

Chapter 19 Lecture Outline

"Aldehydes and Ketones. Nucleophilic Addition to the Carbonyl"

(problems: **25-27**, 28, 30-31, **32-33**, 34, 36, 38, **39-40**, 41-42, 44-45, 49, **51**, 52, 57-59, 61-62, **63, 67**)

I. General Properties & Nomenclature

II. Preparation of Aldehydes

- A. Oxidation of 1° Alcohols by PCC in CH₂Cl₂
- B. Ozonolysis of Alkenes
- C. Controlled Reduction (by DIBAL-H) of Esters

III. Preparation of Ketones

- A. Oxidation of 2° Alcohols by Cr(VI) Reagents
- B. Ozonolysis of Alkenes
- C. Friedel-Crafts Acylation of Arenes
- D. Hydration of Alkynes
- E. Cuprates reaction with Acid Chlorides

IV. Reactions of Aldehydes and Ketones

- A. Oxidation of Aldehydes to Carboxylic Acids (via Aldehyde Hydrate)
- B. Nucleophilic Addition Reactions - Some General Comments
- C. Nucleophilic Addition Reactions
 1. Hydration (addition of H₂O)
 - a. acid catalysis
 - b. base catalysis
 2. Cynaohydrin Formation (addition of HCN)
 3. Alcohol Formation (addition of hydride or Grignard reagents)
 4. Imine Formation (addition of R-NH₂)
 - a. Oxime Formation
 - b. Semicarbazone Formation
 - c. 2,4-Dinitrophenylhydrazone Formation
 5. Wolff-Kishner Reduction (addition of H₂NNH₂ under basic conditions)
 6. Clemmensen Reduction (reduction under acidic conditions)
 7. Enamine Formation (addition of R₂NH)
 8. Acetal Formation (addition of ROH)
 9. Wittig Reaction (addition of phosphonium ylides)

V. Nucleophilic Addition to α,β -Unsaturated Aldehydes and Ketones

- A. Conjugate addition of 1° and 2° amines
- B. Conjugate addition of "R-" as organocuprates (R₂CuLi)

VI. Spectroscopy of Aldehydes and Ketones

- A. IR
- B. NMR (¹H and ¹³C)
- C. MS
 1. McLafferty Rearrangement of aldehyde and ketone radical cations
 2. α -cleavage of aldehyde and ketone radical cations