

# CHM 3140 Organic Chemistry I, Cal Poly Pomona, Dr. Laurie S. Starkey

## Chapter 10 (Klein) Summary: Radical Reactions

- 1) Free Radicals & Radical Mechanisms (10.1, 10.2) **SkillBuilder 10.1**
  - a) electron-deficient, reactive intermediates (like carbocations)
  - b) relative stability: benzyl, allyl  $> 3^\circ > 2^\circ > 1^\circ > \text{methyl}$  **SkillBuilder 10.2**
  - c) radical mechanisms use fishhook arrows to move single electrons **SkillBuilder 10.3**
- 2) Free radical halogenation ( $\text{X}_2$ , with  $h\nu$  or  $\Delta$ ) (10.3 – 10.7)
  - a) Mechanism: chain reaction (initiation, propagation, termination) **SkillBuilder 10.4**
  - b) Relative rates of H atom abstraction: benzyl, allyl  $> 3^\circ > 2^\circ > 1^\circ > \text{methyl}$
  - c) Regioselectivity **SkillBuilder 10.5**
    - i) bromination is more selective than chlorination
    - ii) bromination preferentially occurs at allylic or  $3^\circ$  position (more stable radical = faster reaction)
  - d) Stereochemistry **SkillBuilder 10.6**
    - i) loss of chiral center
    - ii) new chiral centers are formed as both R and S (form racemic mixtures)
  - e) Allylic halogenation (10.7) **SkillBuilder 10.7**
    - i) Either resonance form can lead to halogenated product
  - f) Synthetic use: functionalization of alkanes (10.13)
- 3) Radical addition of HBr to alkenes **SkillBuilder 10.8**
  - a) HBr/ROOR gives anti-Markovnikov addition
  - b) Regiochemistry determined by formation of more stable radical intermediate
- 4) Interesting radical reactions (FYI, not on exam)
  - a) Atmospheric chemistry (ozone layer, 10.8)
  - b) Autooxidation (10.9)
  - c) Radical polymerization (10.11) and cracking (10.12)

## Chapter Outline

- 1) Free Radicals & Radical Mechanisms (10.1, 10.2) **SkillBuilders 10.1, 10.2, 10.3**
- 2) Free radical halogenation ( $\text{X}_2$ ,  $h\nu$  or  $\Delta$ ) (10.3 – 10.7) **SkillBuilders 10.4 – 10.7**
- 3) Radical addition of HBr to alkenes **SkillBuilder 10.8**
- 4) Interesting radical reactions (FYI, not on exam) (10.8, 10.9, 10.11, 10.12)