

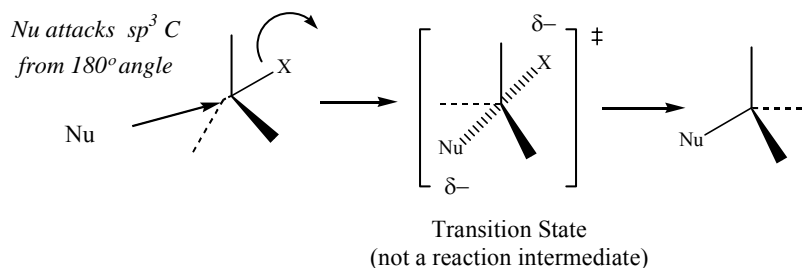
I. PROPERTIES OF ALKYL HALIDES (Section 8.1)

- Alkyl halides contain a halogen bonded to an sp^3 hybridized carbon atom.
- Alkyl halides can be classified as primary, secondary or tertiary depending on the substitution of the carbon atom that bears the halogen.
- The physical properties of alkyl halides differ from their corresponding alkanes (i.e., polarity, solubility, boiling point, etc.).
- Electrophilic nature of alkyl halides

II. NUCLEOPHILIC SUBSTITUTIONS (sp^3 C)

Nucleophilic substitutions occur with molecules that have an sp^3 carbon bonded to a leaving group (-halogen, $-OH_2^+$, -OTs). The reaction occurs when a nucleophile displaces the leaving group. The reaction can occur via two distinct mechanisms.

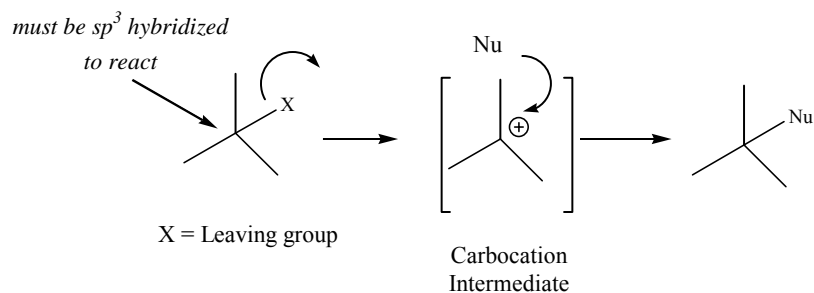
III. SN_2 NUCLEOPHILIC SUBSTITUTION (Section 8.2-8.4)



A. Characteristics of the SN_2 Reaction (Section 8.2-8.4)

- SN_2 substitutions NEVER involve a carbocation intermediate.
 - The rate-determining step of an SN_2 substitution involves bond formation between the attacking Nu and the reacting C atom, and bond cleavage between the leaving group and the reacting C atom.
 - Less substituted alkyl halides react faster than bulky alkyl halides (Rate: $1^\circ > 2^\circ > 3^\circ$)
 - Polar, aprotic solvents enhance the rate of an SN_2 substitution. Protic solvents slow down the rate of SN_2 substitutions.
 - STEREOCHEMISTRY OF SN_2 NUCLEOPHILIC SUBSTITUTIONS
 - Attack of a nucleophile on an alkyl halide in an SN_2 substitution ALWAYS occurs at an angle of 180° to the carbon leaving group bond. This type of nucleophilic attack results in inversion of the configuration (i.e., R inverts to S and S inverts to R) of the reacting carbon atom IF THAT CARBON ATOM IS CHIRAL.
 - Nucleophiles
 - Halides
 - Alkoxides
 - Organometallics
 - Grignard Reagents
 - Alkyl Lithium Reagents
 - Gilman Reagents (Dialkyl lithium Cuprate Reagents)
 - Amines
- B. SN_2 Reactions with Different Functional Groups (Section 8.1; 10.110.3; 10.6-10.8)
- Alkyl Halides
 - Alcohols
 - Ethers

IV. SN₁ NUCLEOPHILIC SUBSTITUTION



- A. Characteristics of the SN₁ Reaction (**Section 8.5-8.7**)
1. SN₁ nucleophilic substitutions always involve a carbocation intermediate.
 2. The rate-determining step of an SN₁ reaction is formation of the carbocation.
 3. The rate at which an SN₁ reaction occurs will be determined by the stability of the carbocation generated in the reaction. More highly substituted alkyl halides react faster than less substituted alkyl halides because their corresponding carbocations are more stable. (Rate: $3^\circ > 2^\circ > 1^\circ$)
 4. Polar solvents enhance the rate of an SN₁ substitution.
 5. STEREOCHEMISTRY OF SN₁ NUCLEOPHILIC SUBSTITUTIONS
 - a. Attack of a nucleophile on a carbocation can occur from the top face or the bottom face
 - b. NO STEREOCHEMICAL BIAS IS OBSERVED when alkyl halides with no chiral centers or when the only chiral center in the molecule is the reacting carbon atom
 - c. STEREOCHEMICAL BIAS IS OBSERVED when an alkyl halide which contains a chiral center that is not the reacting carbon
- B. Benzylic and Allylic Halides in the SN₁ Reaction (Section 8.8)

V. COMPETITION BETWEEN SN₁ AND SN₂ REACTIONS (SECTION 8.9)