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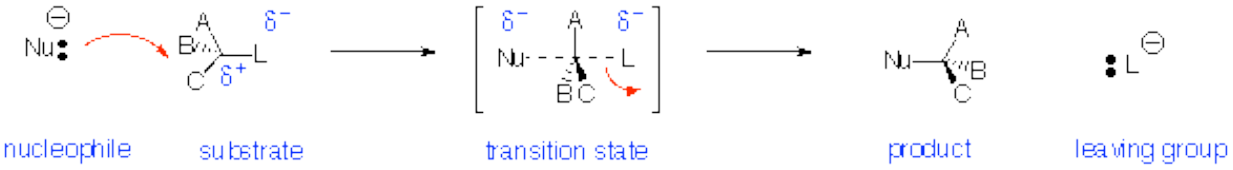
Class : Semester-2
Paper: C4T: Organic Chemistry
Topic : Substitution and Elimination Reaction (Introduction)

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

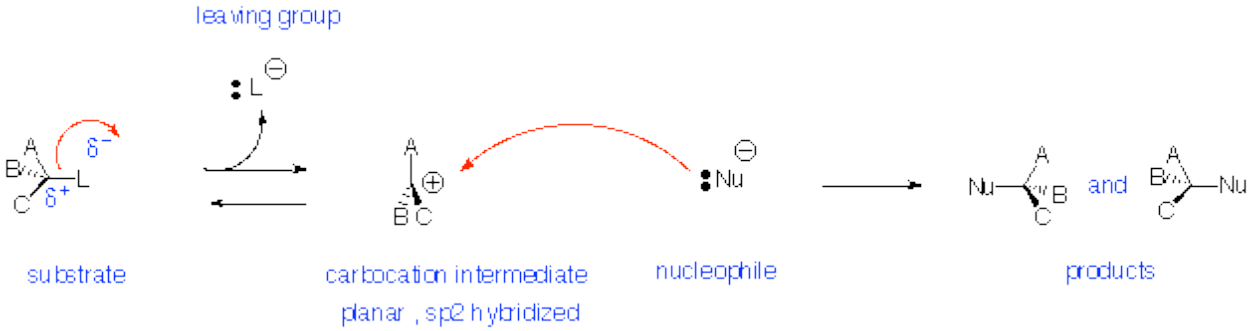
- **Nucleophilic Substitution Reactions (SN2 and SN1) replace a leaving group with a nucleophile (Nu: or Nu: -)**
- **Elimination Reactions (E2 and E1) generate a double bond by loss of " A+ " and " B: - "**
- **They may compete with each other**

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 , RNH_2 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 (CH_3SOCH_3), dimethylformamide ($HCON(CH_3)_2$), acetonitrile (CH_3CN).
  - Protic solvents (e.g. H_2O 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

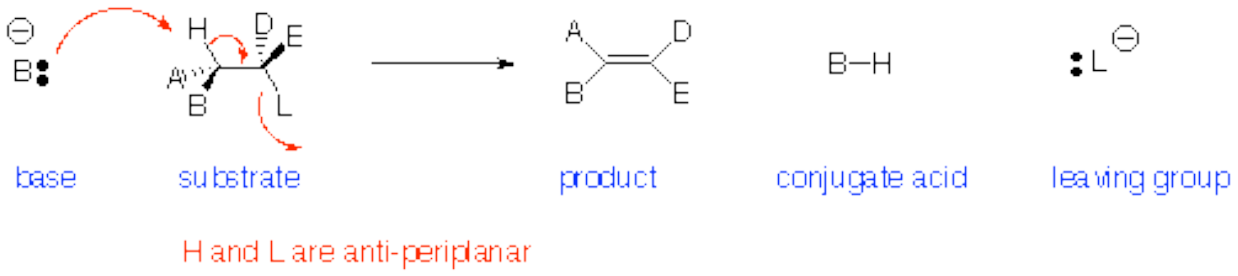
- **Substrate:**
  - Best if tertiary or conjugated (benzylic or allylic) carbocation can be formed as leaving group departs
  - never primary

- **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) > I- > Br- > Cl- > F- (poor)
  - However, tertiary or allylic ROH or ROR' can be reactive under strongly acidic conditions to replace OH or OR

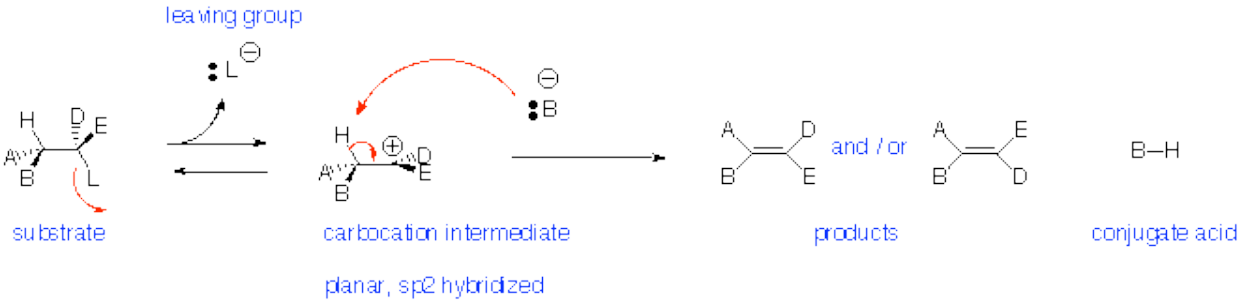
- **Solvent:**
  - Same as SN2
  - Polar Aprotic (i.e. no OH) is best
  - Examples: dimethylsulfoxide (CH_3SOCH_3), dimethylformamide ($HCON(CH_3)_2$), acetonitrile (CH_3CN).
  - Protic solvents (e.g. H_2O or ROH) deactivate but can be used in some cases

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 H_2O or OR as HOR if tertiary or conjugated carbocation can be formed