CHEM 108

FUNDAMENTALS OF ORGANIC CHEMISTRY

FOR B.Sc. PROGRAMS OF SCIENTIFIC COLLEGES

PRE-REQUISITES COURSE; CHEM 101

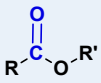
CREDIT HOURS; 4 (3+1)

Chemistry Department, College of Science, King Saud University

CHAPTER 6

ALDEHYDES & KETONES

Common Classes of Carbonyl Compounds

Class	General Formula	Class	General Formula
Ketones		Aldehydes	
Carboxylic acids		Acid Chlorides	
Esters		Amides	

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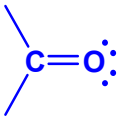
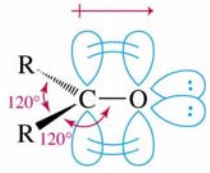
The Carbonyl Group



The carbonyl group

- Carbon is sp^2 hybridized.
- C=O bond is shorter, stronger, and more polar than C=C bond in alkenes.



	length	*energy*
ketone C=O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
alkene C=C bond	1.34 Å	146 kcal/mol (611 kJ/mol)

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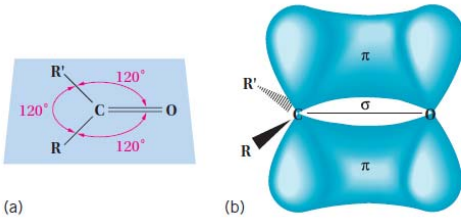
The Carbonyl Group

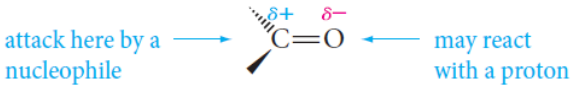
- **The structure and properties of the carbonyl group.**
  - The carbon–oxygen double bond consists of a sigma bond and a pi bond.
  - The carbon atom is sp^2-hybridized. The three atoms attached to the carbonyl carbon lie in a plane with bond angles of 120°.
  - The pi bond is formed by overlap of a *p* orbital on carbon with an oxygen *p* orbital.
  - There are also two unshared electron pairs on the oxygen atom.
  - The C=O bond distance is 1.24A, shorter than the C-O distance in alcohols and ethers (1.43A) .



The Carbonyl Group

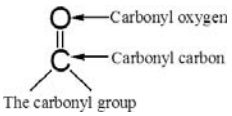
- Oxygen is much more electronegative than carbon. Therefore, the electrons in the C=O bond are attracted to the oxygen, producing a highly polarized bond.

- As a consequence of this polarization, *most carbonyl reactions involve* nucleophilic attack *at the carbonyl carbon,* often accompanied by addition of a proton to the oxygen (electron rich).



Structure of Aldehydes and Ketones

- **Aldehydes and ketones** are characterized by the presence of the carbonyl group.

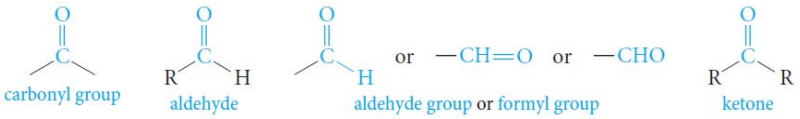


- **Aldehydes** have at least one hydrogen atom attached to the carbonyl carbon atom.

  The remaining group may be another hydrogen atom or any aliphatic or aromatic organic group.

  The -CH=O group characteristic of aldehydes is often called a formyl group.

- In **ketones,** the carbonyl carbon atom is connected to two other carbon atoms.



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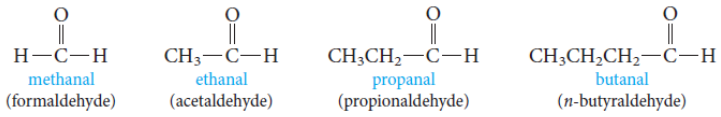
Nomenclature of Aldehydes

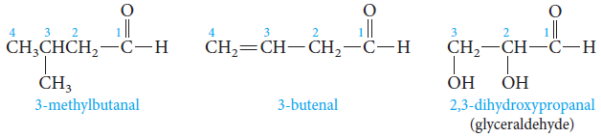
IUPAC System

- *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,*** *we number the chain starting with the aldehyde carbon.*
  - *-CH=O group is assigned the number 1 position.*
  - *Aldehyde group has priority over a double bond or hydroxyl group.*



