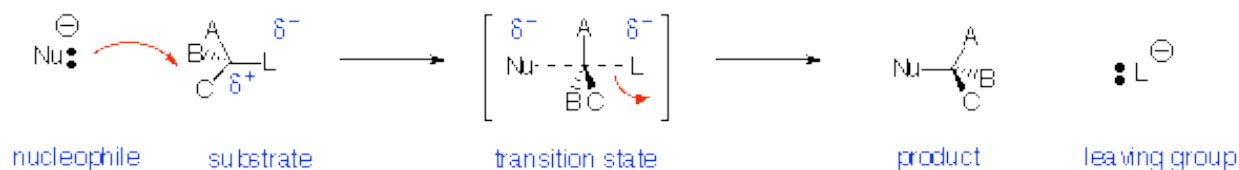


SN2 , SN1 , E2 , & E1: Substitution and Elimination Reactions

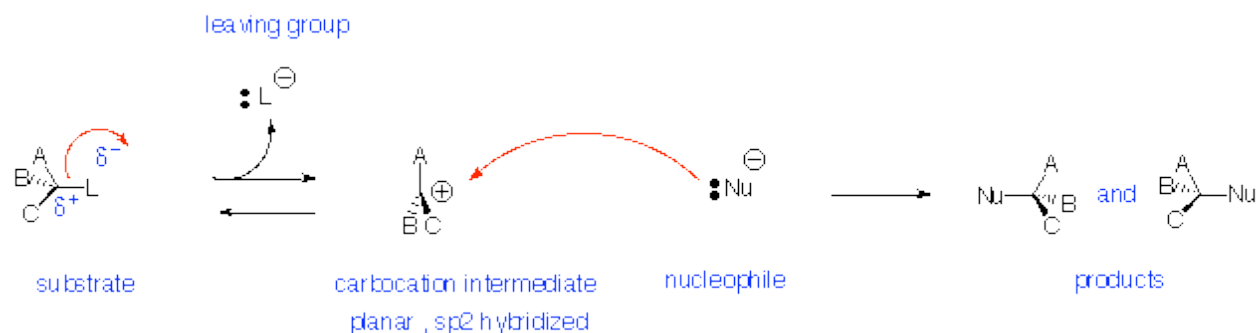
- **Nucleophilic Substitution Reactions (SN2 and SN1) replace a leaving group with a nucleophile (Nu: or Nu: -)**
- **Elimination Reactions (E2 and E1) generate a double bond by loss of " A+ " and " B: - "**
- **They may compete with each other**

Nucleophilic Substitution Reactions - SN2 Reaction:



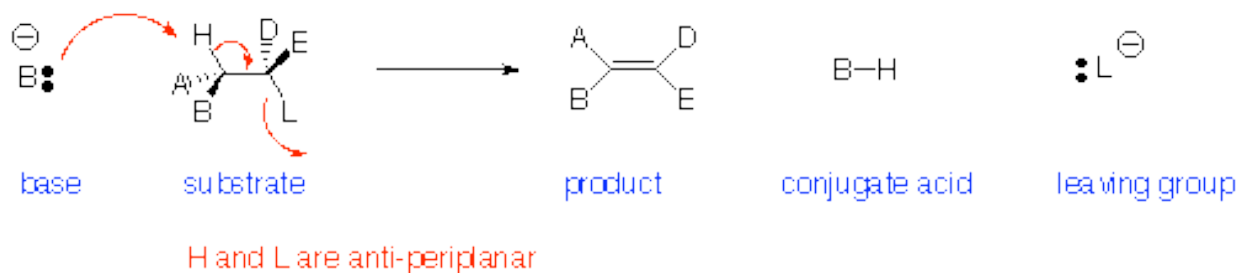
- **Reaction is:**
 - Stereospecific (Walden Inversion of configuration)
 - Concerted - all bonds form and break at same time
 - Bimolecular - rate depends on concentration of both nucleophile and substrate
- **Substrate:**
 - Best if **primary** (one substituent on carbon bearing leaving group)
 - works if secondary, fails if tertiary
- **Nucleophile:**
 - Best if more reactive (i.e. more anionic or more basic)
- **Leaving Group:** Best if more stable (i.e. can support negative charge well):
 - TsO⁻ (very good) > I⁻ > Br⁻ > Cl⁻ > F⁻ (poor)
 - RF , ROH , ROR , RNH₂ are NEVER Substrates for SN2 reactions
 - Leaving Groups on double-bonded carbons are never replaced by SN2 reactions
- **Solvent:** Polar Aprotic (i.e. no OH) is best.
 - For example dimethylsulfoxide (CH₃SOCH₃), dimethylformamide (HCON(CH₃)₂), acetonitrile (CH₃CN).
 - Protic solvents (e.g. H₂O or ROH) deactivate nucleophile by hydrogen bonding but can be used in some case

