

Organic Chemistry

CHEM 145

2 Credit hrs

Chemistry Department

College of Science

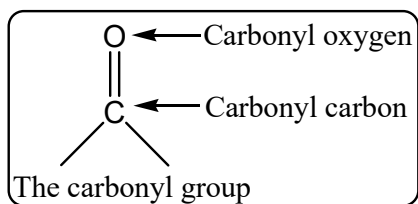
King Saud University

By

Prof. Mohamed El-Newehy

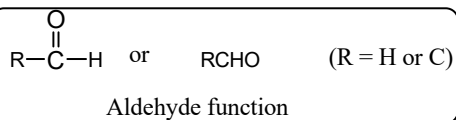
Aldehydes and Ketones

➡ **Aldehydes and ketones** are organic compounds that contain the **carbonyl group**.



Aldehydes: Structure

➔ **Aldehydes** have the general formula.

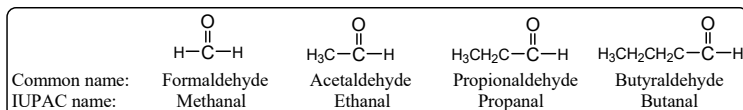


Aldehydes: Nomenclature

IUPAC system

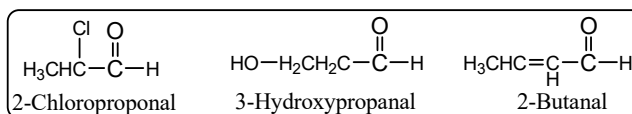
➔ **Aliphatic aldehydes** are named by **dropping the suffix -e** from the name of the hydrocarbon that has the same carbon skeleton as the aldehyde and replacing it with the suffix **-al**.

Alkane -e + al = Alkanal

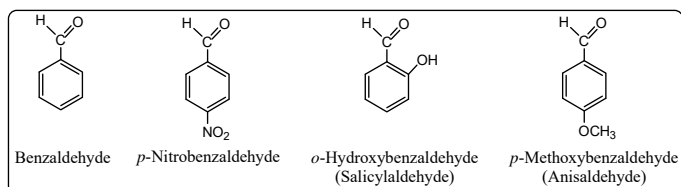


➔ **Substituted aldehydes** are named in the usual ways:

- ➔ By numbering and alphabetically listing the substituents.
- ➔ The **CHO group** is assigned the number **1 position**.
- ➔ The **CHO group** takes precedence over other functional groups such as **-OH, C=C, or C-C triple bond**.

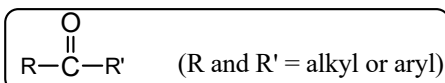


➔ **Aromatic aldehydes** are usually designated as **derivatives of the simplest aromatic aldehyde, benzaldehyde**.



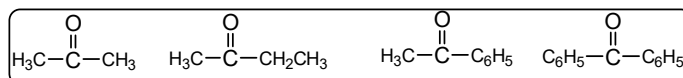
Ketones: Structure

➔ **Ketones** have the general formula.

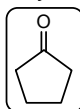


➔ The **carbonyl group** may appear at any of various positions in the chain, *except at the end*.

➔ The **R groups need not be the same**; either or both may be aliphatic or aromatic.



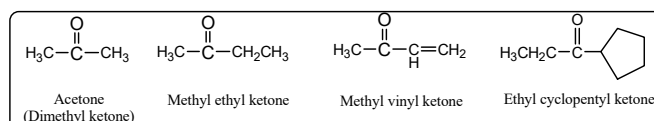
➔ In **ketones** the **carbonyl group** may also be **part of a cyclic structure**.



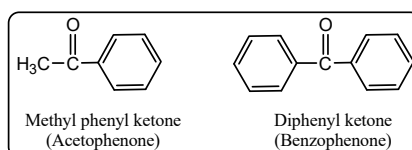
➔ By listing the alkyl substituents attached to the carbonyl group, followed by the word **ketone**.

Alkyl **ketone**

➔ The **simplest aliphatic ketone**, **dimethyl ketone**, is usually called **acetone**.



➔ When the **carbonyl group of a ketone is attached to a benzene ring**, the ketone may be similarly named, or it may be given a special name.




➔ In the **IUPAC system**,

We name ketones in the usual manner.