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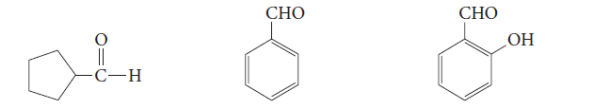
Nomenclature of Aldehydes

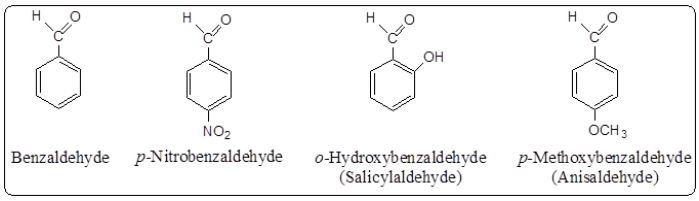
IUPAC System

- *Cyclic aldehydes, the suffix –carbaldehyde is used.*



cyclopentanecarbaldehyde (formylcyclopentane) | benzaldehyde (benzenecarbaldehyde) | salicylaldehyde (2-hydroxybenzenecarbaldehyde)

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



Benzaldehyde | *p*-Nitrobenzaldehyde | *o*-Hydroxybenzaldehyde (Salicylaldehyde) | *p*-Methoxybenzaldehyde (Anisaldehyde)

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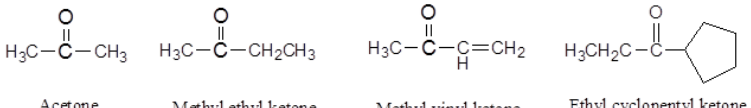
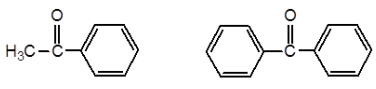
Nomenclature of Aldehydes

Common Names

- Common names of ketones are formed by adding the word *ketone* to the names of the alkyl or aryl groups attached to the carbonyl carbon. Alkyl ketone.
- In still other cases, traditional names are used.



Acetone (Dimethyl ketone) | Methyl ethyl ketone | Methyl vinyl ketone | Ethyl cyclopentyl ketone



Methyl phenyl ketone (Acetophenone) | Diphenyl ketone (Benzophenone)

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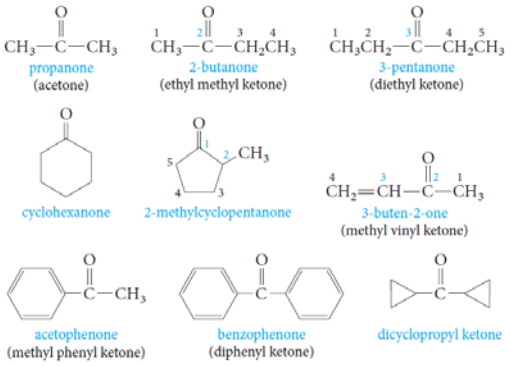
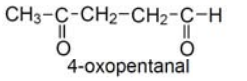
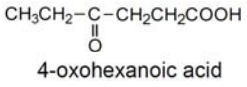
Nomenclature of Ketones

IUPAC System

- In the IUPAC system, the ending for ketones is -one.
- The chain is numbered so that the carbonyl carbon has the lowest possible number.
- For cyclic ketones, numbering always starts from the C=O group.
- The prefix "oxo" is used when the ketone is not the principal functional group.







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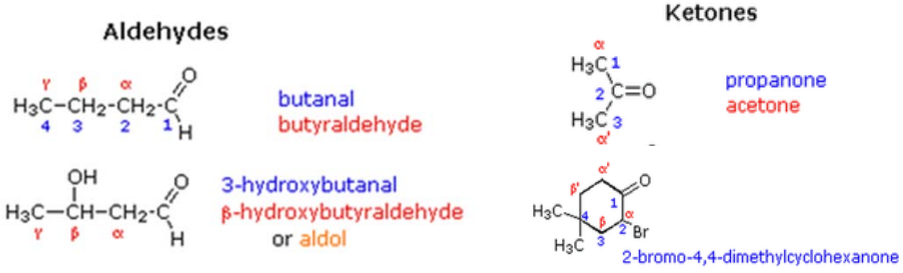
Nomenclature of Aldehydes Ketones

NOTES

- In common names carbon atoms near the carbonyl group are often designated by Greek letters.
- The atom adjacent to the function is *alpha (α)*, the next removed is *beta (β)* and so on. Since ketones have two sets of neighboring atoms, one set is labeled *α, β* etc., and the other *α′, β′* etc.



