BOOKS

1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition

2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle

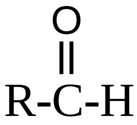
3) Organic Chemistry: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,

4) Organic Chemistry: A Brief Course, R. C. Atkins, F.A. Carey

3. ALDEHYDES AND KETONES

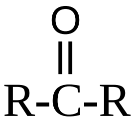
3. ALDEHYDES AND KETONES

Aldehydes and ketones both contain the **carbonyl group**—a group in which a carbon atom has a double bond to oxygen. The carbonyl group of an aldehyde is bonded to one hydrogen atom and one carbon atom (except for formaldehyde, which is the only aldehyde bearing two hydrogen atoms). The carbonyl group of a ketone is bonded to two carbon atoms. Using R, we can designate the general formulas for aldehydes and ketones as follows:



$$R-\overset{\overset{O}{\|}}{C}-H$$

Aldehyde



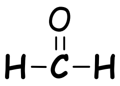
$$R-\overset{\overset{O}{\|}}{C}-R$$

Ketone

3.1 Nomenclature of Aldehydes and Ketones

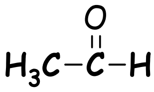
Aliphatic aldehydes are named substitutively in the IUPAC system by replacing the final **-e** of the name of the corresponding alkane with **-al**. Aliphatic ketones are named substitutively by replacing the final -e of the name of the corresponding alkane with -**one**.

The chain is then numbered in the way that gives the carbonyl carbon atom the lower possible number, and this number is used to designate its position. Some aldehydes and ketones have common names that are retained in the IUPAC system:



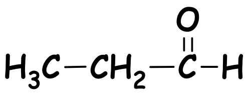
$$H-\overset{\overset{O}{\|}}{C}-H$$

Methanal
(Formaldehyde)



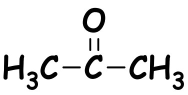
$$H_3C-\overset{\overset{O}{\|}}{C}-H$$

Ethanal
(Acetaldehyde)



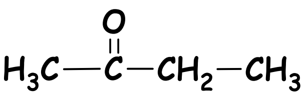
$$H_3C-CH_2-\overset{\overset{O}{\|}}{C}-H$$

Propanal
(Propionaldehyde)



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3$$

Propan-2-one
(Acetone)



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

Butan-2-one
(Ethyl methyl ketone)

3.2 Synthesis of Aldehydes and Ketones

1. Oxidation of alcohols: The oxidation state of an aldehyde lies between that of a 1° alcohol and a carboxylic acid. Aldehydes can be prepared from 1° alcohols by oxidation with pyridinium chlorochromate

($C_5H_5NH^+CrO_3Cl^-$, or PCC). Ketones can be prepared from secondary alcohols by oxidation.

$$RR^1CH_2OH \xrightarrow{[O]} RCHO$$

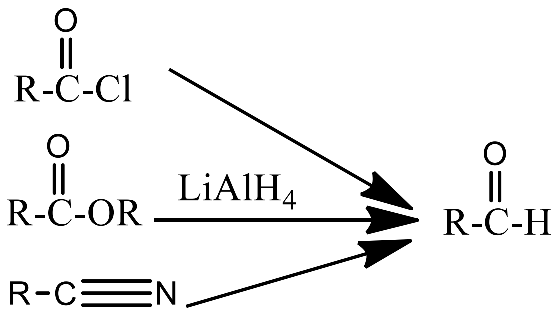
$$RR^1CHOH \xrightarrow{[O]} RCOR$$

R^1 = H, primary alcohol
R^1 = alkyl, seconder alcohol
[O]: $KMnO_4$ / H_2SO_4; $K_2Cr_2O_7$ /H_2SO_4

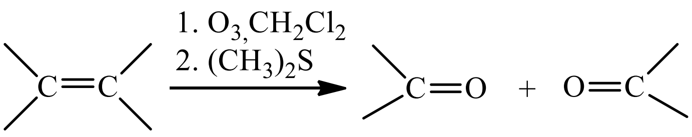
R^1 = H, aldehyde
R^1 = alkyl, ketone

2. Aldehydes by Reduction of Acyl Chlorides, Esters, and Nitriles:

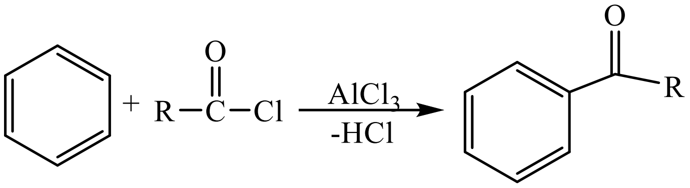
Acyl chlorides (RCOCl), esters (RCO_2R^1), and nitriles (RCN) are all easily prepared from carboxylic acids, and they all are more easily reduced. When any carboxylic acid derivatives are treated with $LiAlH_4$, they are reduced all the way to the 1° alcohol.



