

Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

Credit hrs.: (2+1)

King Saud University

College of Science, Chemistry Department

Learning Objectives

At the end of this chapter, students will be able to:

- Know the structural differences between aldehydes and ketones
- Know how to draw aldehydes and ketones
- know the common and IUPAC nomenclature of aldehydes and ketones
- Know the physical properties of aldehydes and ketones
- Know how to synthesize an aldehyde or a ketone.
- Know the different nucleophilic addition reactions at the carbonyl carbon.

Common Classes of Carbonyl Compounds

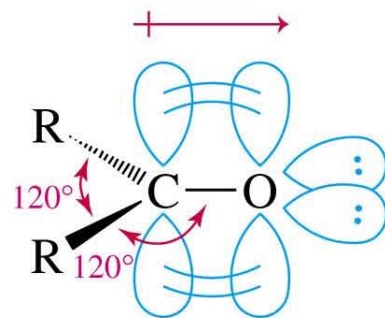
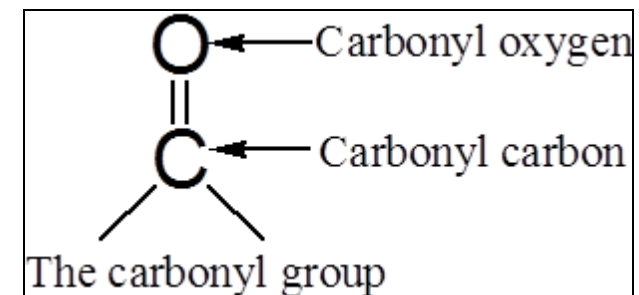


Class	General Formula	Class	General Formula
Ketones	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$	Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}'-\text{C}-\text{H} \end{array}$
Carboxylic acids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$	Acid Chlorides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}'-\text{C}-\text{Cl} \end{array}$
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$	Amides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}'-\text{C}-\text{NH}_2 \end{array}$

The Carbonyl Group

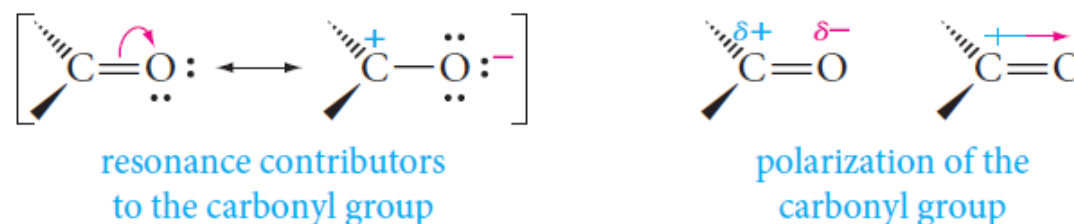
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- The carbon–oxygen double bond consists of a sigma bond and a pi bond.
- The carbon atom is sp^2 -hybridized.
- The three atoms attached to the carbonyl carbon lie in a plane with bond angles of 120° .
- The pi bond is formed by overlap of a p orbital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

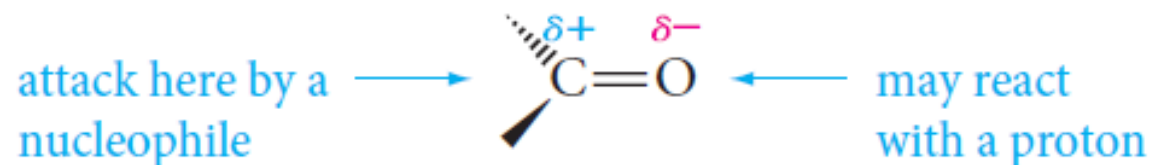


	<i>length</i>	<i>energy</i>
ketone C=O bond	1.23 Å	178 kcal/mol (745 kJ/mol)
alkene C=C bond	1.34 Å	146 kcal/mol (611 kJ/mol)

- 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**.



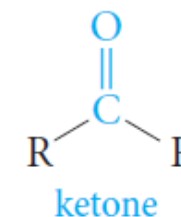
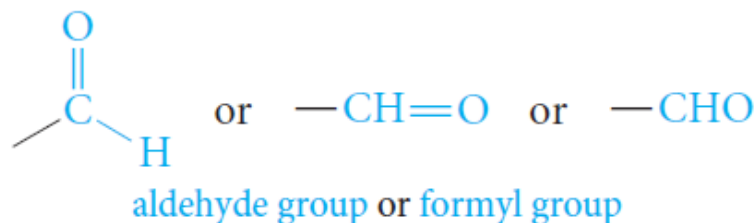
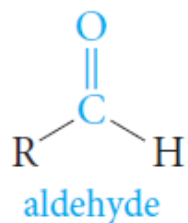
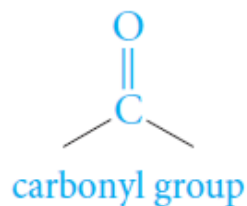
- As a consequence of this polarization, *most carbonyl reactions involve nucleophilic attack at the carbonyl carbon*, often accompanied by addition of a proton to the oxygen (electron rich).



