

1 Halogenoalkanes

1.1 Structure of Halogenoalkanes

Halogenoalkanes are derivatives of alkanes compounds with F, Cl, Br, I groups. Halogenarenes are derivatives of arenes with benzylic H replaced by a F, Cl, Br, I group.

Halogenoalkanes can be classified according to the degree of substitution of C that the halogen is bonded to.

1.2 Physical Properties of Halogenoalkanes

Halogenoalkanes contain polar R–X bonds which increase their melting and boiling point. For compounds with the same R group, the molecule with a larger X electron cloud has stronger id-id interactions and hence a larger melting and boiling point.

Though they are polar, halogenoalkanes are still poorly soluble in water. Fluoroalkanes and monochloroalkanes are less dense than water while other R–X compounds are denser than water.

1.3 Formation of Halogenoalkanes

1.3.1 From Alkanes

Mono and polyhalogenated products can be formed from alkanes. Refer to 'Free Radical Substitution' in Alkanes.

1.3.2 From Alkenes

Mono and dihalogenated products can be formed from alkenes. Refer to 'Electrophilic Substitution' in Alkenes.

1.3.3 From Alcohols

Refer to 'Nucleophilic Substitution' in Hydroxy Compounds.

1.4 Reaction of Halogenoalkanes

Halogenoalkanes typically undergo nucleophilic substitution reactions.

The rate of reaction primarily depends on the nature of the R–X bond, with weaker bonds reacting faster despite the change in electronegativity, hence rate of reaction increases in the order C–Cl, C–Br and C–I.

1.4.1 Nucleophilic Substitution

Definition 1.1: Nucleophile

A Nucleophile Nu is a particle which has at least one pair of free electrons and can act as an electron donor. Nucleophiles are attracted to electron-poor sites.

Note that nucleophiles are not necessarily charged.

Nucleophilic substitution can occur through two mechanisms, characterized by the study of these mechanism's kinetic properties.

Definition 1.2: S_N2

The S_N2 mechanism of nucleophilic substitution involves two molecules in its slow (and only) step.

S_N2 reactions involve the backside attack of a nucleophile to the halogenoalkane at the opposite side of the C–X bond, forming an intermediate molecule both bonded to the nucleophile and X, after which X is ejected. This reaction preserves the enantiomeric quality of a molecule if the original alkane displays enantiomerism about the C with X due to the spatial requirements of a backside attack.

Definition 1.3: S_N1

The S_N1 mechanism of nucleophilic substitution involves molecules in its slow step.

S_N1 reactions involve the spontaneous ejection of the X group in its slow step to form a carbocation which will then react with a nucleophile. The later addition of the nucleophile will happen at equal probabilities at either side of the

trigonal planar C^+ , hence any enantiomeric products about C will be racemic.

Only draw stereochemistry of a reaction if the original molecule displays enantiomerism about the C bonded to X. The mechanism at which a S_N reaction occurs depends primarily on the degree of substitution of the C bonded to X. C with more alkyl groups bonded to it will generally follow the S_N1 mechanism because it will form a more stable C^+ whereas C with less alkyl groups bonded to it will follow the S_N2 mechanism due to the free space around C leaving it susceptible to backside attack.

Formation of Alcohol

Reagents: NaOH

Conditions: Aqueous, heat

A polyhalogenoalkane may react to form alcohol groups, which may then alter the reaction environment to give an Alcoholic medium which can then lead to elimination of HX. Refer to Elimination Reactions.

Formation of Amines

Reagents: Concentrated NH_3 in excess

Conditions: Alcoholic, heat, sealed tube

If NH_3 is not in excess, a primary amine can act as a nucleophile in later reactions and form a chain reaction to eventually form secondary and tertiary amines and finally a quaternary ammonium salt.

Formation of Nitriles

Reagents: KCN

Conditions: Alcoholic, heat

In practice, a mixture of alcohol and water is used so that all reactants can be dissolved. Nitriles can be further reduced to form primary amines (H_2 , Ni and Heat OR $LiAlH_4^-$, dry ether and heat) or undergo hydrolysis to form carboxylic acids ($H_2SO_4(aq)$, heat) and carboxylate ions ($NaOH(aq)$, heat).

Williamson Ether Synthesis

Reagents: Alcohol, Na OR $R-O^-Na^+$

Conditions: heat

1.4.2 Elimination

Though the benzene ring itself is unreactive, any alkyl chains bonded to a benzene ring can undergo oxidation, replacing the alkyl group with a COOH group. However, the reaction requires that the benzylic carbon has at least 1 H or 1 O atom bonded to it, otherwise a case such as a tert-butyl benzene will not be oxidised due to steric effect of CH_3 groups attached to the benzylic C.

Dehydrohalogenation

Reagents: NaOH

Conditions: Alcoholic, heat

Dehydrohalogenation can only occur if there is a H in some C adjacent to the C-X group.

1.5 Halogenoarenes

Halogenoarenes are compounds with X bonded to benzene rings.

Halogenoarenes burn with a sooty flame and are insoluble in and denser than water.

Refer to 'Electrophilic Substitution' in Arenes for methods of preparation.

Halogenoarenes generally do not undergo nucleophilic substitution reactions. Extension of the πe^- cloud over C-X causes the formation of a partial double bond character, the benzene ring physically blocks approaching nucleophiles, the e^- density of the benzene ring repels approaching nucleophiles and the presence of the e^- cloud prevents the

formation of C^+ . However, reactions may occur under extreme conditions (150 atm, 350 °C).

Halogenoarenes can also undergo electrophilic substitution, much like other arenes. However, X are electron-withdrawing and electronegative, hence they are deactivating groups and the reactivity of the arene decreases as more X groups are added. X is a 2,4-directing group.

1.6 Distinguishing Test

1.6.1 '4-step Test'

1. Heat with NaOH(aq)
2. Cool
3. Acidify with HNO_3
4. Add $AgNO_3$

Positive tests will form a AgX precipitate. The identity of X can be determined according to the color of the precipitate.

1.6.2 Ethanolic $AgNO_3$

1. Heat with ethanolic $AgNO_3$

Ethanol acts as a nucleophile.

1.7 Applications of Halogenoalkanes