3. Ozonolysis of Alkenes: Alkenes can be cleaved by ozonolysis of their double bond. The products are aldehydes and ketones.



4. Ketones from arenes by Friedel-Crafts acylations: Aromatic ketones can be prepared from arenes by Friedel-Crafts acylations



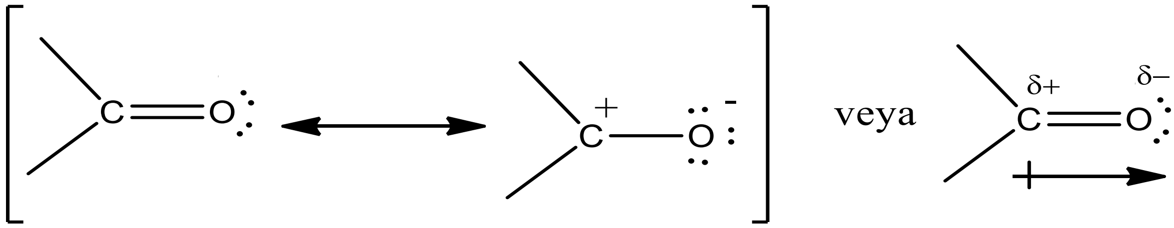
3.3 The Carbonyl Group

Aldehydes and ketones have a trigonal planar arrangement of groups around the carbonyl carbon atom. The carbon atom is sp^2 hybridized.

The trigonal planar arrangement of groups around the carbonyl carbon atom means that the carbonyl carbon atom is relatively open to attack from above or below the plane of the carbonyl group.

- The positive charge on the carbonyl carbon atom means that it is especially susceptible to attack by a nucleophile.
- The negative charge on the carbonyl oxygen atom means that nucleophilic addition is susceptible to acid catalysis.

Resonance structure of carbonyl group:



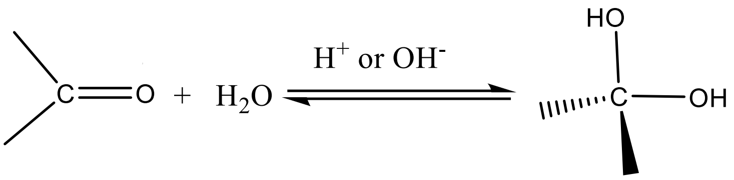
The carbonyl group is a polar group; therefore, aldehydes and ketones have higher boiling points than hydrocarbons of the same molecular weight. However, since aldehydes and ketones cannot have strong hydrogen bonds between their molecules, they have lower boiling points than the corresponding alcohols.

3.4 Nucleophilic Addition to the Carbon-Oxygen Double Bond

Aldehydes and ketones are especially susceptible to nucleophilic addition because of the structural feature.

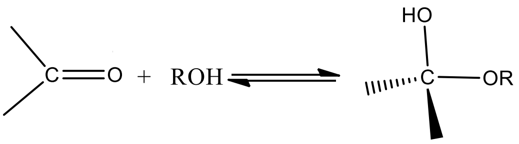
3.4.1 The Addition of Water

Geminal diols occur by addition of H_2O to aldehydes and ketones.

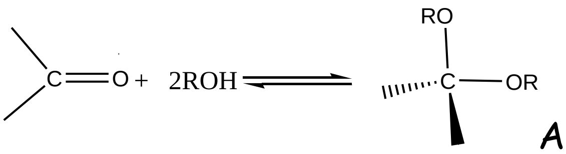


3.4.2 The Addition of Alcohols

Aldehydes and ketones react with alcohols to form hemiacetals and acetals by an equilibrium reaction.



