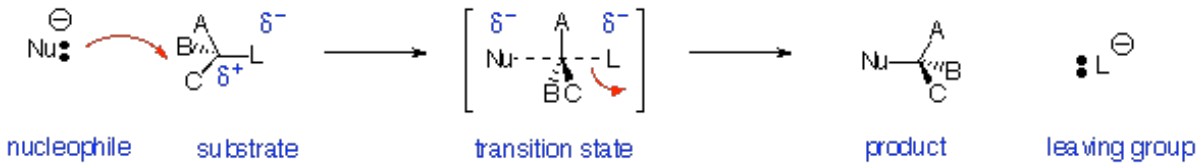
SN2 , SN1 , E2 , & E1:
Substitution and Elimination Reactions

- **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 cases

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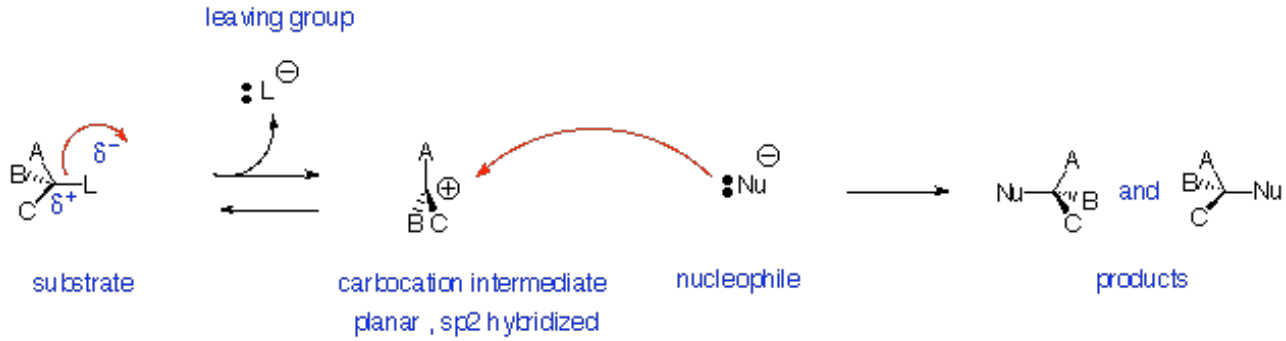
Nucleophilic Substitution Reactions - SN1 Reaction:



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):

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: for example dimethylsulfoxide (CH3SOCH3), dimethylformamide (HCON(CH3)2), acetonitrile (CH3CN). Protic solvents (e.g. H2O or ROH) deactivate but can be used in some cases

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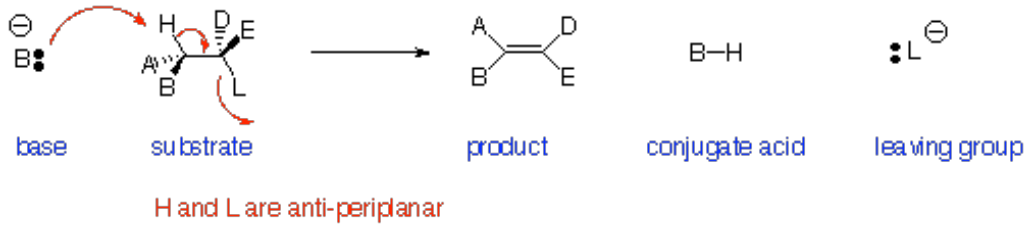
Elimination Reactions - E2 Reaction:



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

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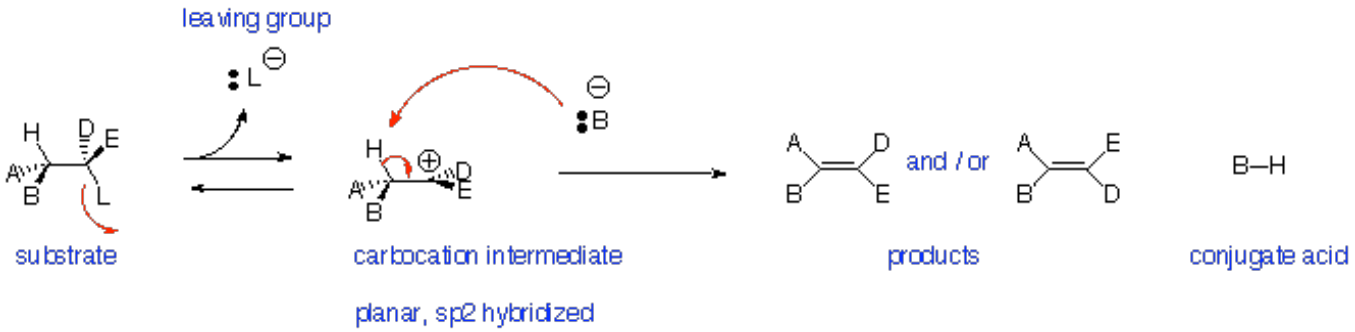
Elimination Reactions - E1 Reaction:



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

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