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.



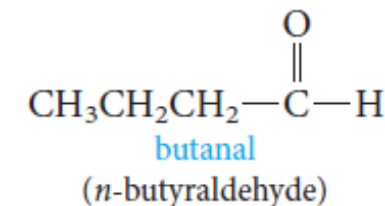
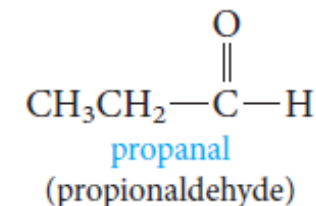
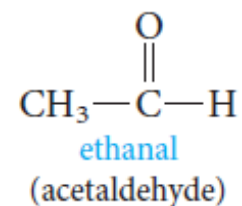
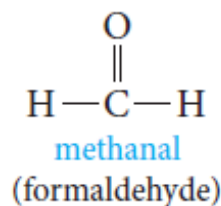
Nomenclature of Aldehydes

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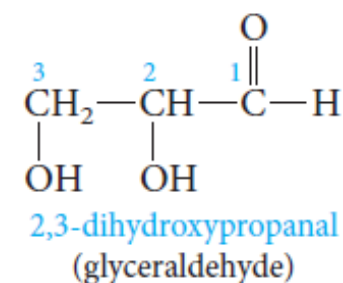
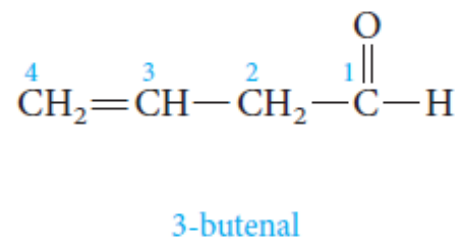
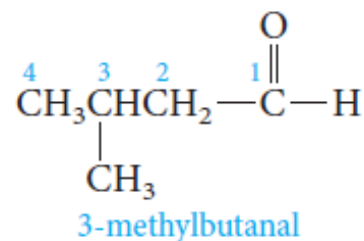
IUPAC System

- **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**.

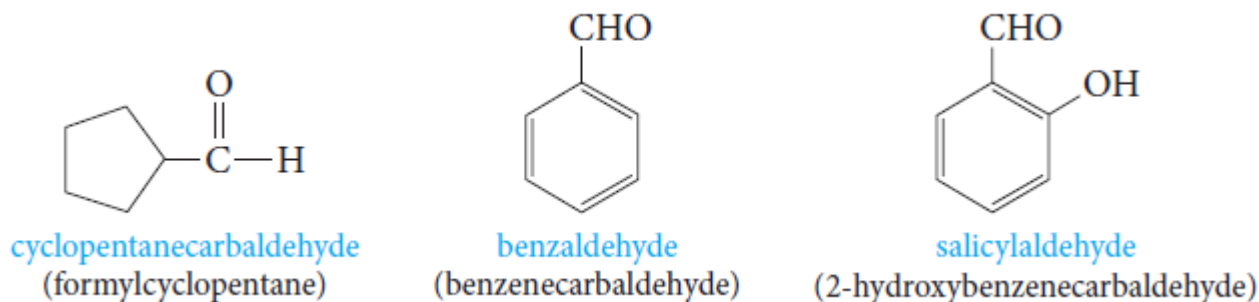
Alkane - e + al = Alkanal



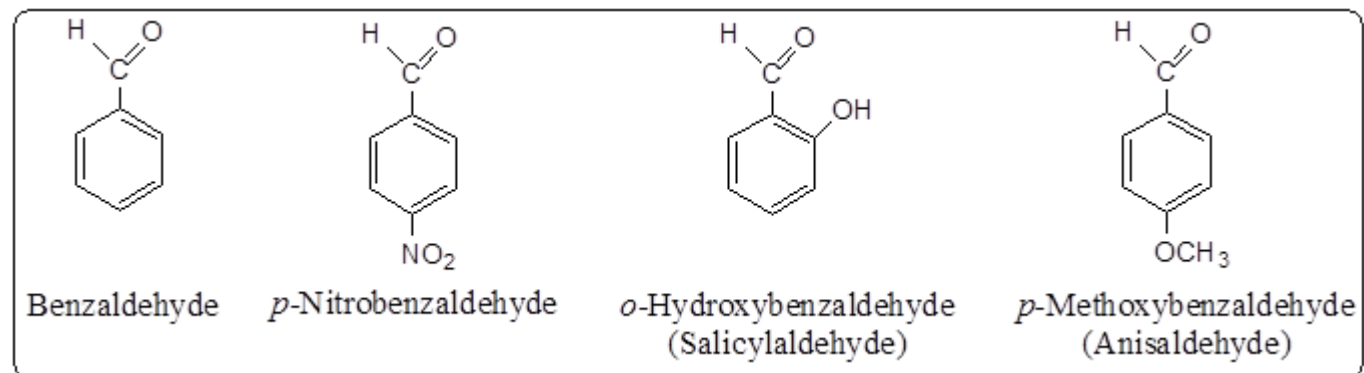
- **Substituted aldehydes**, we number the chain starting with the aldehyde carbon.
 - **-CH=O group** is assigned the number **1 position**.
 - Aldehyde group has priority over a double bond or hydroxyl group.