- The functional group priority order in nomenclature system is as following:
  Acid and derivatives > aldehyde > ketone > alcohol > amine > alkene > alkyne > ether

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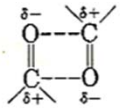
Physical Properties of Aldehydes and Ketones

Boiling Points

- Carbonyl compounds boil at higher temperatures than hydrocarbons, but at lower temperatures than alcohols of comparable molecular weight.

$CH_3(CH_2)_4CH_3$ hexane (bp 69°C) $CH_3(CH_2)_3CH{=}O$ pentanal (bp 102°C) $CH_3(CH_2)_3CH_2OH$ pentanol (bp 118°C)

- This is due to the intermolecular forces of attraction, called dipole-dipole interactions, which is stronger than van der Waals attractions but not as strong as hydrogen bonds.

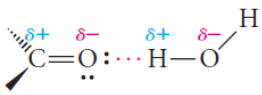


Dipole–dipole attractions among carbonyl compounds

Physical Properties of Aldehydes and Ketones

Solubility

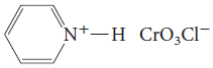
- Carbonyl compounds as aldehydes and ketones have a C=O bond, but no O-H bond, cannot form hydrogen bonds with themselves.
- The polarity of the carbonyl group also affects the solubility properties of aldehydes and ketones.
- Carbonyl compounds with low molecular weights are soluble in water as they can form hydrogen bonds with O-H or N-H compounds.



Preparation of Aldehydes and Ketones

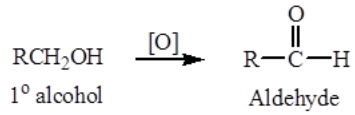
1) Oxidation of Primary and Secondary Alcohols

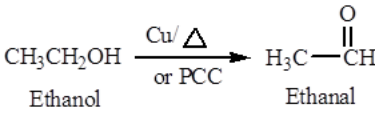
- Chromium reagents, such as pyridinium chlorochromate (PCC), are commonly used in the laboratory.



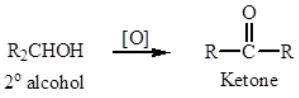
pyridinium chlorochromate (PCC)

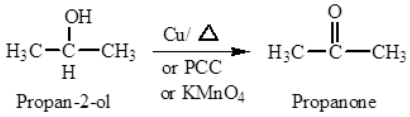
- Oxidation of primary alcohols, under controlled conditions, yields aldehydes.





- Oxidation of secondary alcohols yields ketones.





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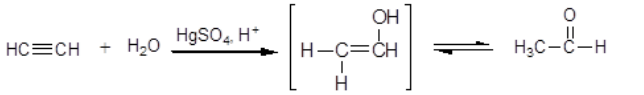
Preparation of Aldehydes and Ketones

2) Hydration of Alkynes

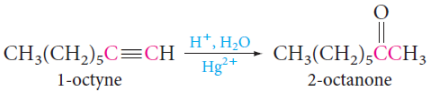
- Hydration of acetylene yields acetaldehyde (catalyzed by acid and mercuric).

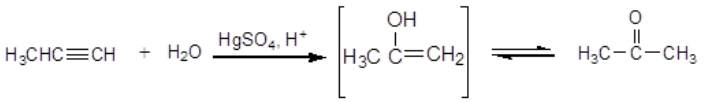


Vinyl alcohol (enol form of acetaldehyde, unstable) (<1%)

Acetaldehyde (keto form, stable) (>99%)

- Hydration of terminal alkynes EXCEPT acetylene yields ketones (catalyzed by acid and mercuric).





(enol form, unstable) (<1%)

(keto form, stable) (>99%)

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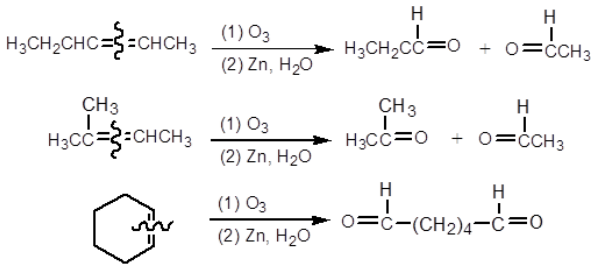
Preparation of Aldehydes and Ketones