- We find the **longest continuous chain carrying the carbonyl group**.
- Name the parent structure by **dropping the suffix -e**, **lowest possible number to the C=O group**.

$$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$$

Butanone
(no number needed, the position of C = O is unambiguous)



Cyclopentanone

$$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_3$$

2-Pentanone
(not 4-Pentanone)

$$\text{H}_3\text{CH}_2\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$$

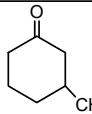
3-Pentanone

➔ **Substituted ketones** are named by numbering and listing the substituents alphabetically.

➔ **For cyclic ketones**, numbering always starts from the C=O group.

$$\text{H}_3\text{CH}_2\text{CH}(\text{Cl})-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$$

3-Chloro-2-pentanone
(not 3-Chloro-4-pentanone)



3-Ethylcyclohexanone
(not 5-Methylcyclohexanone)

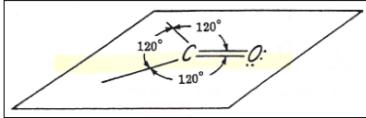
$$\text{H}_3\text{C}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$$

3-Penten-2-one
(not 2-Penten-4-one)

The Carbonyl Group

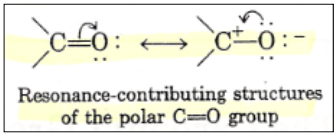
➔ The **carbon-oxygen double bond** is a combination of a **sigma (σ) bond** and a **pi (π) bond**.

➔ **Geometry of the carbonyl group:** planar, 120° angles.



➔ The π bond of the carbonyl group is **polarized**.

➔ The polar character of the carbonyl group can be described by **resonance-contributing structures**.

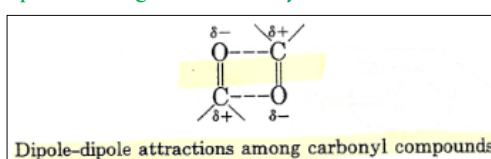


Resonance-contributing structures of the polar C=O group

Physical Properties of Aldehydes and Ketones

Boiling Points

- Because of the polarity of the carbonyl group, Aldehydes and ketones are polar compounds.
- The polar character of the molecules gives rise to intermolecular attractions.
- These attractive forces, called dipole-dipole attractions, occur between the partial negative charge on the carbonyl oxygen of one molecule and the partial positive charge on the carbonyl carbon of another molecule.



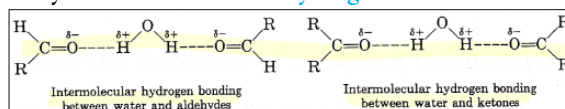
- Dipole-dipole attractions, although important, are not as strong as interactions due to hydrogen bonding.

- So the boiling points of aldehydes and ketones are
 - ➔ higher than those of nonpolar alkanes, of comparable molecular weights.
 - ➔ lower than those of alcohols, of comparable molecular weights.

CH_3CH_3 Ethane (mol wt 30; bp -12°C)	$\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ Formaldehyde (mol wt 30; bp -21°C)	CH_3OH Methyl alcohol (mol wt 32; bp 64.5°C)
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array}$ Isobutane (mol wt 58; bp -12°C)	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ Acetone (mol wt 58; bp 56°C)	$\begin{array}{c} \text{OH} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{H} \end{array}$ Isopropyl alcohol (mol wt 60; bp 82.5°C)

Solubility in Water.

- The lower aldehydes and ketones are soluble in water. Because aldehydes and ketones form hydrogen bonds with water.

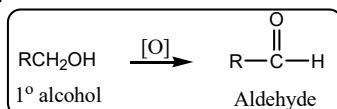


- As the hydrocarbon portion of the molecule increases, the solubility in water decreases rapidly.
- Aldehydes and ketones with more than six carbons are essentially insoluble in water.

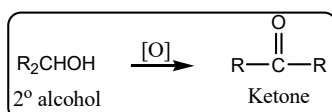
Preparation of Aldehydes and Ketones

Oxidation of Primary and Secondary Alcohols

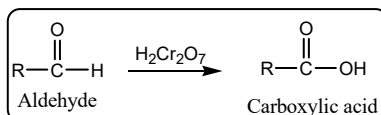
- Oxidation of **primary alcohols**, under controlled conditions, yields **aldehydes**.



- Oxidation of **secondary alcohols** yields **ketones**.

