



# Fundamentals of Organic Chemistry

## CHEM 109

*For Students of Health Colleges*

Credit hrs.: (2+1)

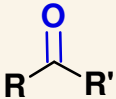
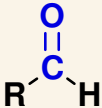
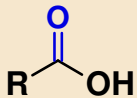
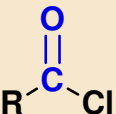
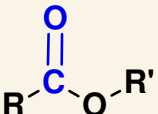
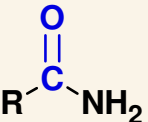
*King Saud University*

College of Science, Chemistry Department

# Common Classes of Carbonyl Compounds

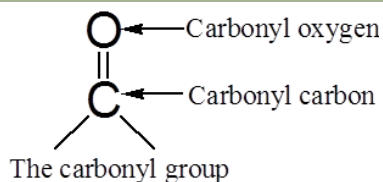


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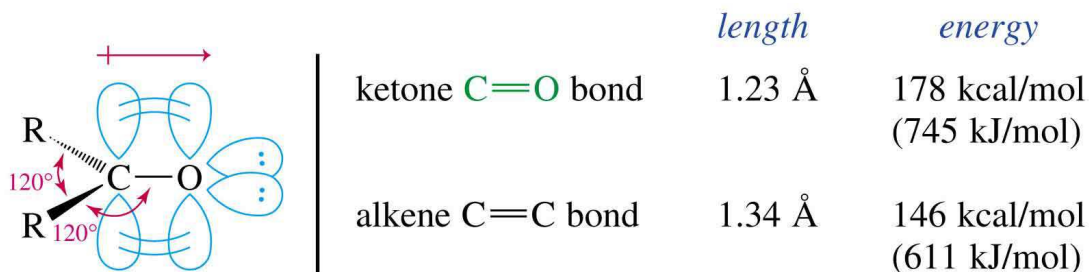
Class	General Formula	Class	General Formula
Ketones		Aldehydes	
Carboxylic acids		Acid Chlorides	
Esters		Amides	

# The Carbonyl Group

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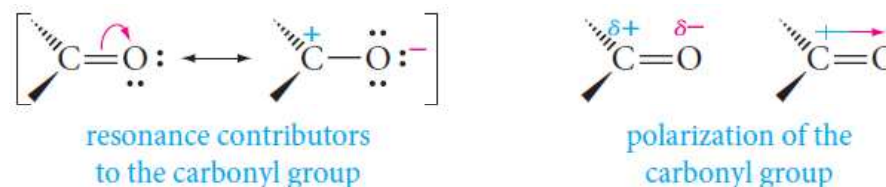
- The carbon–oxygen double bond consists of a sigma bond and a pi bond.
- The carbon atom is  $sp^2$ -hybridized.
- The three atoms attached to the carbonyl carbon lie in a plane with bond angles of  $120^\circ$ .
- The pi bond is formed by overlap of a  $p$  orbital on carbon with an oxygen  $p$  orbital.
- 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).



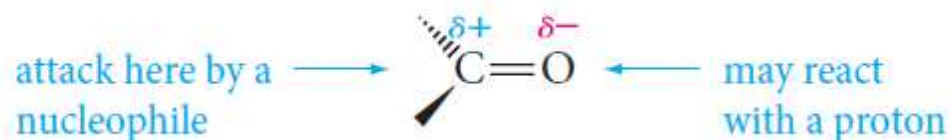
# The Carbonyl Group

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- 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**.

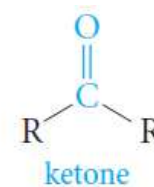
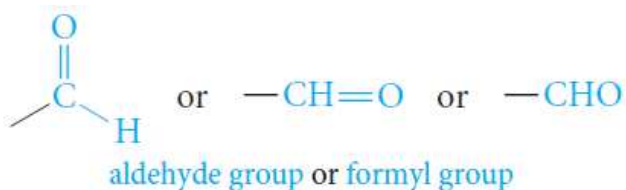
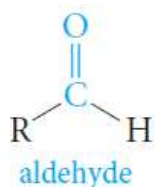


- As a consequence of this polarization, *most carbonyl reactions involve nucleophilic attack at the carbonyl carbon*, often accompanied by addition of a proton to the oxygen (electron rich).