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



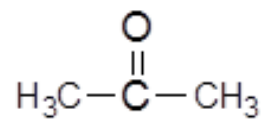
- **Aromatic aldehydes** are usually designated as derivatives of the simplest aromatic aldehyde, **benzaldehyde**.



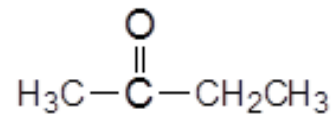
Nomenclature of Ketones

Common Names

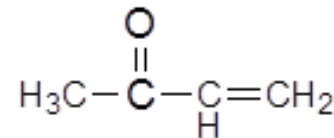
- Common names of ketones are formed by adding the word *ketone* to the names of the alkyl or aryl groups attached to the carbonyl carbon. **Alkyl ketone.**
- In still other cases, traditional names are used.



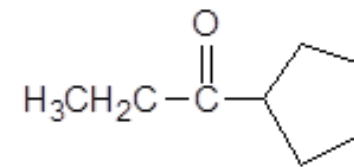
Acetone
(Dimethyl ketone)



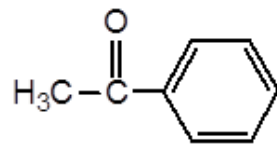
Ethyl methyl ketone



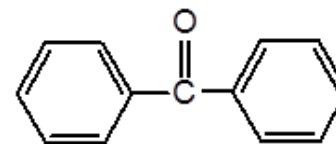
Methyl vinyl ketone



Cyclopentyl ethyl ketone



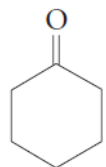
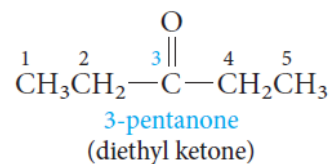
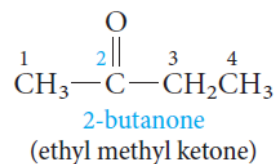
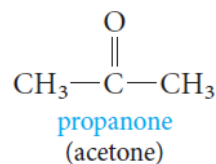
Methyl phenyl ketone
(Acetophenone)



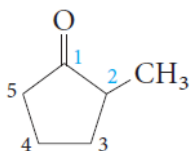
Diphenyl ketone
(Benzophenone)

IUPAC System

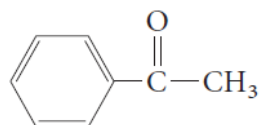
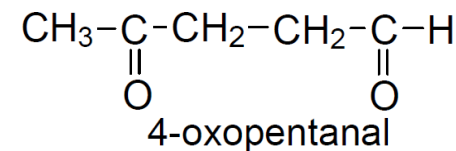
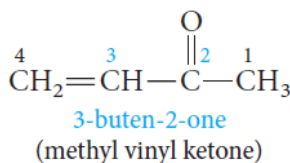
- In the IUPAC system, **the ending for ketones is -one.**
- The chain is numbered so that the **carbonyl carbon has the lowest possible number.**
- For **cyclic ketones**, numbering always starts from the C=O group.
- The prefix "**oxo**" is used when the ketone is not the principal functional group.



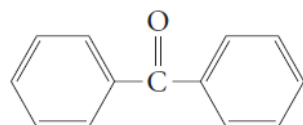
cyclohexanone



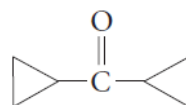
2-methylcyclopentanone



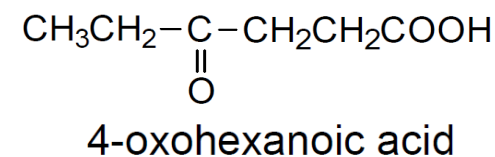
acetophenone
(methyl phenyl ketone)
1-phenylethanone



benzophenone
(diphenyl ketone)
Diphenylmethanone



dicyclopropyl ketone
Dicyclopropylmethanone

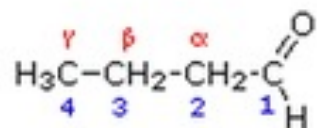


Nomenclature of Aldehydes and Ketones

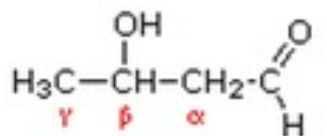
NOTES

- **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.