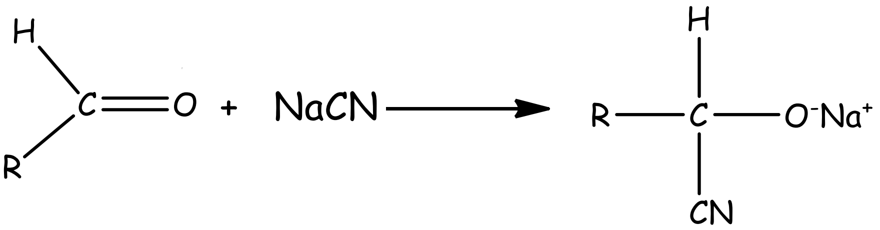
Hemiacetal

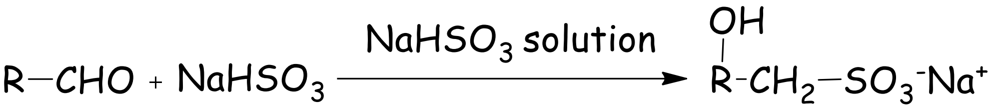


Acetal

3.4.3 The Addition of Hydrogen Cyanide and Sodium bisulfide

Hydrogen cyanide adds to the carbonyl groups of aldehydes and most ketones to form compounds called cyanohydrins. (Ketones in which the carbonyl group is highly hindered do not undergo this reaction).

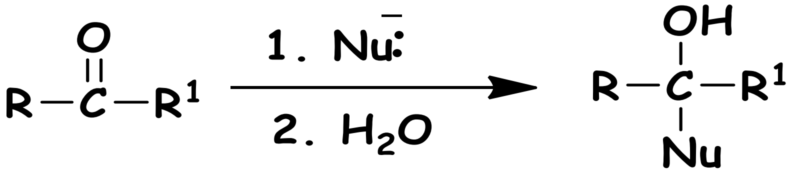




$$R{-}CHO + NaHSO_3 \xrightarrow{NaHSO_3\ \text{solution}} \overset{OH}{\overset{|}{R}}{-}CH_2{-}SO_3^{-}Na^{+}$$

3.4.4 The Addition of Strong Nucleophile

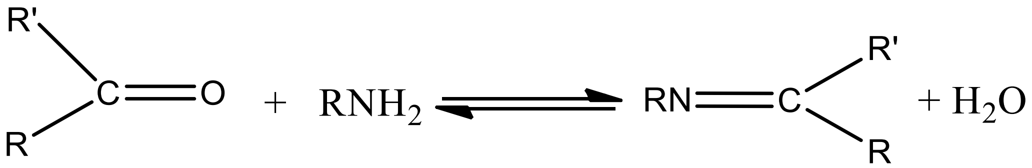
When the reagent is a strong nucleophile ($Nu:^-$), addition usually takes place in the following way, converting the trigonal planar aldehyde or ketone into a tetrahedral product. In the second step, the oxygen atom accepts a proton. This happens because the oxygen atom is now much more basic; it carries a full negative charge as an alkoxide anion.



$$R-\overset{O}{\overset{\|}{C}}-R^1 \xrightarrow[2.\ H_2O]{1.\ \bar{Nu:}} R-\underset{\underset{Nu}{|}}{\overset{\overset{OH}{|}}{C}}-R^1$$

3.4.5 The Addition of Primary and Secondary Amines

Aldehydes and ketones react with primary amines to form imines and with secondary amines to form enamines.



3.5 Oxidation and Reduction of Carbonyl Compounds

Aldehydes are much more easily oxidized than ketones. Aldehydes are readily oxidized by strong oxidizing agents such as potassium permanganate, and they are oxidized by such mild oxidizing agents as silver oxide.

The ease with which aldehydes undergo oxidation differentiates them from most ketones. Mixing aqueous silver nitrate with aqueous ammonia produces a solution known as Tollens' reagent. The reagent contains the diamminosilver(I) ion, $Ag(NH_3)_2^+$. Although this ion is a very weak oxidizing agent, it oxidizes aldehydes to carboxylate anions. As it does this, silver is reduced from the +1 oxidation state [of $Ag(NH_3)_2^+$] to metallic silver. Tollens' reagent gives a negative result with all ketones.

$$RCHO + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow \downarrow 2Ag + RCOOH + 4NH_3 + H_2O$$