# 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.

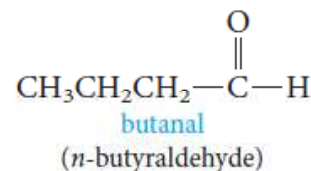
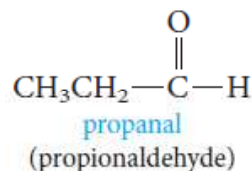
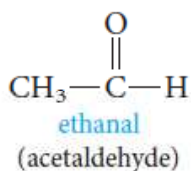
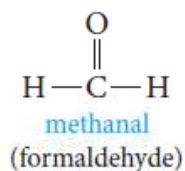


## IUPAC System

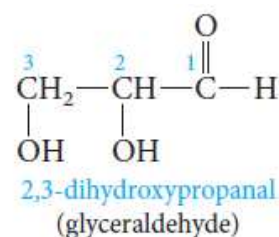
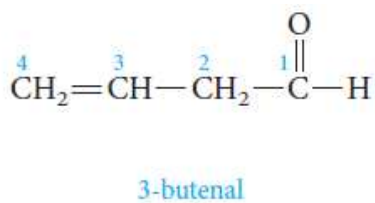
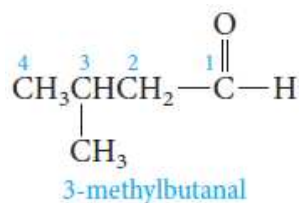
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- **Aliphatic aldehydes** are named by dropping the suffix **-e** from the name of the hydrocarbon that has the same carbon skeleton as the aldehyde and replacing it with the suffix **-al**.

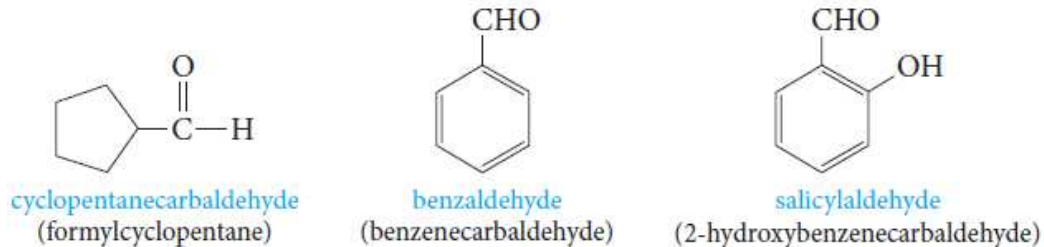
**Alkane - e + al = Alkanal**



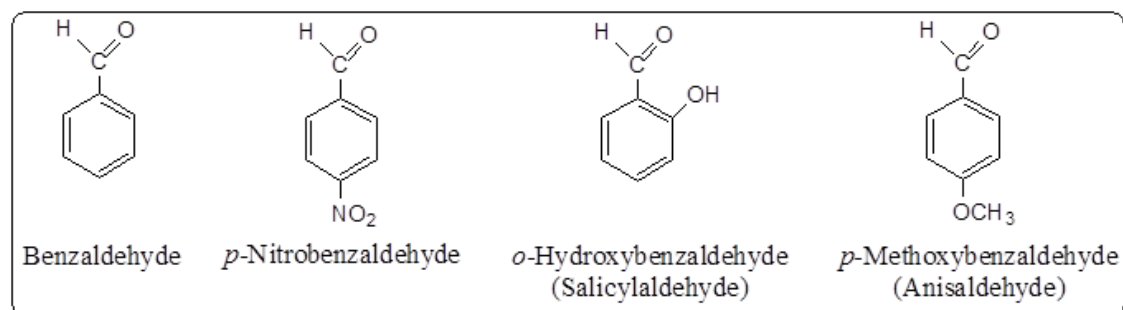
- **Substituted aldehydes**, we number the chain starting with the aldehyde carbon.
  - **-CH=O group** is assigned the number **1 position**.
  - Aldehyde group has priority over a double bond or hydroxyl group.



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



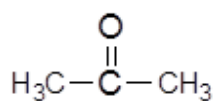
- Aromatic aldehydes** are usually designated as derivatives of the simplest aromatic aldehyde, **benzaldehyde**.



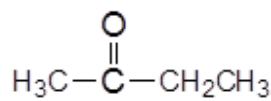
## Common Names

# Nomenclature of Aldehydes

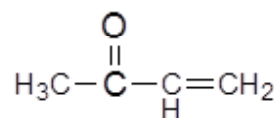
- Common names of ketones are formed by adding the word *ketone* to the names of the alkyl or aryl groups attached to the carbonyl carbon. **Alkyl ketone.**
- In still other cases, traditional names are used.



