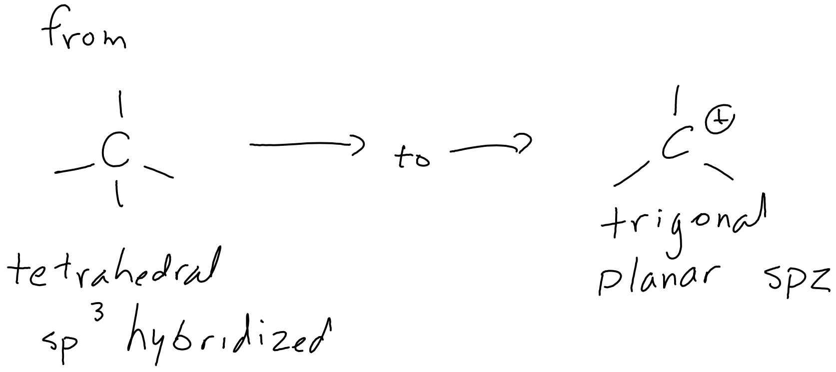
Notes: 4-3

Tuesday, April 03, 2007
5:38 PM

Last Time: Substituion Reactions, SN1, 1st order reaction

① $R-X \rightarrow R^+ + X^-$ rate determining step $r = k[Rx]$

② $R^+ \; Nu \rightarrow R-Nu$ fast



Today:
- Factors affecting the mechanism
- Rearrangments of SN1 mechanisms
- SN2 reactions

- SN1 mechanism (first order)
  - Two step mechanism
  - Unimolecular
    - Rate=k[alkyl halide]
  - Racemization of chirality at carbon
  - Reactivity of alkyl halides: 3° > 2° > 1°
- SN2 mechanism (2nd order)
  - Bimolecular reaction
    - Rate=k[alkyl halide][nucleophile]
  - Inversion of chirality at carbon
  - Reactivity of alkyl halides: 1° > 2° > 3°
- Alkyl Halide (substrate)
  - Steric effects: carbon I sbeing attacked by the nucleophil in an Sn2 mechanism
    - Steric strain experienced by nucleophile increases in the order 1° < 2° << 3°
    - So reactivity is CH3X > 1°> 2°
  - Carbocation: intermediate in the Sn1 mechanism
    - Electron-donation by attached carbons stabilizes carbocation intermediates: 3° > 2° > 1°

- On the board
  - SN1
    - Favored:
      - ☐ Alkyl halide is 3°

- X is good leaving group
- No weak (neutral) because strong Nucelphile will directly attack the C if not sterically hindered (2nd order reaction)
- Solvent is polarprotic (common solvents are ethanol, methanol, acetic acid, and formic acid)

- Things to look at:
  - Alkyl halide/alcohol
  - 3°> 2°, allylic, benzylic
  - Carboctaion rearrangement is possible
  - Leaving group - reaction proceeds fastest when x is a weak base
    - Leaving groups: P-toluensesolfonate (Ots) > I>Br>>Cl>F>OH
- Nucleophile
  - Weak Nu favored SN1
  - Often neutral
- Solvent
  - Polar protic solvents
    - H-bonding capability
      - Commonly alcohols, water, carboxylic acids
  - The solvent stabilizes transition states

- SN1 Rearrangements (SN2 does not do this since it does not have carbocations)
  - Carbocations frequently undergo structural changes call rearrangements to form more stable carbocations
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