

Summary of CH17 Aldehydes and Ketones

I. Nomenclature

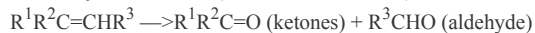
- Common names
- IUPAC name

II. Synthesis of aldehydes and ketones

- Oxidation of alcohols (review section 8.6)

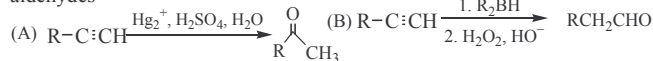


- Ozonolysis of alkenes (review section 12.11)

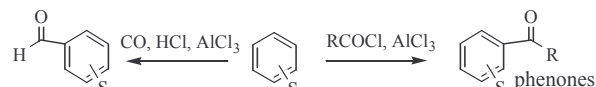


- Hydration of alkynes (review section 13.8 & 13.9)

(A) Markovnikov hydration to ketones, (B) anti-Markovnikov hydration to aldehydes



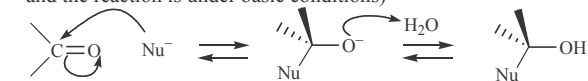
- Friedel-Crafts acylation (review section 15.14)



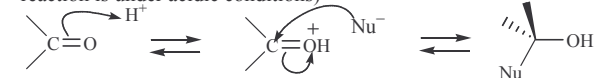
benzaldehydes

III. General mechanisms for nucleophilic addition to C=O

- Nucleophilic addition-protonation (if Nu is a strong nucleophile and the reaction is under basic conditions)



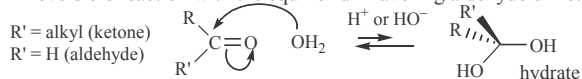
- Electrophilic protonation-addition (if Nu is a weak nucleophile and the reaction is under acidic conditions)



IV. Addition of H-OH to form hydrates

- Acid or base catalysis

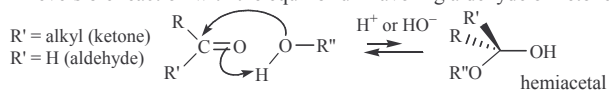
- Reversible reaction with the equilibrium favoring aldehyde or ketone



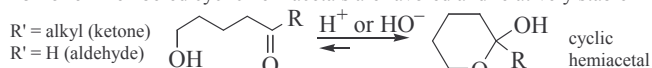
V. Addition of H-OR to form acetals

- Acid or base catalysis

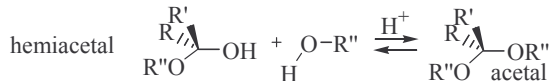
- Reversible reaction with the equilibrium favoring aldehyde or ketone



- 5- or 6- membered cyclic hemiacetals are favored and relatively stable



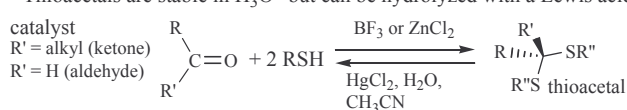
- Hemiacetals are further converted into acetals under acidic conditions



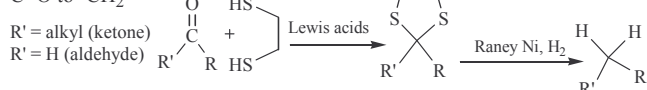
VI. Addition of H-SR to form thioacetals

- Thioacetal formation requires a Lewis acid catalyst such as BF₃ or ZnCl₂

- Thioacetals are stable in H₃O⁺ but can be hydrolyzed with a Lewis acid as catalyst

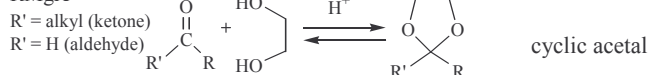


- Thioacetal formation - hydrogenolysis provides a method to reduce C=O to -CH₂-

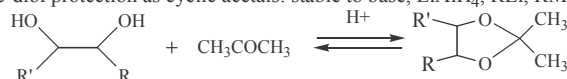


VII. Acetals and thioacetals as protecting groups in synthesis

- ketone/aldehyde protection as cyclic acetal: stable to base, LiAlH₄, RLi, RMgX



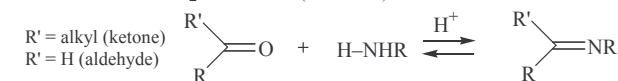
- Ketone/aldehyde protection as cyclic thioacetal (see VI above): stable to base and H₃O⁺, LiAlH₄, RLi, RMgX, etc. (complementary to cyclic acetals)
- vic-diol protection as cyclic acetals: stable to base, LiAlH₄, RLi, RMgX, etc.