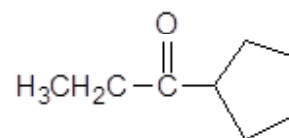
Acetone  
(Dimethyl ketone)



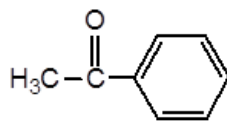
Ethyl methyl ketone



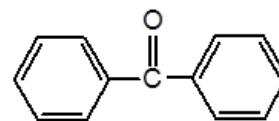
Methyl vinyl ketone



Cyclopentyl ethyl ketone



Methyl phenyl ketone  
(Acetophenone)



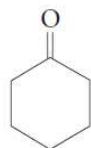
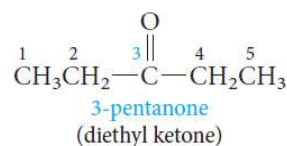
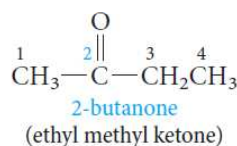
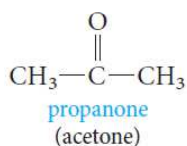
Diphenyl ketone  
(Benzophenone)



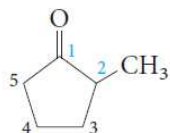
## IUPAC Names

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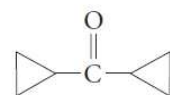
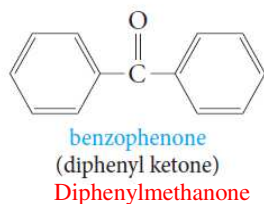
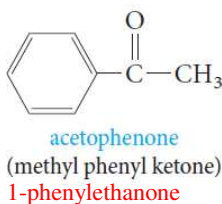
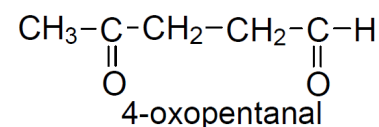
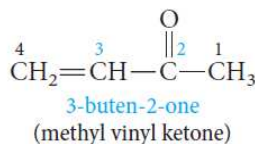
- In the IUPAC system, **the ending for ketones is -one.**
- The chain is numbered so that the **carbonyl carbon has the lowest possible number.**
- For **cyclic ketones**, numbering always starts from the C=O group.
- The prefix "**oxo**" is used when the ketone is not the principal functional group.



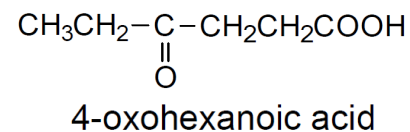
cyclohexanone



2-methylcyclopentanone



dicyclopropyl ketone  
Dicyclopropylmethanone



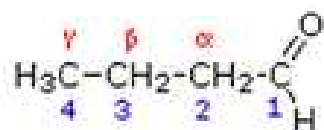
## NOTES

# Nomenclature of Aldehydes and Ketones

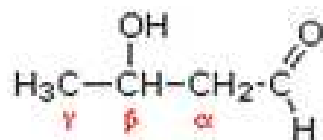
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- **In common names** carbon atoms near the carbonyl group are often designated by **Greek letters**.
- The atom adjacent to the function is *alpha* ( $\alpha$ ), the next removed is *beta* ( $\beta$ ) and so on. Since ketones have two sets of neighboring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

### Aldehydes

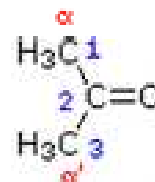


butanal  
butyraldehyde



3-hydroxybutanal  
 $\beta$ -hydroxybutyraldehyde  
or **aldol**

### Ketones



propanone  
acetone



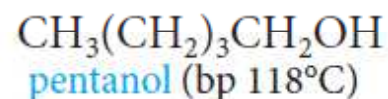
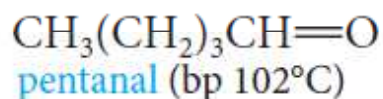
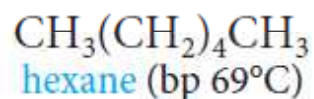
2-bromo-4,4-dimethylcyclohexanone

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

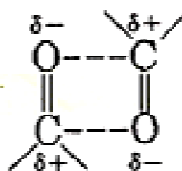
# Physical Properties of Aldehydes and Ketones

## 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.

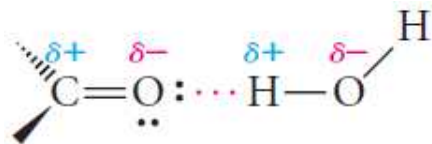


Dipole-dipole attractions among carbonyl compounds

# Physical Properties of Aldehydes and Ketones

## Solubility

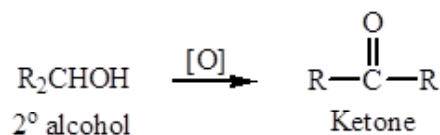
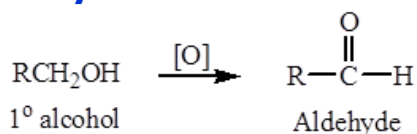
- Carbonyl compounds as aldehydes and ketones have a C=O bond, but no O-H bond, cannot form hydrogen bonds with themselves.
- The polarity of the carbonyl group also affects the solubility properties of aldehydes and ketones.
- Carbonyl compounds with low molecular weights are soluble in water as they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



