

Chapter 16

Aldehydes and Ketones

Chapter 16 suggested problems: 24, 26, 28, 30, 38, 40, 42, 46, 50, 56, 58, 62, 64, 66

Class Notes

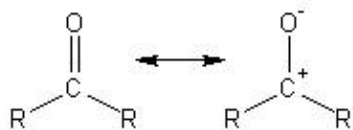
I. Carbonyl compounds: variation stems from those groups attached to the carbonyl carbon

- A. Aldehydes
- B. Ketones
- C. Carboxylic acids
- D. Acyl (acid) halides
- E. Acid anhydrides
- F. Esters
- G. Amides

II. The carbonyl group and its chemistry

A. Properties of the carbonyl group

1. Hybridization - both the C and O are sp^2 hybridized
2. Trigonal planar geometry - flat, 120° bond angles
3. The reactivity of the carbonyl group
 - a. The C=O is quite a polar bond (e.g., 1-butene with a dipole moment of 0.3 D as compared to propanal with a dipole moment of 2.5 D)
 - b. Resonance and the carbonyl group



- c. The cloud of pi electrons can provide an electron source for electrophiles
- d. The characteristic reactions of aldehydes and ketones are nucleophilic additions, the addition of electrophiles to the carbonyl group

4. Aldehydes and ketones can form polar bonds with water, alcohols, and other polar solvents
5. Cannot form hydrogen bonds alone but can accept hydrogen bonds from water, alcohols, carboxylic acids, and other hydrogen bond donors

B. Physical properties of aldehydes and ketones

1. BP higher than alkanes, alkenes, alkynes and ethers but lower than alcohols
2. More soluble than alkanes, alkenes, alkynes, but less soluble than alcohols
3. Solubility decreases as the number of carbon atoms increases, as per alcohols

III. Sources of aldehydes and ketones

- A. Common and naturally occurring in many products, e.g., sugars and carbohydrates
- B. Oxidation of 1° and 2° alcohols
- C. Ozonolysis of alkenes
- D. Reduction of organic acids to 1° alcohols and oxidation to aldehydes (difficult in actual practice)

IV. Naming aldehydes and ketones

A. Aldehydes

1. Longest continuous chain that contains the CHO group
2. Substitute "al" for "e" for alkane name
3. Aldehydes are always terminal groups
4. Substitute "dial" if the molecule contains two aldehyde functionalities
5. When a formyl group is attached to a ring (-CH=O) the ring name is followed by the suffix "carbaldehyde"
6. Acceptable common names of aldehydes (IUPAC - common name)
 - a. Methanal - formaldehyde
 - b. Ethanal - acetaldehyde
 - c. Propanal - propionaldehyde
 - d. Butanal - butyraldehyde
 - e. Benzaldehyde - benzaldehyde

B. Ketones

1. Longest continuous chain that contains the carbonyl group
2. Substitute "one" for "e" for alkane name
3. Number the chain such that the carbonyl carbon is numbered as low as possible

4. Substitute "dione" if the molecule contains two ketone functionalities
5. Functional class nomenclature is also acceptable; groups are named alphabetically
6. Acceptable common names of ketones (IUPAC - common name)
 - a. 2-propanone - acetone
 - b. 2-butanone - ethyl methyl ketone (commonly MEK or methyl ethyl ketone)

V. Reactions of aldehydes and ketones

A. Oxidation of aldehydes and ketones

1. Combustion of aldehydes and ketones
2. Selective oxidation and colorimetric determination of aldehydes and ketones
 - a. With permanganates and dichromates, aldehydes are oxidized to carboxylic acids while ketones are not further reduced
 - i. Ketones lack the hydrogen on the carbonyl carbon that is essential for further oxidation
 - ii. Permanganates and dichromates cannot differentiate between aldehydes and 1° and 2° alcohols
 - b. Tollen's reagent: specific for aldehydic carbonyl groups, reduction of colorless solution of silver diamine complex ion results in formation of metallic silver - "silver mirror" test
 - c. Benedict's reagent: determination of alpha-hydroxy aldehydes and ketones from simple aldehydes and ketones through reduction of blue Cu^{2+} solution to red Cu^+ solution
 - i. alpha-hydroxy aldehydes and ketones
 - ii. Important in the determination of hexoses