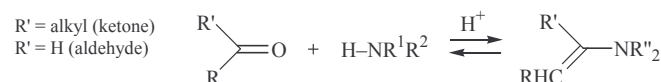
VIII. Addition of H-NH₂ and its derivatives to form imines, enamines, oximes, hydrazones, semicarbazones

- All additions are under acid catalysis.

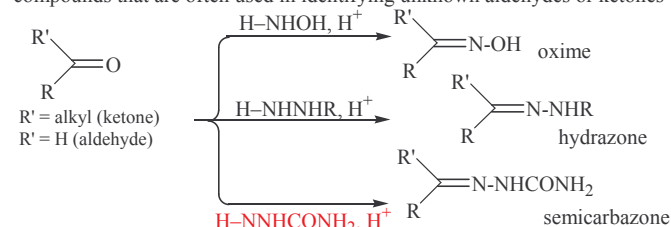
- Addition of H-HN₂ or H-NHR (1° amine) to C=O forms imine



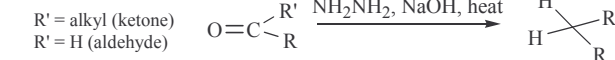
- Addition of H-NR¹R² (2° amine) to C=O containing α-H forms enamine



- Additions of H-NHOH, H-NHNHR, or H-NHNH₂CONH₂ form crystalline compounds that are often used in identifying unknown aldehydes or ketones



- Wolff-Kishner reduction: to reduce C=O to -CH₂- under strong basic conditions

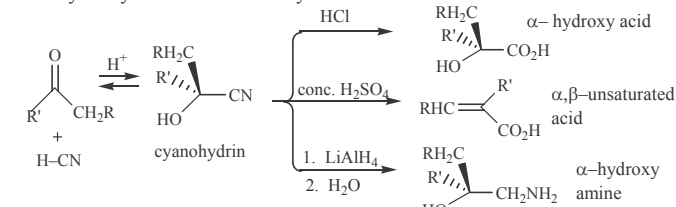


- Compare the C=O to -CH₂-reduction by Wolff-Kishner reduction, Clemmensen reduction, or thioacetal-hydrogenolysis reactions and their respective limitations.

IX. Addition of H-CN to form cyanohydrins

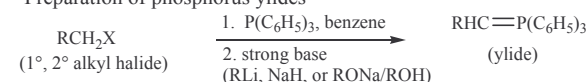
- Acid-catalyzed addition

- Cyanohydrins are versatile synthetic intermediates

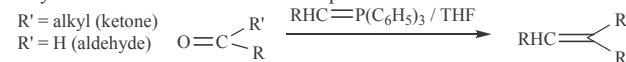


X. Addition of phosphorus ylides: The Wittig reaction

- Preparation of phosphorus ylides

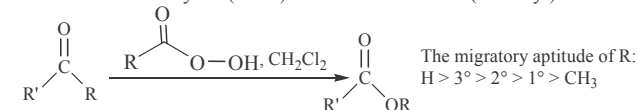


- Synthesis of alkene from C=O compounds



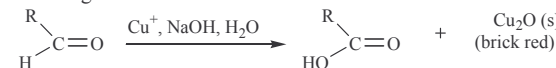
XI. Addition of H-OOCOR: The Baeyer-Villiger oxidation

- Conversion of aldehydes (R'=H) to acids and ketones (R'=alkyl) to esters



XII. Oxidative chemical tests for aldehydes

- Fehling's test



- Tollen's test

