5.S: ALDEHYDES AND KETONES (SUMMARY)

CONCEPTS & VOCABULARY

19.0 Chapter Objectives and Preview of Carbonyl Chemistry

- Aldehydes are carbonyl compounds with an R group and a hydrogen attached to the carbonyl carbon.
- Ketones are carbonyl compounds with two R groups attached to the carbonyl carbon.

19.1 Naming Aldehydes and Ketones

- Aldehydes are named following IUPAC rules with the standard ending -al.
- Ketones are named following IUPAC rules with the standard ending -one.
- Aldehydes have priority over ketones when both appear in the same molecule.

19.2 Preparing Aldehydes and Ketones

- Primary alcohols can be oxidized to aldehydes with PCC (pyridinium chlorochromate) or DMP (Dess-Martin Periodinane).
- Terminal alkynes can be hydrated to form aldehydes through hydroboration-oxidation reactions.
- Esters can be reduced to aldehydes with DIBAL-H.
- Acid chlorides can be reduced to aldehydes with hydrides.
- Nitriles can be reduced to aldehydes with DIBAL-H.
- Secondary alcohols can be oxidized to ketones with chromic acid/Jones reagent.
- Alkynes can be hydrated to form ketones.
- Aryl ketones can be formed by Friedel-Crafts acylation of aromatic rings.
- Nitriles can be reacted with Grignard reagents to form ketones.
- Alkenes can be cleaved with ozone to form aldehydes or ketones.
- Acid halides can be converted to ketones by reacting with Gilman reagents.

19.3 Oxidation of Aldehydes and Ketones

- Aldehydes can be oxidized more easily than ketones due to the aldehyde hydrogen.
- Jones reagent is a mixture of CrO_3 and aqueous acid.
- Aldehydes can be oxidized to carboxylic acids with chromium trioxide/Jones reagent.
- Ketones can undergo oxidative cleavage with very strong oxidizing agents such as potassium permanganate.
- Ketones can be oxidized to esters by peroxycarboxylic acids in a reaction known as Baeyer-Villiger oxidation.

19.4 Nucleophilic Addition Reactions of Aldehydes and Ketones

- Carbonyl bonds are polarized with a partial positive charge on the carbon making it an electrophile and a target for attack by nucleophiles.
- Neither aldehydes nor ketones have a good leaving group causing both to undergo nucleophilic addition reactions.
- Aldehydes are more reactive than ketones to nucleophilic addition reactions.

19.5 Nucleophilic Addition Reactions of Water: Hydration

- Gem-diols are molecules that have two hydroxide groups attached to the same carbon.
- Aldehydes and ketones can react with water under either acidic or basic conditions to form gem-diols.

19.6 Nucleophilic Addition Reactions of HCN: Cyanohydrin Formation

- Cyanohydrins are molecules with a cyanide and a hydroxide attached to the same carbon.
- Cyanohydrins can be formed from aldehydes or ketones by reacting with cyanide ion and a weak acid.

19.7 Nucleophilic Addition Reactions of Hydride and Grignard Reagents: Alcohol Formation

- Metal hydrides can reduce aldehydes and ketones to alcohols.
- Organometallic reagents include carbon bonds to metals which react similarly to carbanions.
- Grignard reagents (R-Mg-X) and organolithium compounds add to aldehydes and ketones to form alcohols.

19.8 Nucleophilic Addition of Amines: Imine and Enamine

- Imines are characterized by a carbon-nitrogen double bond.
- Reaction of aldehydes and ketones with primary amines can form imines.
- Reaction of aldehydes and ketones with secondary amines can form enamines.

19.9 Nucleophilic Addition of Hydrazine - The Wolff-Kishner Reaction

- Hydrazine will react with aldehydes and ketones to form hydrazones (similar to imine formation). Heating of the hydrazone with base converts it to an alkane.
- The combination of hydrazone formation and reduction (of aldehydes and ketones) is called the Wolff-Kishner reaction.

19.10 Nucleophilic Addition of Alcohols: Acetal Formation

- Hemiacetals have one hydroxide and one ether attached to a carbon.
- Acetals have two ethers attached to a carbon.
- Reaction of an aldehyde or ketone with an alcohol under acidic conditions forms a hemi-acetal. Continuation of the same reaction results in an acetal.
- Acetals can reform the aldehyde or ketone by reacting with acid.
- Acetals are useful as protecting groups due to the reversible nature of acetal formation.

19.11 Nucleophilic Addition of Phosphorun Ylides: The Wittig Reaction

- A molecule with positive and negative charges on adjacent atoms is called an ylide.
- Wittig reagents are organophosphorus ylides which can be drawn as a double bonded structure called a phosphorane.
- The Wittig reaction is used to convert an aldehyde or ketone into an alkene by reacting with an organophosphrous ylide.
- Oxaphosphetane intermediates containing a 4 membered ring including one oxygen and one phosphorus atom occur during the Wittig reaction.

