Organic Chemistry II CHM 3150, Dr. Laurie S. Starkey, Cal Poly Pomona
Chapter 20 Summary (Klein), Carboxylic Acids & Their Derivatives

I. Physical Properties (20.3)
- A) water solubility of RCO_2H and RCO_2Na
- B) acidity of RCO_2H (see pK_a Table 3.1)
  - i) look at inductive and/or resonance effects to stabilize the conjugate base

II. Preparation of RCO_2H (20.4)
- A) oxidation of aldehydes and 1˚ alcohols (12.10) and ozonolysis of alkynes (9.9)
  - i) $Na_2Cr_2O_7$, H_2SO_4 (chromic acid, Jones)
  - ii) $KMnO_4$, NaOH, H_2O (permanganate)
  - iii) Ag_2O, NaOH, H_2O (Tollens test for aldehydes)
- B) organometallic reagents + CO_2
- C) hydrolysis of carboxylic acid derivatives, RCN or RCO*LG*
  - i) *Addition* of H_2O/*Elimination* of LG = *acyl substitution*
  - ii) acid- and base-catalyzed mechanisms (**SkillBuilder 20.1**)
  - iii) saponification reaction: lipids, fats, oils and soaps
  - iv) nitrile hydrolysis (20.13) and its use in synthesis (19.10)

III. Preparation of Carboxylic Acid Derivatives
- A) features of the leaving group, LG (20.7)
  - i) electrophilicity trends and leaving group ability: compare derivatives!
- B) acid halides (20.8)
- C) anhydrides (20.9)
- D) esters (20.10)
- E) amides (20.12)

IV. Reactions of Carboxylic Acids and Derivatives with Nucleophiles (20.11, 20.12)
- A) reduction reactions of carboxylic acids and derivatives (12.4)
  - i) adds 2 equiv. of $LiAlH_4$ (LAH) to give an alcohol (N.R. with $NaBH_4$)
  - ii) mechanism (Mechanism 12.3, **SkillBuilder 12.4**)
    - a) addition of LAH ("H:$^-$" nu:) to C=O carbon (E^+)
    - b) collapse of CTI to eliminate LG
    - c) addition of 2nd equiv. of LAH
    - d) protonation of O^- by H_3O^+ workup to give alcohol product
  - iii) exception: LAH reduction of amides and nitriles give <u>amine</u> products
- B) organometallic reagents (12.6, Mechanism 12.5)
  - i) adds 2 equiv. of RMgX or RLi to give an <u>alcohol</u> product
  - ii) mechanism: same as above but carbon nu: ("R:$^-$") instead of hydride, "H:$^-$"
- C) FYI: special reagents (cuprates, modified LAH)

V. Synthesis (20.14, **SkillBuilder 20.2, SkillBuilder 20.3**)

VI. Nomenclature (20.1, 20.2)
- A) alkanoic acid (RCO_2H)
- B) alkanoyl halide (RCOX)
- C) alkanoic anhydride (RCO_2COR)
- D) alkyl' alkanoate (RCO_2R')
- E) alkanamide ($RCONH_2$), *N*-alkyl'alkanamide (RCONHR')
- F) alkanenitrile (RCN)