Aldehydes

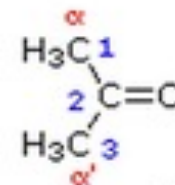


butanal
butyraldehyde

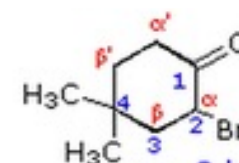


3-hydroxybutanal
 β -hydroxybutyraldehyde
or aldol

Ketones



propanone
acetone



2-bromo-4,4-dimethylcyclohexanone

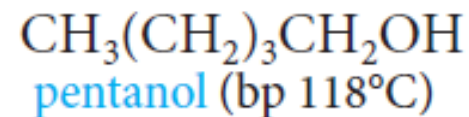
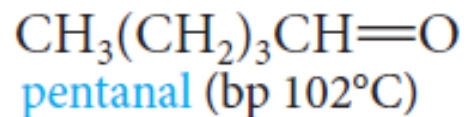
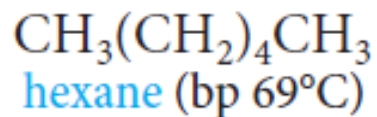
- **The functional group priority order in nomenclature system** is as following:
Acid and derivatives > aldehyde > ketone > alcohol > amine > alkene > alkyne > ether

Physical Properties of Aldehydes and Ketones

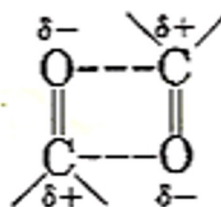


Boiling Points

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



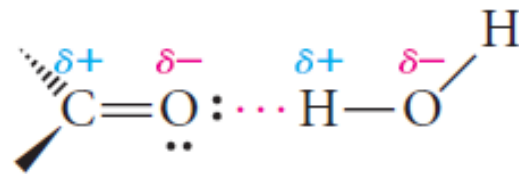
- This is due to the intermolecular forces of attraction, called dipole-dipole interactions, which is stronger than van der Waals attractions but not as strong as hydrogen bonds.



Dipole-dipole attractions among carbonyl compounds

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.



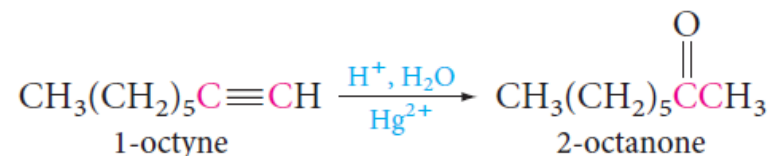
Preparation of Aldehydes and Ketones

1) Oxidation of Primary and Secondary Alcohols

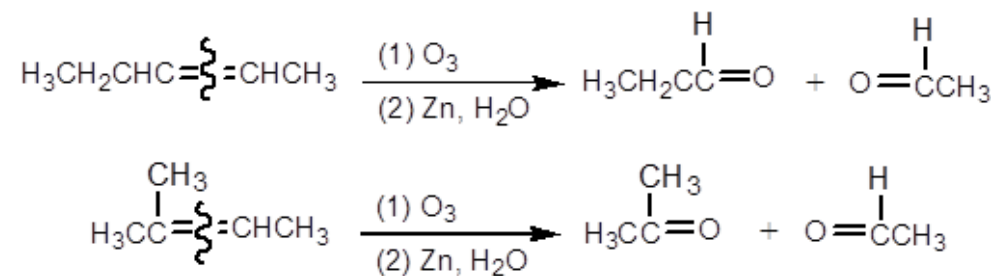


2) Hydration of Alkynes

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

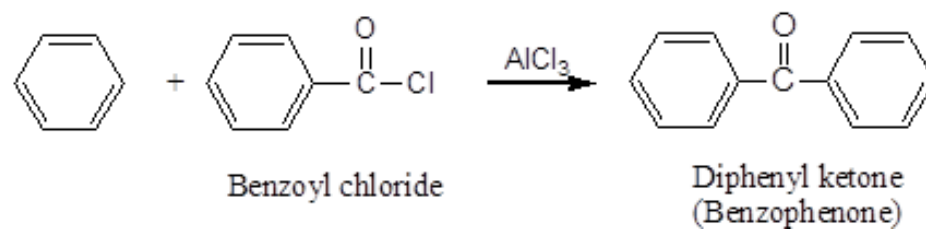
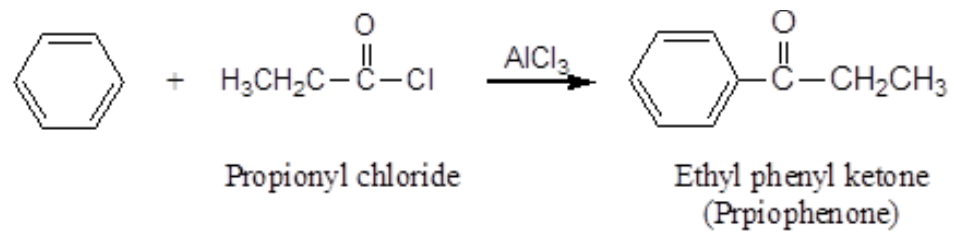


