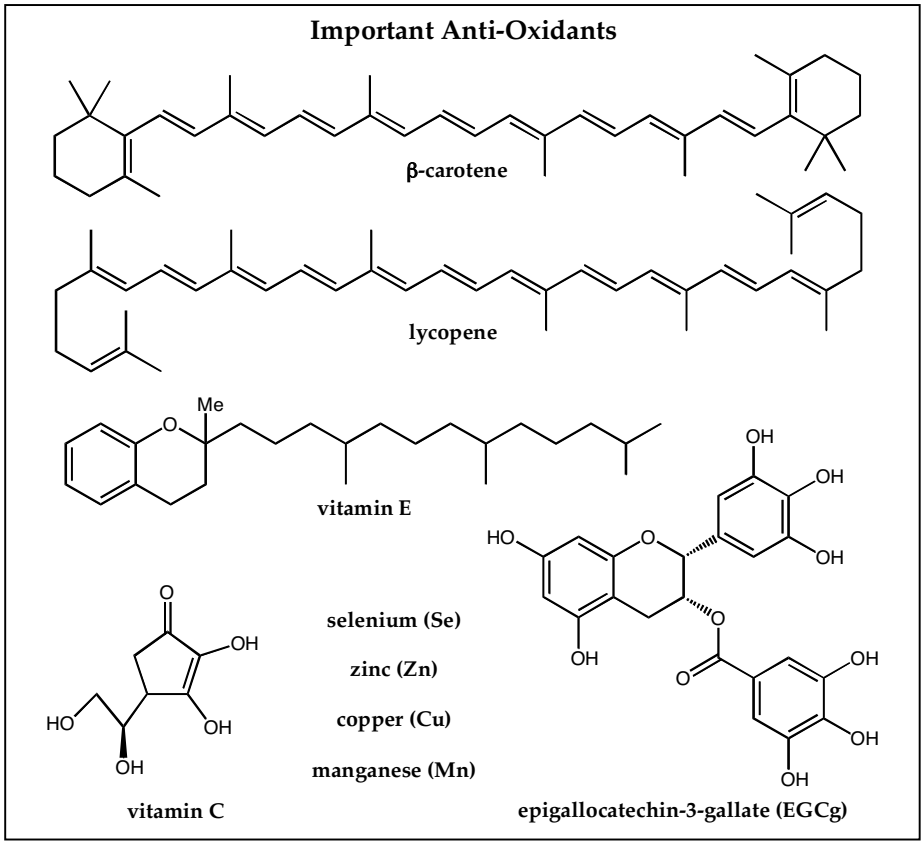
Massachusetts Institute of Technology

5.13: Organic Chemistry II *Fall 2003*

Outline & Study Guide for Unit VIII. Radicals



Free Radicals: Friend or Foe?

Free radicals exist naturally in our bodies and play important roles in many essential biochemical processes; however, research has shown that an excess of free radicals can trigger destructive chain reactions in cells. Free radical oxidation has been linked to premature aging, high blood pressure, arthritis, cancer, and many other ailments. No wonder Americans spend millions of dollars every year on vitamins containing anti-oxidants! It's even hard to buy face cream that doesn't claim to fight free radicals. From the old essentials like β-carotene and vitamin C, to compounds like lycopene and EGCg that are receiving more recent attention, it appears that anti-oxidants are the lucrative weapons of choice in the endless battle against free radicals.

The same highly reactive species that wreak havoc on our bodies have been tamed and harnessed in the chemistry laboratory. Methods have been developed for the selective formation of organic radicals under mild conditions, and a great deal of work has focused on understanding and predicting the reactivity of free radicals once they are formed. Organic radicals have proven to be synthetically useful and mechanistically intriguing. Over the next few lectures, you will gain some insight into the incredible potential of free radical intermediates.

VIII. Radicals

- A. Introduction
  - 1. Structure
  - 2. Stability
- B. Generation of Radicals
  - 1. Thermal Bond Cleavage
    - a) Acyl Peroxides
    - b) Alkyl Peroxides
    - c) Halides
    - d) Azo Compounds (AIBN)
  - 2. Photochemical Bond Cleavage
- C. Termination Reactions
  - 1. Radical-Radical Coupling
  - 2. Disproportionation
- D. Propagation Reactions
  - 1. Abstraction
    - a) Selectivity
    - b) Intramolecular Abstraction
    - c) Halogen Abstraction with Tin Radical
  - 2. Addition to π-Bonds
    - a) Intramolecular Addition Reactions
  - 3. Fragmentation
  - 4. Rearrangement
- E. Chain Reactions
  - 1. Chain Length
  - 2. Solvent Effects
  - 3. Cage Effects