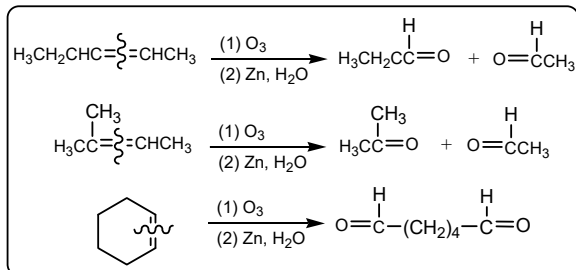


- **Aldehydes** are very easily oxidized to **carboxylic acids**.



Ozonolysis of Alkenes

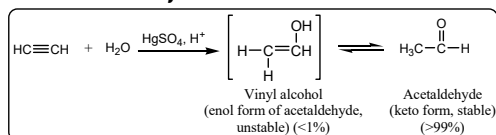
- Oxidation of alkenes by ozonolysis.
- The net result, the presence of **two C=O bonds for every C=C**.



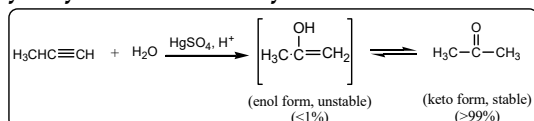
Hydration of Alkynes

- Addition of water to alkyne follows Markovnikov's rule.
- The **only aldehyde** that can be obtained by this method is **acetaldehyde**.

➤ Addition of water to acetylene.

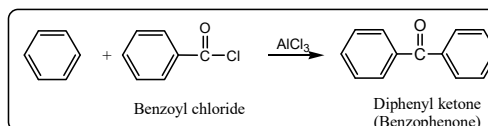
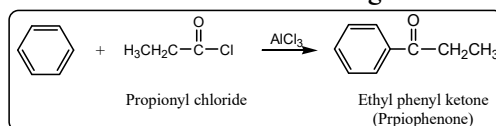


➤ All other alkynes yield **ketones** on hydration.



Friedel-Crafts Acylation

➤ Preparing ketones that contain an aromatic ring.

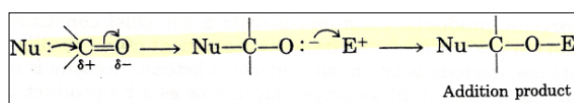


Nucleophilic Addition Reactions of Aldehydes and Ketones

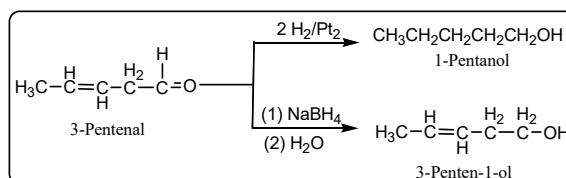
➤ Nucleophilic addition reactions to the **carbon-oxygen double bond**.

➤ In nucleophilic addition reactions

- The **partially positive carbonyl carbon** undergoes attack by electron-rich reagents, or **nucleophiles (Nu):**
- The **partially negative carbonyl oxygen** is attacked by electron-deficient reagents, or **electrophiles (E⁺)**.

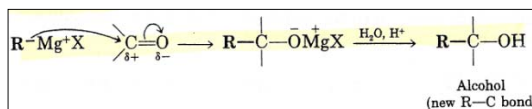


Reduction of the Carbonyl Group



Addition of Grignard Reagents: Formation of Alcohols

- Addition of Grignard reagents, $R-Mg^+X$, to the carbonyl group is used for synthesizing all kinds of **alcohols**.
- The addition product, after it is formed, is **hydrolyzed** with aqueous acid to give an alcohol.



- It is possible to prepare **1°, 2°, or 3° alcohols**, depending on what **kind of carbonyl compound** undergoes the addition reaction.

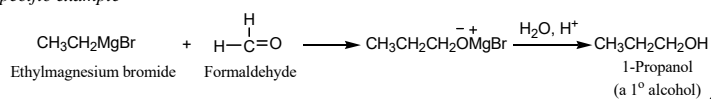
➤ **For example;**

➔ **Formaldehyde yields primary alcohols.**

General equation



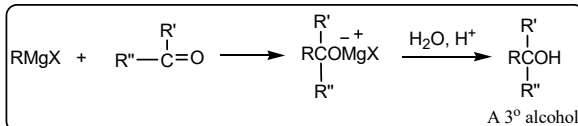
Specific example



➔ **Aldehyde other than formaldehyde yields secondary alcohols.**

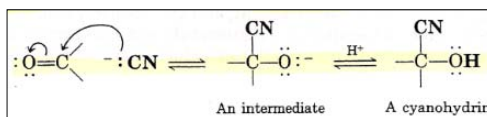


➔ **Ketones yields tertiary alcohols.**



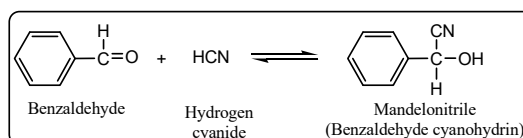
Addition of Hydrogen Cyanide: Formation of Cyanohydrins

→ The addition is catalyzed by cyanide ion (good nucleophile).