3) Ozonolysis of Alkenes

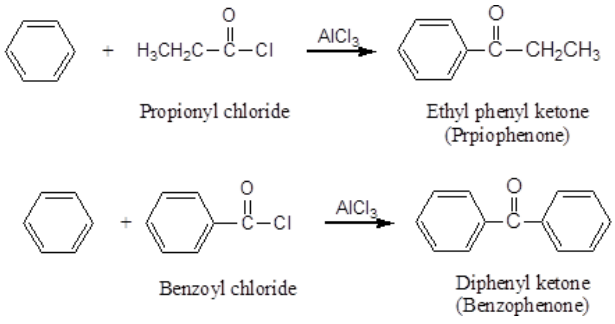
Product (aldehyde or ketone) depends on the structure of alkene.



Preparation of Aldehydes and Ketones

4) Friedel-Crafts Acylation

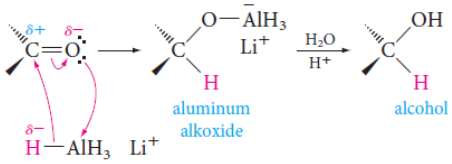
Preparing ketones that contain an aromatic ring.



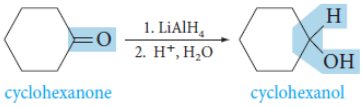
Reactions of Aldehydes and Ketones

A) Reduction of Carbonyl Compounds

- Aldehydes and ketones are easily reduced to primary and secondary alcohols, respectively.
- The most common metal hydrides used to reduce carbonyl compounds are lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$).



- **Example:**



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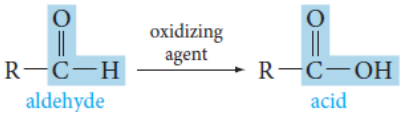
Reactions of Aldehydes and Ketones

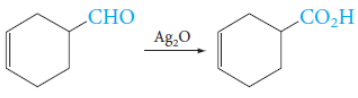
B) Oxidation of Carbonyl Compounds

- Oxidation of aldehydes gives a carboxylic acid with the same number of carbon atoms.
- Because the reaction occurs easily, many oxidizing agents, such as $KMnO_4$, CrO_3, Ag_2O and peracids will work.



- **Example:**

$$CH_3(CH_2)_5CH{=}O \xrightarrow[\text{(Jones' reagent)}]{CrO_3,\ H^+} CH_3(CH_2)_5CO_2H$$



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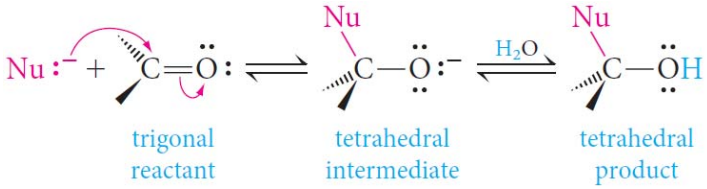
Reactions of Aldehydes and Ketones

C) Nucleophilic Addition Reactions

- Nucleophiles attack the carbon atom of a carbon-oxygen double bond because that carbon has a partial positive charge.
- The overall reaction involves addition of a nucleophile and a proton across the pi bond of the carbonyl group (when carried out in alcohol or water).



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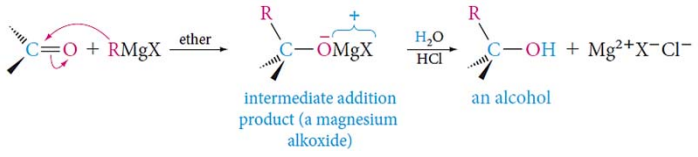
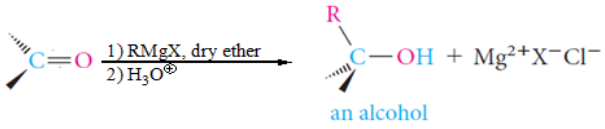
Reactions of Aldehydes and Ketones; C) Nucleophilic Addition Reactions

1) Addition of Grignard Reagents: Formation of Alcohols

- *Grignard reagents act as carbon nucleophiles toward carbonyl compounds.*
- The reaction of a Grignard reagent with a carbonyl compound provides a useful route to alcohols.





- The type of carbonyl compound chosen determines the class of alcohol produced.