3) Ozonolysis of Alkenes



4) Friedel-Crafts Acylation

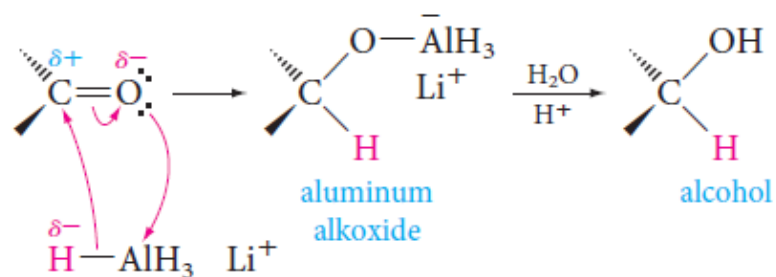
Preparing ketones that contain an aromatic ring.



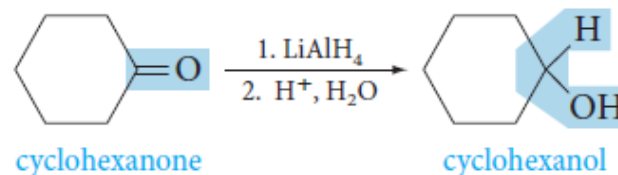
Reactions of Aldehydes and Ketones

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).

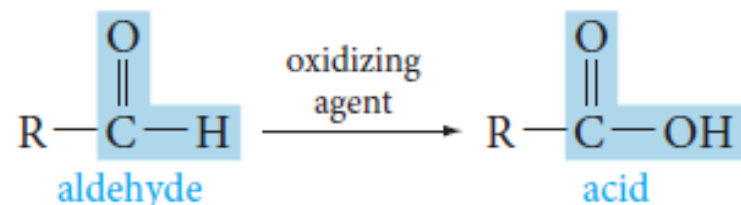


○ Example:

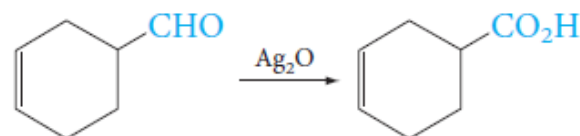
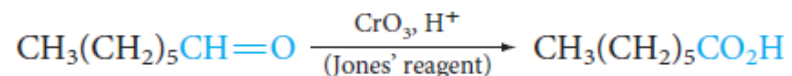


B) Oxidation of Carbonyl Compounds

- 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.

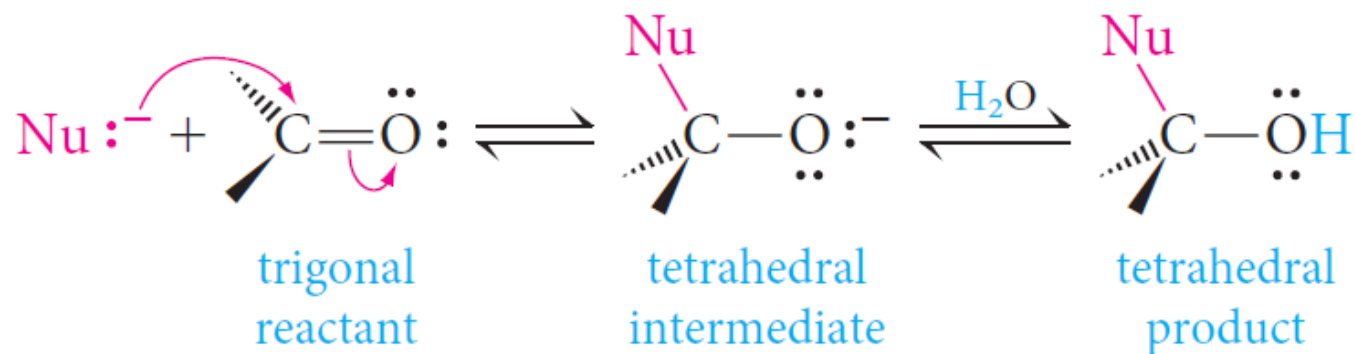


○ Example:



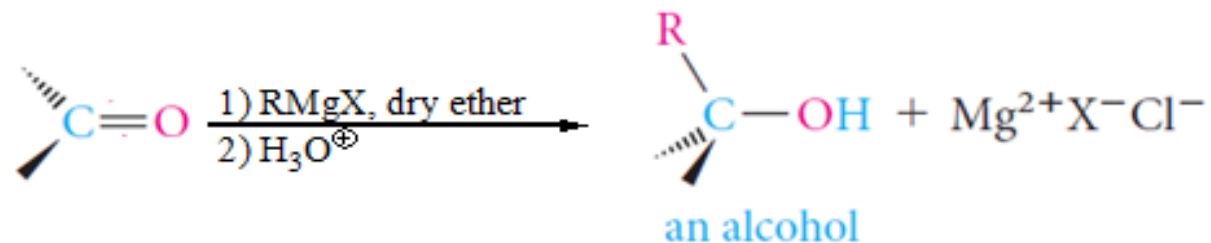
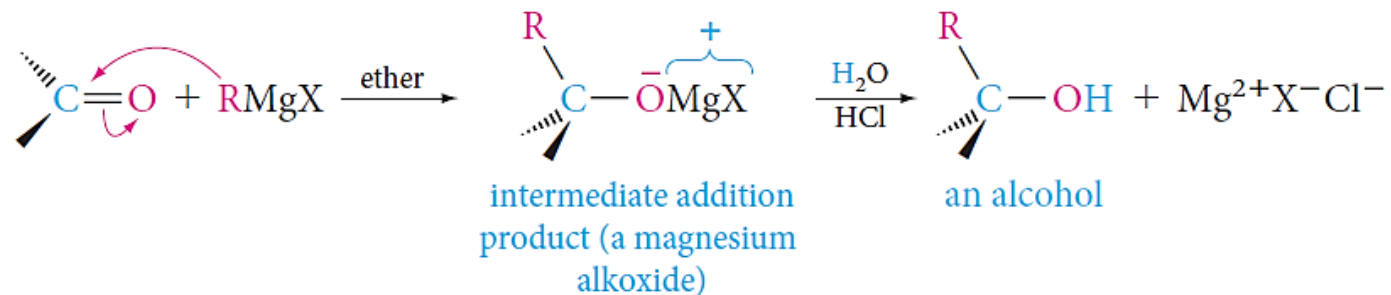
C) Nucleophilic Addition Reactions

- 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).



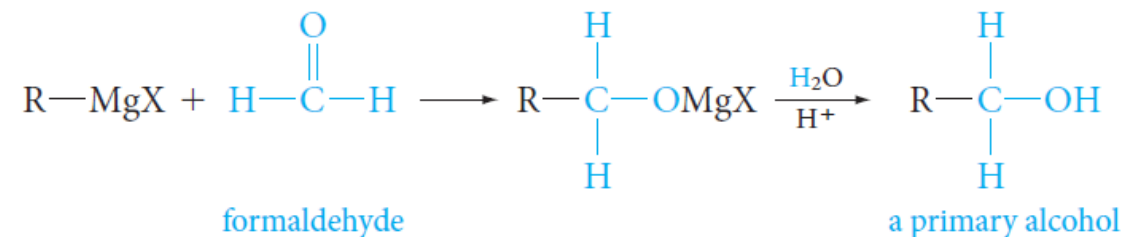
1) Addition of Grignard Reagents: Formation of Alcohols

- 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.

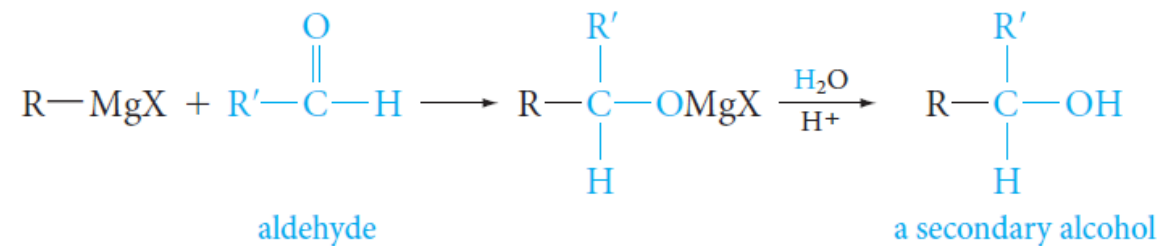


- The type of carbonyl compound chosen determines the class of alcohol produced.

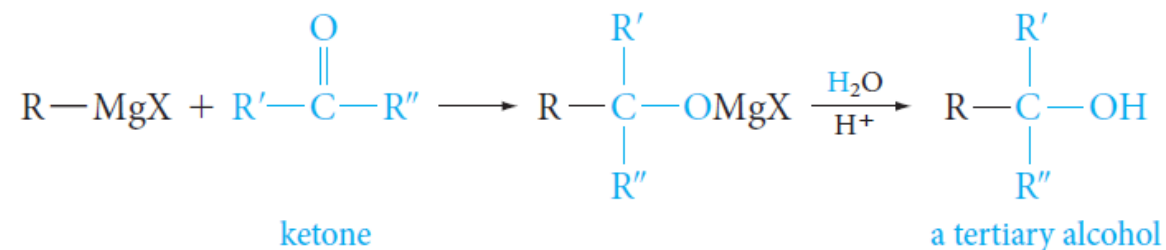
- *Formaldehyde gives primary alcohols.*