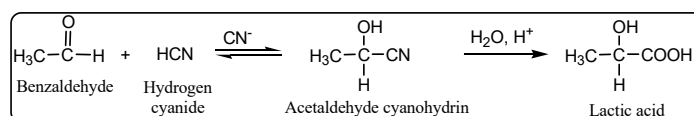
→ **Example**

Mandelonitrile, the cyanohydrin obtained when hydrogen cyanide is added to benzaldehyde.



→ **Cyanohydrins** are valuable synthetic intermediates.

► On treatment with aqueous acid (**hydrolysis**), they yield **hydroxy acids** one more carbon than the starting aldehyde or ketone.



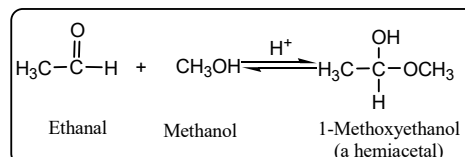
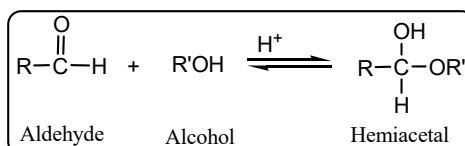
Addition of Alcohols: Formation of Hemiacetals and Acetals

A. Hemiacetals (and Hemiketals)

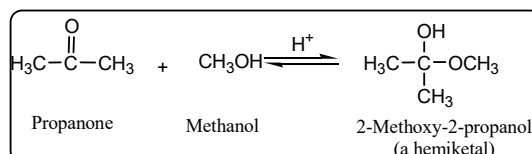
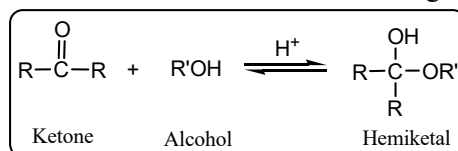
→ **Water and alcohols (weak nucleophiles)**, can add to the carbonyl group of aldehydes and ketones.

→ An acid catalyst is required to speed the rate of reaction.

► The addition of **one mole of an alcohol** to the **carbonyl group of an aldehyde** yields a **hemiacetal**.



➤ The addition of **one mole of an alcohol** to a **ketone** gives a **hemiketal**.

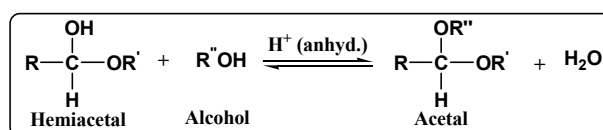


➤ **Hemiacetals and hemiketals** have an **alkoxy group (OR)** and a **hydroxy group (OH)** attached to the **same carbon**.

B. Acetals

When **hemiacetals** are treated with an **additional mole of alcohol** in the presence of anhydrous acid, they are converted to **Acetals**.

➤ **Acetals** have **two alkoxy groups (OR)** on the **same carbon**.

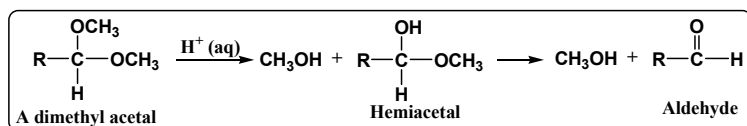


➤ **Acetals** are **stable compounds**.

➤ **Acetals, like ethers, do not react with bases, oxidizing agents and reducing agents.**

➤ **Acetals, unlike ethers, are sensitive to aqueous acids.**

Acetals gives an **aldehyde** and **2 moles of alcohols**.



Addition of Ammonia and Ammonia Derivatives

► The addition of nitrogen nucleophile, such as ammonia (NH_3) and substituted ammonia ($\text{NH}_2\text{-Y}$).