19.12 Biological Reductions

- The Cannizzaro reaction allows an aldehyde to react with another like molecule in strong base to form one oxidized molecule (carboxylic acid) and one reduced molecule (alcohol).
- NADH, one of the most important biological reducing agents, uses a similar mechanism to the Cannizzaro reaction while reducing ketones in biological systems to alcohols while being converted to NAD^+.

19.13 Conjugate Nucleophilic Addition of alpha, beta-Unsaturated Aldehydes and Ketones

- α, β-unsaturated carbonyls have an alkene attached to the carbonyl carbon.
- Due to resonance delocalization, the β-carbon of an α, β-unsaturated carbonyl is electrophilic and will react with nucleophiles.
- α, β-unsaturated carbonyls can undergo 1,2 or 1,4 addition.
- 1,4 addition is also called conjugate addition.
- Lithium diorganocopper reagents are called Gilman reagents.
- Gilman reagents typically react with α, β-unsaturated carbonyls via conjugate addition.

19.14 Spectroscopy of Aldehydes and Ketones

- IR of aldehydes and ketones is defined strongly by the carbonyl stretching vibration.
- ^1H NMR of aldehydes show the aldehyde proton between 10 and 11 ppm as well as the protons on carbon adjacent to the carbonyl at about 2.5 ppm.
- ^1H NMR of ketones show the protons on carbon adjacent to the carbonyl at about 2.5 ppm.
- ^{13}C NMR of aldehydes and ketones show the carbonyl carbon at about 200 ppm.
- Mass spectra of aldehydes and ketones typically yield moderately intense molecular ions, M^+. They also can undergo some rearrangements that yield common fragmentation patterns.

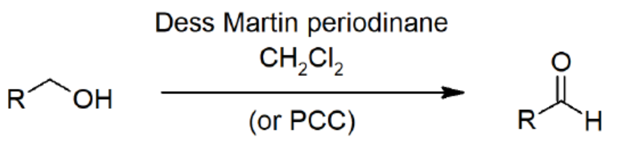
SKILLS TO MASTER

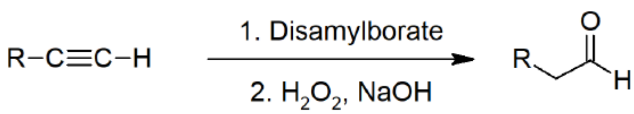
- Skill 19.1 Explain the relative reactivity of aldehydes vs. ketones to nucleophiles, based on carbonyl bond polarity.
- Skill 19.2 Name aldehydes and ketones using IUPAC rules.
- Skill 19.3 Draw the structure of an aldehyde or ketone from the IUPAC name.
- Skill 19.4 Interpret common names of aldehydes and ketones.
- Skill 19.5 Describe methods for preparing aldehydes and ketones.
- Skill 19.6 Draw mechanisms for oxidations of aldehydes and ketones.
- Skill 19.7 Explain general reactivity of aldehydes and ketones through the nucleophilic addition mechanism.
- Skill 19.8 Draw mechanisms for nucleophilic addition reactions to aldehydes and ketones including
  - Hydration
  - Cyanohydrin formation
  - Hydride Reduction
  - Organometallic reactions
  - Addition of amines
  - Wolff-Kishner reaction
  - Acetal formation

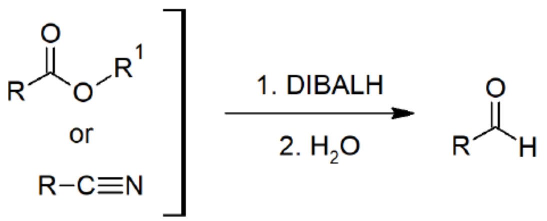
- Wittig reaction
- Cannizzaro reaction
- Conjugate addition
- Skill 19.9 Use IR, NMR and MS to identify aldehydes and ketones.