- *Other aldehydes give secondary alcohols*

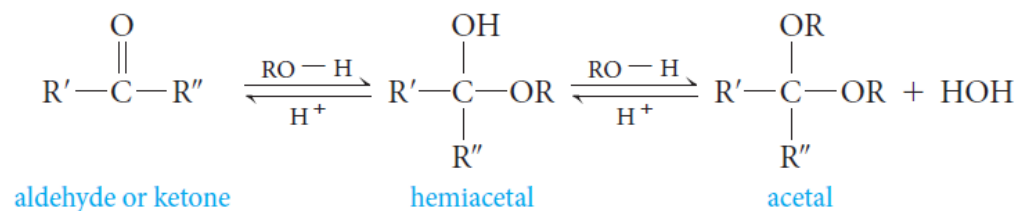


- *Ketones give tertiary alcohols.*

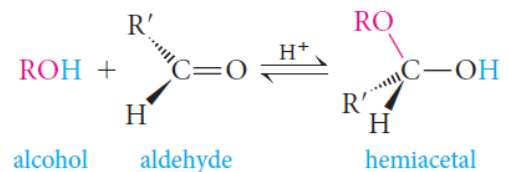


3) Addition of Alcohols: Formation of Hemiacetals and Acetals

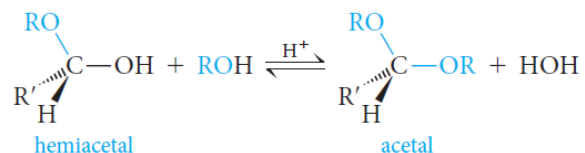
- Alcohols add to the C=O bond, the OR group becoming attached to the carbon and the proton becoming attached to the oxygen.
- Aldehydes and ketones react with alcohols to form, first, [hemiacetals](#) and then, if excess alcohol is present, [acetals](#).



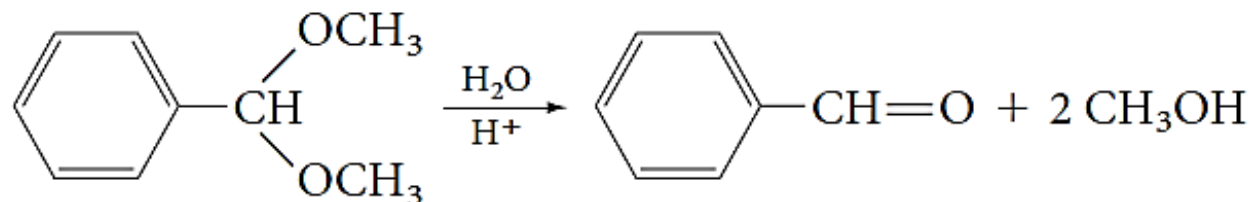
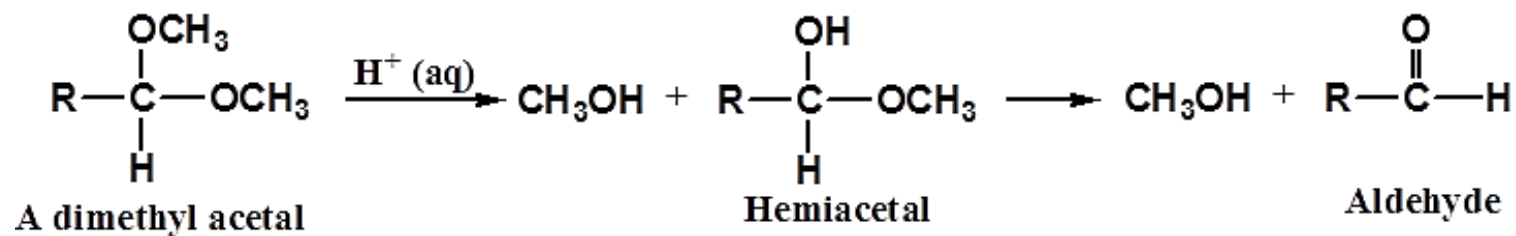
- Hemiacetals**; it contains both alcohol and ether functional groups on the same carbon atom.



