Organic Chemistry II CHM 3150, Dr. Laurie S. Starkey, Cal Poly Pomona

Chapter 19 Summary (Klein): Aldehydes & Ketones

I. Introduction to the reactivity of the carbonyl (19.1)
   a) C=O carbon is electrophilic (δ^+) and reacts with nucleophiles
   b) C=O oxygen is δ^- and can be protonated
   c) α-hydrogens are acidic (covered in Chapter 21)

II. Nomenclature (19.1, 19.2): alkan**al** or #-alkan**one** (C=O is highest priority F.G.) ***SkillBuilder 19.1***

III. Preparation of ketones & aldehydes: a review (19.3)
   a) oxidation of alcohols (12.10)
   b) ozonolysis of alkenes (8.12)
   c) hydration of alkynes (9.7)

IV. Reactions with nucleophiles; all add to δ^+ carbonyl carbon (19.4)
   a) Hydride Nu: (12.4, 19.9)
      i) $LiAlH_4$ or $NaBH_4$ as sources of hydride, "$H:^-$"
      ii) a reduction reaction that gives an alcohol product
   b) Carbon Nu: makes C–C bonds!! (19.10)
      i) NaC≡N and NaC≡CH carbanions give alcohol products
      ii) organometallic reagents (12.6)
         A) Grignard (RMgX) and organolithium (RLi) reagents
         B) use in synthesis, consider retrosynthesis of alcohols ***SkillBuilders 12.5 & 13.7***
      iii) Wittig reaction
         A) Wittig reagent prepared from alkyl halide (Ph_3P, then base)
         B) Wittig reagent reacts with carbonyl to give C=C double bond
      i) use in synthesis, consider retrosynthesis of alkenes ***SkillBuilder 19.6***
   c) Oxygen Nu: (19.5)
      i) addition of H_2O gives hydrate (only formaldehyde, compounds like chloral)
      ii) addition of ROH gives acetal (TsOH is acid catalyst) ***SkillBuilder 19.2***
         A) mechanism for acetal formation (via tetrahedral intermediates)
         B) mechanism for acetal hydrolysis (reverse of formation) (19.7) ***SkillBuilder 19.5***
   d) Nitrogen Nu: (19.6)
      i) addition of 1˚ amines (RNH_2) give imines (mechanism) ***SkillBuilder 19.3***
      ii) addition of 2˚ amines (R_2NH) give enamines (mechanism) ***SkillBuilder 19.4***
      iii) enamines & imines can also be hydrolyzed (H_3O^+) to regenerate C=O (19.7)

V. Oxidations of aldehydes to carboxylic acids
   a) $RCHO \rightarrow RCO_2H$ (ox. agent: metals, $Na_2Cr_2O_7$ or $KMnO_4$) (ketones N/R)

VI. Reductions of aldehydes and ketones (19.8, 19.9)
   a) to alcohol with LAH or Raney Nickel (Ni-H_2)
   b) to alkane
      i) Clemmenson (Zn-Hg, HCl, H_2O)
      ii) Wolff-Kishner (N_2H_4 to make imine, followed by NaOH/heat)
      iii) via thioacetal ($HSCH_2CH_2SH$, followed by Raney Ni) (19.9)

VII. Applications of acetals
   a) Carbohydrates as examples of cyclic hemiacetals (24.5)
   b) Protective Groups in organic synthesis to hide carbonyls and alcohols (12.7, 19.5)
      i) Synthesis strategies (19.12) ***SkillBuilder 19.7***

SKIP section 19.11 (Baeyer-Villiger Oxidation)
READ on your own section 19.13 (IR/NMR Spectroscopy)