Nucleophilic Substitution Reactions – SN1 Reaction:



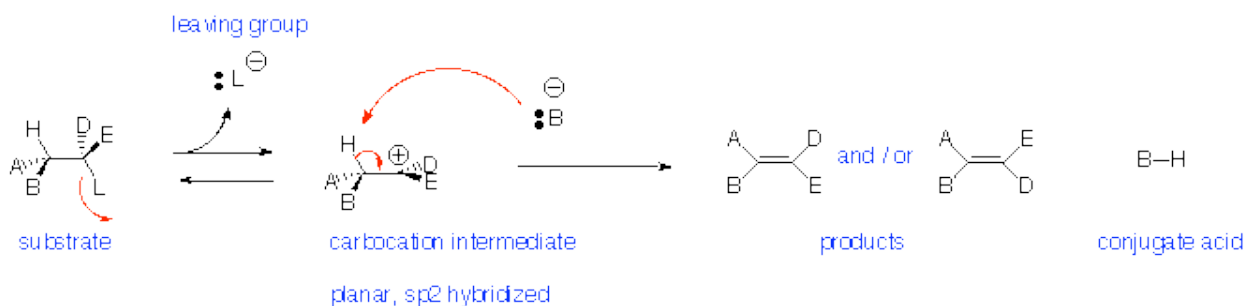
- **Reaction is:**
 - Non-stereospecific (attack by nucleophile occurs from both sides)
 - Non-concerted - has carbocation intermediate
 - Unimolecular - rate depends on concentration of only the substrate
- **Substrate:**
 - Best if tertiary or conjugated (benzylic or allylic) carbocation can be formed as leaving group departs
 - never primary
- **Nucleophile:**
 - Best if more reactive (i.e. more anionic or more basic)
- **Leaving Group:**
 - Same as SN2
 - best if more stable (i.e. can support negative charge well)
 - Examples: TsO^- (very good) $> \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ (poor)
 - However, tertiary or allylic ROH or ROR' can be reactive under strongly acidic conditions to replace OH or OR
- **Solvent:**
 - Same as SN2
 - Polar Aprotic (i.e. no OH) is best
 - Examples: dimethylsulfoxide (CH_3SOCH_3), dimethylformamide ($\text{HCON}(\text{CH}_3)_2$), acetonitrile (CH_3CN).
 - Protic solvents (e.g. H_2O or ROH) deactivate but can be used in some cases

Elimination Reactions - E2 Reaction:



- **Reaction is:**
 - Stereospecific (Anti-periplanar geometry preferred, Syn-periplanar geometry possible)
 - Concerted - all bonds form and break at same time
 - Bimolecular - rate depends on concentration of both base and substrate
 - Favoured by strong bases

Elimination Reactions – E1 Reaction:



- **Reaction is:**
 - Non-stereospecific- follows Zaitsev (Saytseff) Rule
 - Non-concerted - has carbocation intermediate - favoured for tertiary leaving groups
 - Unimolecular - rate depends on concentration of only the substrate
 - Does NOT occur with primary alkyl halides (leaving groups)
 - Strong acid can promote loss of OH as H₂O or OR as HOR if tertiary or conjugated carbocation can be formed