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

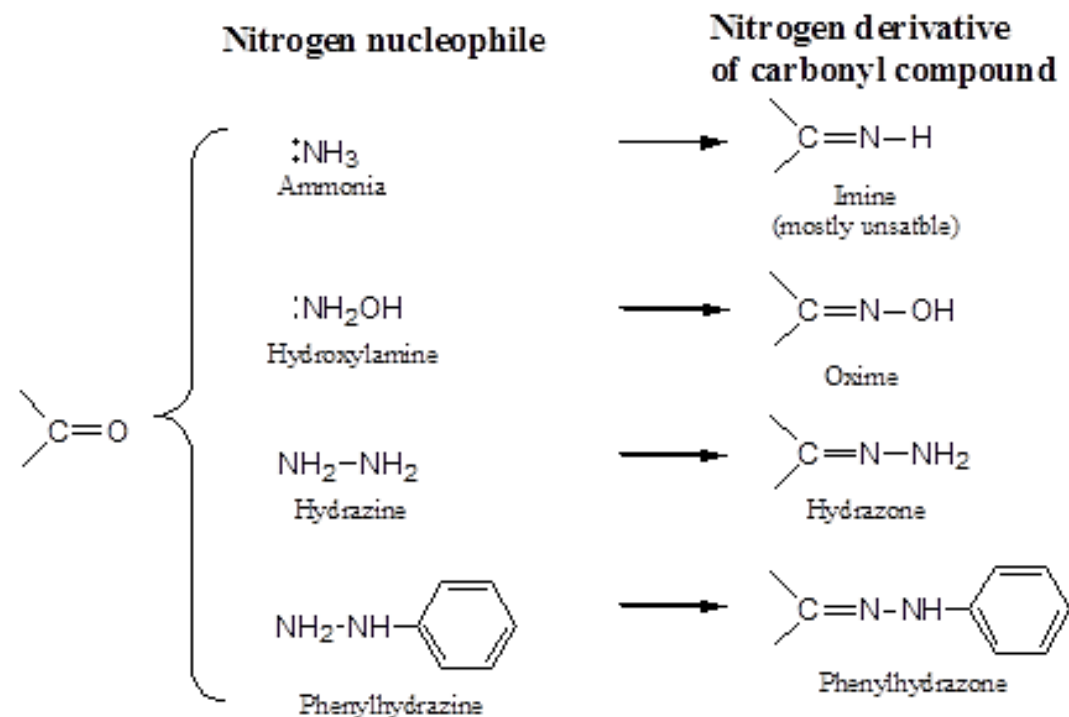
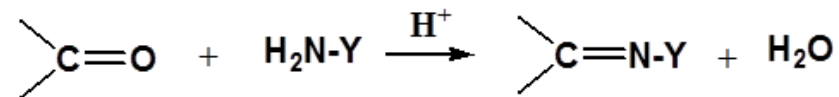


- The reverse of acetal formation, called acetal hydrolysis.
- Acetal can be hydrolyzed to its aldehyde or ketone and alcohol components by treatment with excess water in the presence of an acid catalyst.



4) Addition of Ammonia and Ammonia Derivatives

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



Uses of Aldehydes and ketones

Aldehydes and ketones find application in different sectors such as pharmaceutical, food, fragrance, cosmetics because of their chemical properties.

- ❑ **Formaldehyde** is found in the gaseous form.
 - Formaldehyde with 40% solution in water forms formalin, helps in the preservation of biological specimens.
 - It is essential during industrial processes manufacture of polymeric products.
 - It acts as germicide, insecticide, and fungicides.
 - It helps in the testing of drugs. It is also used in photography.
 - It forms with ammonia a tricyclic condensation product called methenamine (hexamethylenetetramine).

Methenamine is used for the treatment of urinary tract infection: it decomposes at an acid pH to formaldehyde and ammonia, and the formed formaldehyde is bactericidal.

The applications of aldehydes and ketones are used in different sectors such as pharmaceutical, food, fragrance, cosmetics industry.

❑ **Acetaldehyde**

- It is used for the production of acetic acid and pyridine derivatives.
- Its derivative, paraldehyde was once used as sedative and hypnotic drug.

❑ **Benzaldehyde**

- It is an essential component for the production of perfumes, cosmetic products, and dyes.
- is added to incorporate almond flavor into various food products.
- It also acts as a bee repellent.

❑ **Anisaldehyde, vanillin or cinnamaldehyde** are mainly used in cosmetics, but also in drug formulation.

❑ **Glutaraldehyde** is used to disinfect medical and dental equipment.

Therapeutic applications of aldehydes and ketones

Compound	Name in the Pharmacopoeia	Application
Aldehydes and analogues		
Formaldehyde	Formaldehydi solution (35 per centum)	antiseptic
Paraldehyde	Paraldehydum	sedative and hypnotic
Chloral hydrate	Chlorali hydras	sedative and hypnotic
Methenamine	Methenaminum	antiseptic
Vanillin	Vanillinum	flavouring additive

Ketone behaves as an excellent solvent for certain types of plastics and synthetic fibers.

❑ **Acetone**

- It act as a paint thinner and a nail paint remover.
- It is also used for medicinal purposes such as chemical peeling procedure as well as acne treatments.

❑ **Butanone**

- It is one of the common solvents.
- It is used in textile production, varnishes production, paint remover production, paraffin wax production, plastic production, etc.

❑ **Cyclohexanone** is an important component in nylon production.

❑ **Acetophenone** is responsible for fragrances such as cherry, jasmine, honeysuckle, almond, strawberry, etc.