Halogen Derivatives

Halogenoalkanes

Halogenoarenes

Preparation of Halogen Derivatives

Free-Radical Substitution of Alkanes

- Refer to Alkane Lecture

Electrophilic Addition of Alkenes

- Refer to Alkene Lecture

Nucleophilic Substitution of Alcohols

$R\text{-}OH \longrightarrow R\text{-}X + H_2O$

Reagent & Condition

Dry HX, heat ($X = Cl, Br, I$)

$3R\text{-}OH + PX_3 \longrightarrow 3R\text{-}X + H_3PO_3$

Reagent & Condition

Anhydrous PX_3, heat ($X = Cl, Br, I$)

$R\text{-}OH + PCl_5 \rightarrow R\text{-}Cl + POCl_3 + \underline{HCl}^*$

Reagent & Condition

Anhydrous PCl_5, rtp

$R\text{-}OH + SOCl_2 \rightarrow R\text{-}Cl + SO_2 + \underline{HCl}^*$

Reagent & Condition

Anhydrous $SOCl_2$, heat

*Obs: white fumes of HCl that turn damp blue lithmus paper red

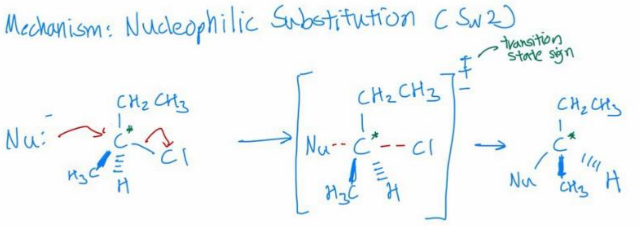
Electrophilic Substitution of Arenes

- Refer to Arenes Lecture

Nucleophilic Substitution Reactions of Halogenoalkanes

S_N2 Mechanism

Mechanism: Nucleophilic Substitution (S_N2)



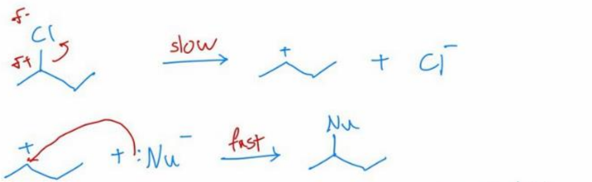
Note: Inversion of stereochemistry

Rate Eqn: Rate = $k[RX][Nu]$ → both reactants involved in one-step reaction

Note: Look at steric hindrance about carbon -> more steric hindrance = harder for nucleophile to attack carbon -> reaction not preferred

S_N1 Mechanism

Mechanism: Nucleophilic Substitution (S_N1)

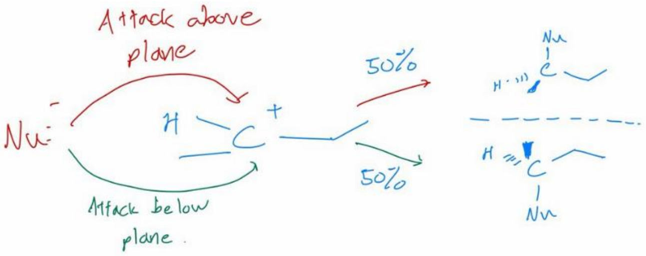


Rate Eqn: Rate = $k[RX]$ → only RX involved in slow step

Note: 2-step reaction means energy profile of reaction has 2 humps.

Note: Look at stability of carbocation formed -> more electron-donating R groups attached to carbocation = more stable carbocation = reaction preferred

Note: If the Carbocation turns into a chiral carbon, this means the reaction can form a racemic mixture of enantiomers



Note: Carbocation Trigonal Planar

Enantiomers formed in 50:50 ratio
↳ Racemic mixture

Reactivity of Halogenoalkanes by Nucleophilic Substitution Reactions

Size of Halogens increase down the group -> valence orbital used in bonding is larger and more diffused -> orbital overlap btwn X and C atoms become less effective

- Therefore, Bond Strength of C-I < C-Br < C-Cl < C-F, lower bond strength means lower Ea for reaction, thus reactivity higher
- C-F bond too strong -> Unreactive