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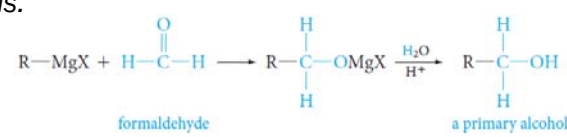
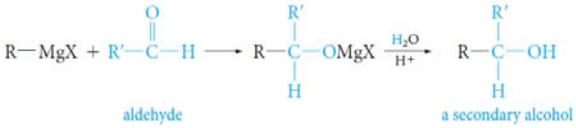
Reactions of Aldehydes and Ketones; C) Nucleophilic Addition Reactions

1) Addition of Grignard Reagents: Formation of Alcohols

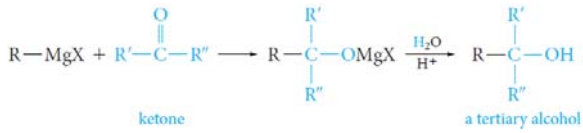
- *Formaldehyde gives primary alcohols.*



- *Other aldehydes give secondary alcohols*



- *Ketones give tertiary alcohols.*



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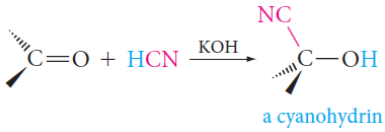
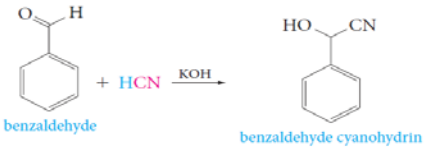
Reactions of Aldehydes and Ketones; C) Nucleophilic Addition Reactions

2) Addition of Hydrogen Cyanide: Formation of Cyanohydrins

- Hydrogen cyanide adds to the carbonyl group of aldehydes and ketones to form cyanohydrins, compounds with a hydroxyl and a cyano group attached to the same carbon.



- Example



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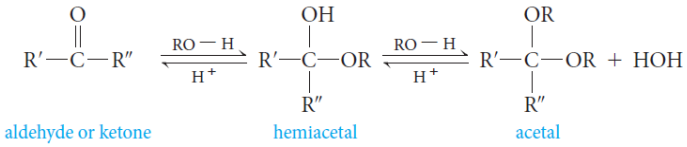
Reactions of Aldehydes and Ketones; C) Nucleophilic Addition Reactions

3) Addition of Alcohols: Formation of Hemiacetals and Acetals

- *Alcohols add to the C=O bond, the OR group becoming attached to the carbon and the proton becoming attached to the oxygen.*
- Aldehydes and ketones react with alcohols to form, first, hemiacetals and then, if excess alcohol is present, acetals.



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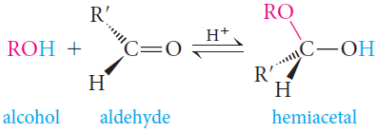
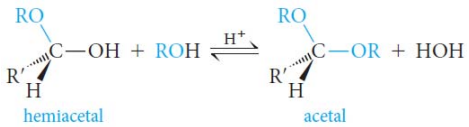
Reactions of Aldehydes and Ketones; C) Nucleophilic Addition Reactions

3) Addition of Alcohols: Formation of Hemiacetals and Acetals

- Hemiacetals; it contains both alcohol and ether functional groups on the same carbon atom.



- Acetals have two ether functions at the same carbon atom.

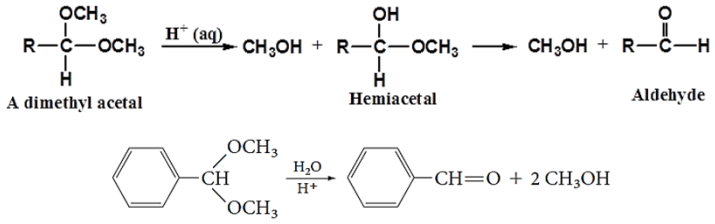


Dr Mohamed El-Newehy

Reactions of Aldehydes and Ketones; C) Nucleophilic Addition Reactions

3) Addition of Alcohols: Formation of Hemiacetals and Acetals

- The reverse of acetal formation, called acetal hydrolysis.
- Acetal can be hydrolyzed to its aldehyde or ketone and alcohol components by treatment with excess water in the presence of an acid catalyst.



Reactions of Aldehydes and Ketones; C) Nucleophilic Addition Reactions

4) Addition of Ammonia and Ammonia Derivatives

The addition of nitrogen nucleophile, such as ammonia(NH_3) and substituted ammonia (NH_2-Y).