity of isomeric bromobutanes in SN1 and SN2 reactions.

Solution: SN1: primary < secondary < tertiary; SN2: tertiary < secondary < primary.

Practice Set

- **Level 1 (Easy):** Define ortho, meta, and para substitution in haloarenes with examples.
- **Level 2 (Moderate):** Describe the Sandmeyer reaction and its significance.
- **Level 3 (Challenging):** Explain why nucleophilic substitution is difficult in haloarenes compared to haloalkanes.

Answer Key

- **Level 1:** Ortho: substituents on adjacent carbons (1,2-), meta: substituents separated by one carbon (1,3-), para: substituents opposite each other (1,4-).
- **Level 2:** Sandmeyer reaction replaces diazonium group with halogens using copper salts, useful for synthesizing haloarenes.
- **Level 3:** C–X bond in haloarenes has partial double bond character due to resonance, making nucleophilic attack difficult; also, phenyl cation intermediate is unstable.

Quick Reference Table

Common Mistakes and Misconceptions

Glossary