SUMMARY OF REACTIONS

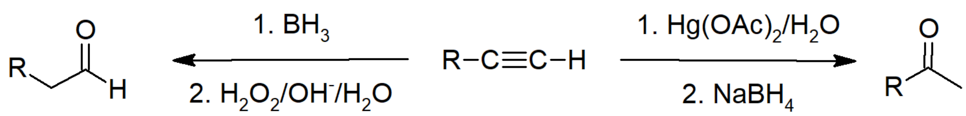
Aldehyde Preparation

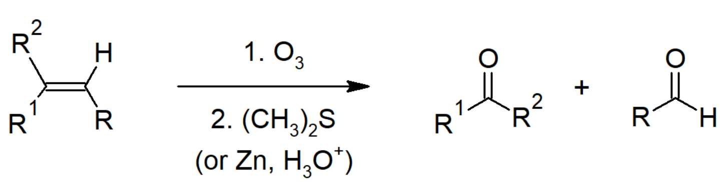




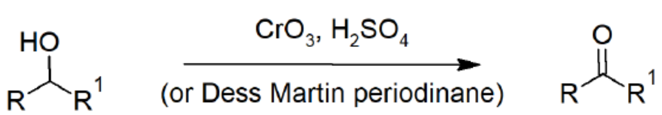


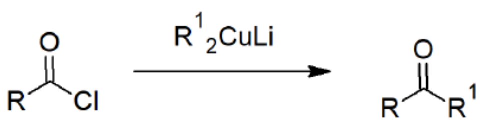
Aldehyde and Ketone Preparation

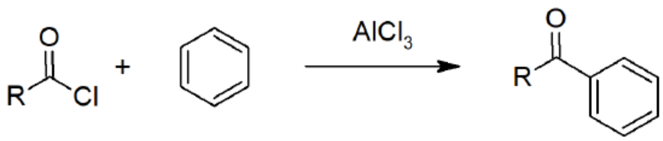


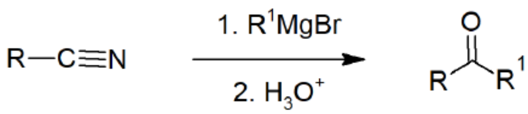


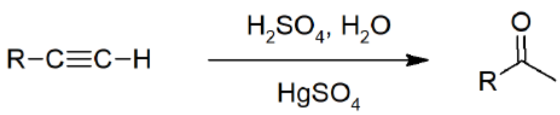
Ketone Preparation



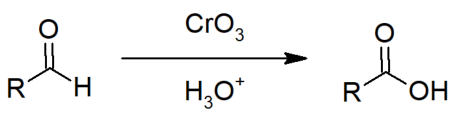


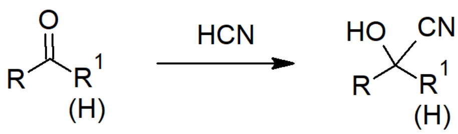


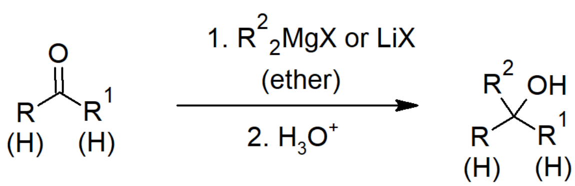


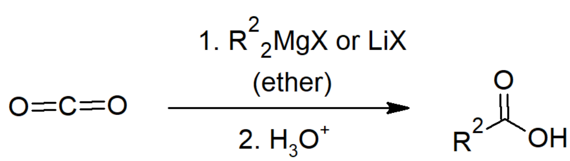


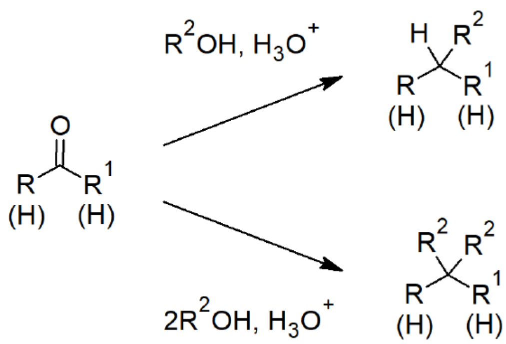
Aldehyde and Ketone Reactions

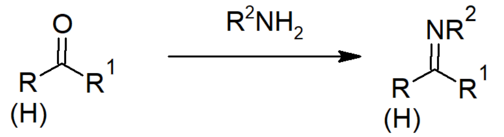


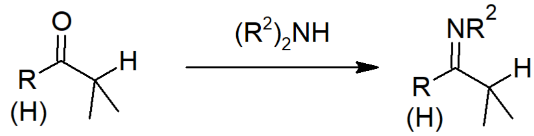


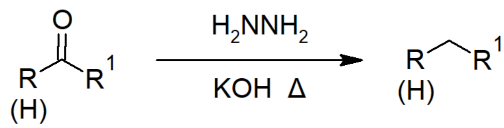




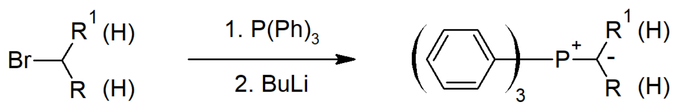








(Wolff-Kishner)



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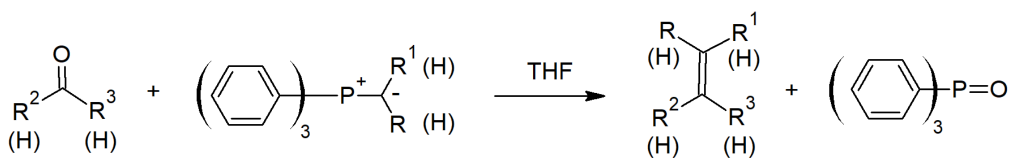

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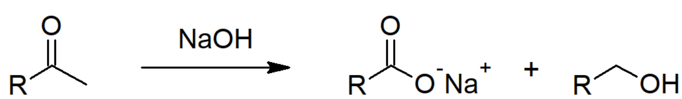
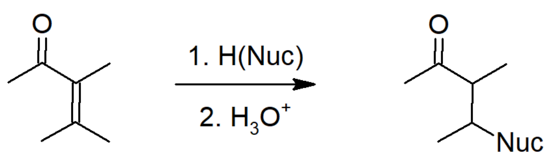


(Cannizzaro)

Conjugated Addition Reactions



where Nuc = OH, OR, SR, NH_2, NHR, Br, CN