Formation of Alcohols

Reagents & Conditions

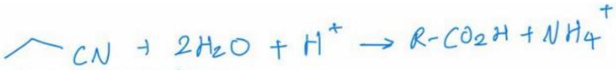
NaOH (aq) or KOH (aq) ; heat

Formation of Nitriles

Reagent & Condition

KCN or NaCN , ethanol ; heat

Hydrolysis of Nitriles



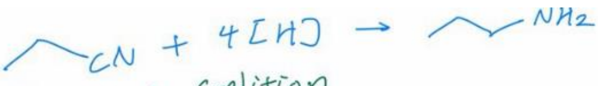
Reagent & Condition

HCl (aq) or H_2SO_4 (aq) , heat

Reagent & Condition

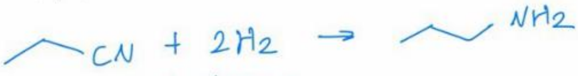
NaOH (aq) or KOH (aq) , heat

Reduction of Nitriles



Reagent & Condition

$LiAlH_4$ in dry ether



Reagent & Condition

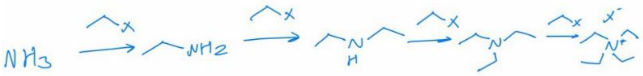
H_2 with Ni or Pd or Pt catalyst, r.t.p

Formation of Amines

Reagent & Condition

Excess NH_3, ethanol ; heat in sealed tube

Note: Multi-substituted products are possible



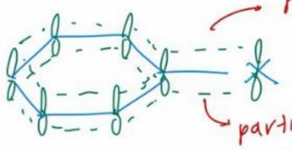
Elimination of Halogenoalkane

- Refer to Alkene Lecture

Reactions of Halogenoarenes

No Nucleophilic Substitution

- C-X bond strengthened



p-orbital overlap – lone pair on X donated to π electron cloud

partial double bond character in C–X bond, stronger bond.

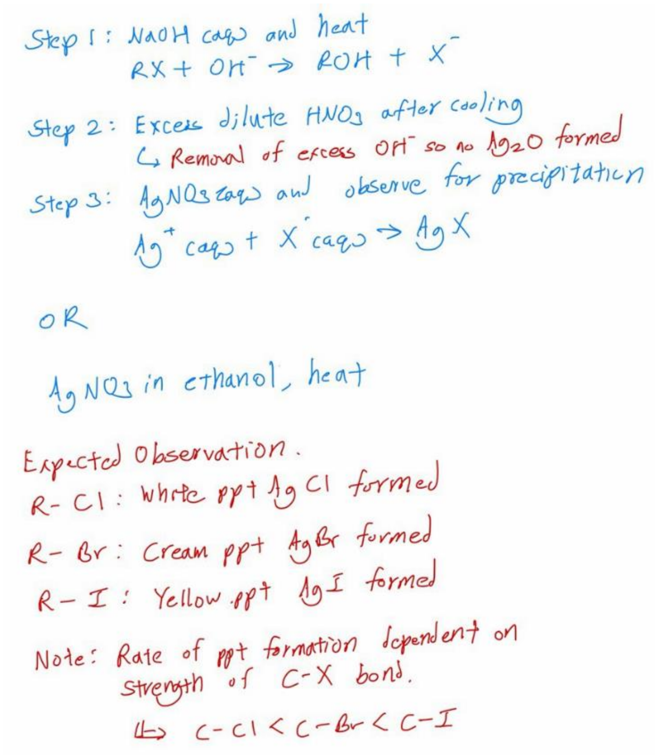
- Steric hindrance
    - Benzene ring sterically hinder S_N2 reaction. C not accessible to nucleophilic attack by the rear side

Electrophilic Substitution of Halogenoarenes

Refer to Arene Lecture

- Halogens are deactivating groups as they are electron-withdrawing -> Electrophilic Substitution happens at lower rate and stronger conditions required

Distinguishing test for Halogenoalkanes



Step 1: NaOH (aq) and heat

$RX + OH^- \rightarrow ROH + X^-$

Step 2: Excess dilute HNO_3 after cooling

↳ Removal of excess OH^- so no Ag_2O formed

Step 3: $AgNO_3$ (aq) and observe for precipitation

$Ag^+ (aq) + X^- (aq) \rightarrow AgX$

OR

$AgNO_3$ in ethanol, heat

Expected Observation.

R-Cl: white ppt AgCl formed

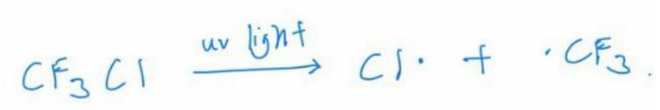
R-Br: Cream ppt AgBr formed

R-I: Yellow ppt AgI formed

Note: Rate of ppt formation dependent on strength of C-X bond.

↳ C-Cl < C-Br < C-I

CFCs



$$CF_3Cl \xrightarrow{\text{uv light}} Cl\cdot + \cdot CF_3 .$$

Cl Radical will react with ozone O_3 in a chain propagation reaction

Substitutes like hydrocarbons, hydrofluorocarbons or fluorocarbons are used.

- C-F bonds are stronger and therefore resist breaking easily to form F radicals