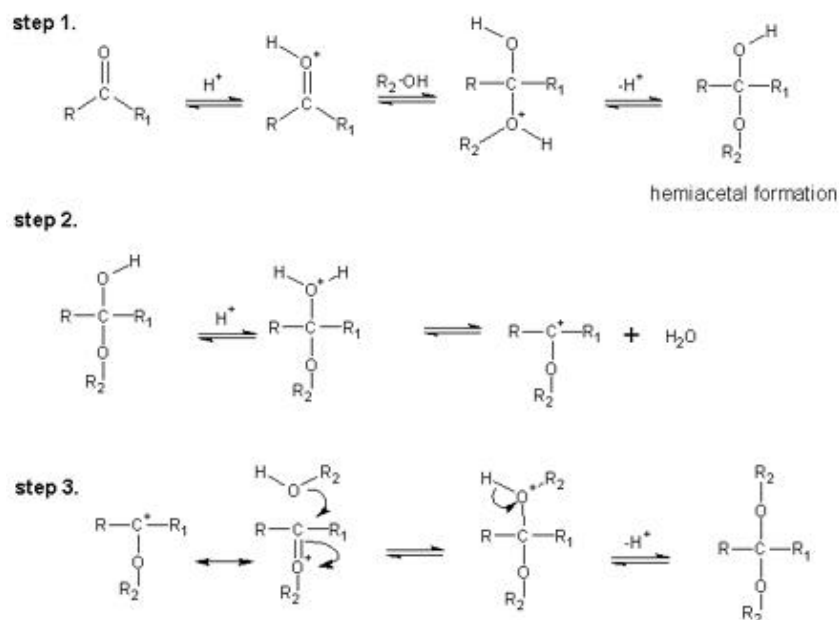
B. Reduction of aldehydes and ketones

1. Reduction to alcohols: the net effect is the addition of a hydrogen atom to the carbonyl carbon and the conversion of the carbonyl oxygen to a hydroxyl group
2. Catalytic hydrogenation: addition of molecular hydrogen (in the presence of Ni/Pt) to both the carbonyl carbon and also to the carbonyl oxygen by breaking pi bond and forming OH
 - a. Aldehydes reduced to primary alcohols, ketones reduced to secondary alcohols
3. Hydride reduction: methods include the use of LiAlH_4 and NaBH_4 , have replaced catalytic hydrogenation as relevant lab-scale preparations
 - a. Since LiAlH_4 reacts violently with water it is a two-step preparation
 - i. First with LiAlH_4 in an anhydrous solvent like diethyl ether

- ii. The product of step 1. must be hydrolyzed in water to form the alcohol
- b. Aldehydes form primary alcohols and ketones form secondary alcohols
- c. Hydride reductions are essential in biological systems and are performed by enzymes

C. Hemiacetal and acetal formation by reaction with alcohol

1. Acetals are geminal diethers prepared by nucleophilic substitution at the carbonyl group of aldehydes and ketones
2. A result of the acid-catalyzed reaction of aldehydes and ketones with alcohols



3. Hemiacetals are extremely unstable, but acetals are extremely stable so the formation of the stable acetal drives the equilibrium to the product side of the reaction
4. Whether the starting material is an aldehyde or a ketone, the resulting products are now called hemiacetals and acetals (as formerly distinguished from hemiketals and ketals)
5. Cyclic hemiacetals are formed when a compound (e.g., pentoses and hexoses) contain both hydroxyl and carbonyl groups
 - a. Hydroxyl oxygen atom attacks carbonyl carbon and forms ring
6. Hemiacetal/acetal formation is an acid-catalyzed reversible reaction
 - a. Equilibrium: $\text{RCOR} + \text{ROH} \rightleftharpoons \text{hemiacetal/acetal} + \text{water}$

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