Organic Halides

Derivatives of alkanes where one or more hydrogen atoms is replaced by a halogen
Nomenclature

- Named in a similar manner as alkanes
- 1. Name the longest continuous carbon chain
- 2. Name & number substituents in alphabetical order.

- Ex. 1:

- Ex. 2:
Reactions of Organic Halides

1. Nucleophilic Substitution Reactions
   - Reagent is the nucleophile; halide is the “leaving group”
   - Halogens are easily displaced by other groups
   - Nucleophile – may be a neutral molecule or a negative ion
     - Must have an unshared pair of electrons with which to bond to the carbon atoms
   - Leaving group – takes with it the pair of electrons that bonded it to the carbon atom
• Elimination reactions compete with substitution reactions

  - To favor substitution - low concentrations of acid or base & high concentration of nucleophile

  - To favor elimination - high concentrations of acid or base catalyst

  - There are two possible nucleophilic substitution reactions: $S_N^1$ or $S_N^2$
$S_N^1$ mechanism

- A two-step process
  
  - a. Spontaneous departure of the leaving group $(X^-)$ generates a carbocation intermediate
  
  - b. Either side of the newly formed carbocation intermediate is open to nucleophilic attack, producing a **racemic** mixture of products

- Ex.: **works best for tertiary alkyl halides**
\textit{S}_N^2 \text{ mechanism}

- A one step direct displacement process
- Nucleophile attacks the C-X bond & the three remaining bonds on that carbon atom become inverted
- The rate at which this proceeds depends on two things: the concentration of the nucleophile and the concentration of the alkyl halide
- **Works for primary and secondary alkyl halides**
I. Reactions with Oxygen Nucleophiles

• 1. Formation of Alcohols
  – A. Hydrolysis - $S_{N1}$ mechanism
    – Ex.:
  – B. Reaction with Aqueous Hydroxide - $S_{N2}$ mechanism
    – Ex.:
2. Formation of Ethers
   - A. Reaction with Alcohols - $S_N^1$ mechanism
     - Ex.: 
   
   - B. Williamson Synthesis - $S_N^2$ mechanism; reacts with sodium alkoxide
     - Ex.: 

   - Ex.: 
II. Reactions with Sulfur Nucleophiles

• 1. Formation of thiols - $S_N^2$ mechanism
  - Ex.
  - Ex.

• 2. Formation of thioethers - $S_N^2$ mechanism
  - Ex.
  - Ex.
III. Reactions with Nitrogen Nucleophiles

• 1. Formation of Primary Amines - $S_N^2$ mechanism; reagent is $\text{NH}_3$
  • Ex.:  

• Ex.:  

• Ex.:
2. Reaction of Primary & Secondary Amines - $S_N^2$ mechanism

- Primary amines form secondary amines
  - Ex.:

- Secondary amines form tertiary amines
  - Ex.;
IV. Reactions with Carbon Nucleophiles

- $S_N^2$ mechanism
- Reagent is cyanide (CN)
- Ex.: 

- Ex.: 

V. Nucleophilic Aromatic Substitution

• Simple aromatic halides are inert to most nucleophiles - NO REACTION
  - Replacement does occur if a strongly electron-withdrawing group (-NO$_2$, CN) is ortho or para to the halogen
Preparation of Organic Halides

1. Halogenation of Hydrocarbons
   - A. Substitution of Alkanes
   - B. Substitution of Alkenes
   - C. Substitution of Aromatics
     - i. Substitution on the ring
     - ii. Substitution on the side chain
• 2. Substitution of Alcohols

• 3. Hydrohalogenation of Alkenes

• 4. Halogen Exchange – used to make iodides & fluorides from bromides & chlorides