Metallic silver

Fehling reagent;

$$RCHO + 2\,Cu^{+2} + 5OH^- \longrightarrow \downarrow Cu_2O + RCOOH + 3H_2O$$

red precipitates

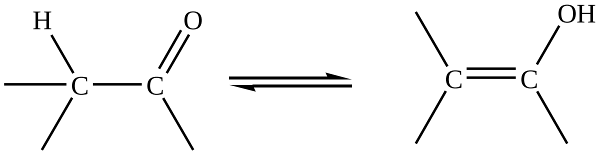
The carbonyl group of a ketone or an aldehyde can be reduced to a C-OH group with catalytic hydrogenations. However, the carbonyl group of a ketone or an aldehyde can be reduced to a CH_2 group. One general method—called the Clemmensen reduction—consists of refluxing the ketone with hydrochloric acid containing amalgamated zinc.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$

$$RCHO \xrightarrow{Zn, Hg / conc.HCl} RCH_3$$

3.6 Keto-Enol Tautomerization

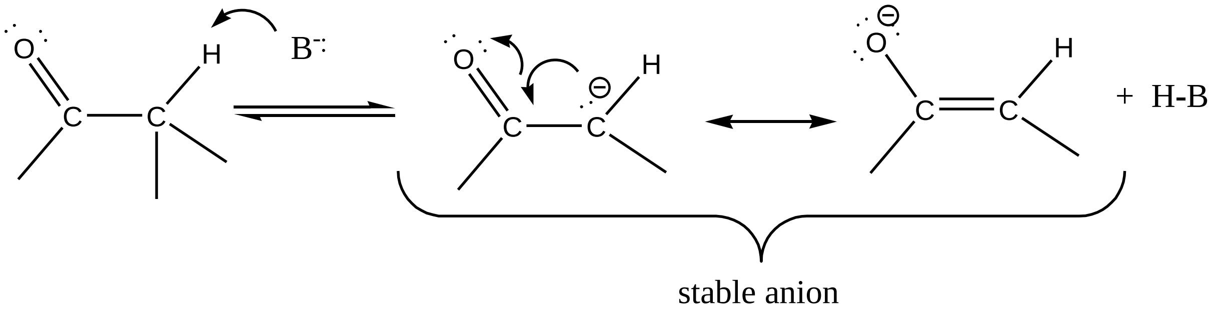
The keto and enol forms of carbonyl compounds are constitutional isomers, but of a special type. Interconvertible keto and enol forms are called tautomers, and their interconversion is called tautomerization. Keto-enol tautomers are not resonance structures. They are constitutional isomers in equilibrium (generally favoring the keto form).



Keto- Enol-

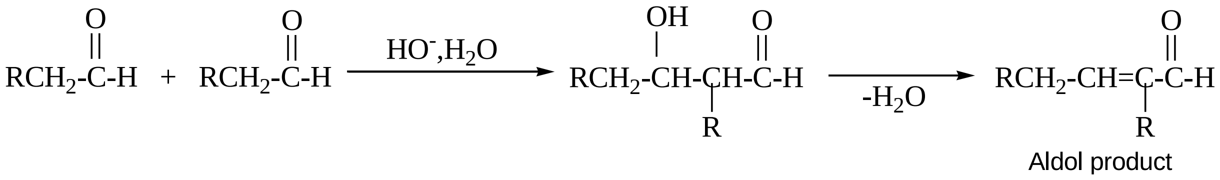
3.7 a-Hydrogen Acidity of Carbonyl Compounds; Enolate Anion

a-hydrogens of carbonyl compounds can be removed by base. A base catalyzes the formation of an enol through the intermediate formation of an enolate anion.



3.8 Aldol Condensation

An aldol reaction begins with addition of an enolate or enol to the carbonyl group of an aldehyde or ketone, leading to a β-hydroxy aldehyde or ketone as the initial product. An aldol addition is an equilibrium reaction when it is conducted in a protic solvent with a base such as hydroxide or an alkoxide. the initial aldol addition product often dehydrates to form an α,β-unsaturated aldehyde or ketone. When this is the result, the overall reaction is an aldol condensation.



3.9 Crossed Aldol Condensations

An aldol reaction that starts with two different carbonyl compounds is called a crossed aldol reaction. Unless specific conditions are involved, a crossed aldol reaction can lead to a mixture of products from various pairings of the carbonyl reactants. Crossed aldol reactions are possible with weak bases such as hydroxide or an alkoxide when one carbonyl reactant does not have a hydrogen. A reactant without a hydrogen cannot self-condense because it cannot form an enolate.