# Preparation of Aldehydes and Ketones

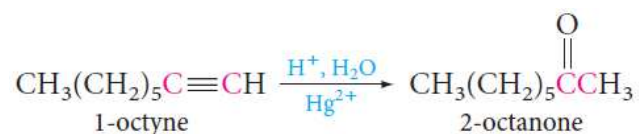


## 1) Oxidation of Primary and Secondary Alcohols

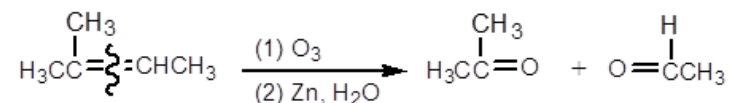
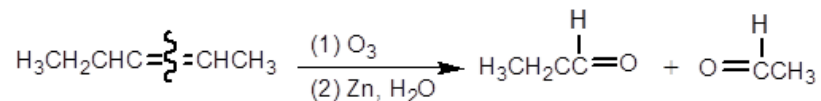


## 2) Hydration of Alkynes

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



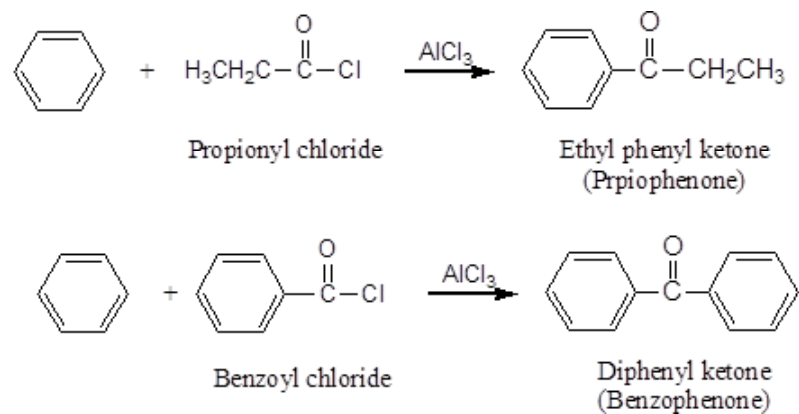
## 3) Ozonolysis of Alkenes



# Preparation of Aldehydes and Ketones

## 4) Friedel-Crafts Acylation

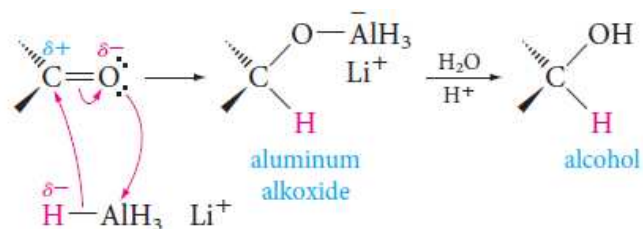
Preparing ketones that contain an aromatic ring.



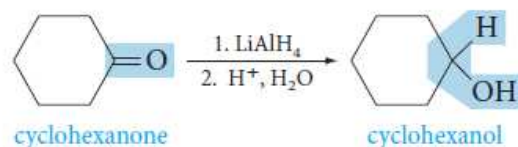
## A) Reduction of Carbonyl Compounds

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- 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 ( $\text{LiAlH}_4$ ) and sodium borohydride ( $\text{NaBH}_4$ ).



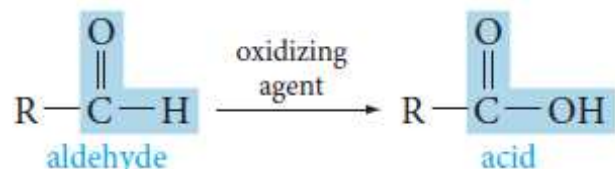
### ○ Example:



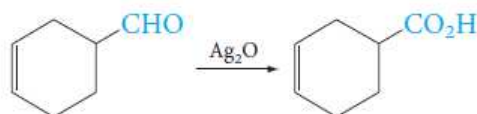
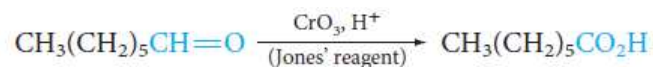
## B) Oxidation of Carbonyl Compounds

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- Oxidation of aldehydes gives a carboxylic acid with the same number of carbon atoms.
- Because the reaction occurs easily, many oxidizing agents, such as  $\text{KMnO}_4$ ,  $\text{CrO}_3$ ,  $\text{Ag}_2\text{O}$  and peracids will work.



### ○ Example:



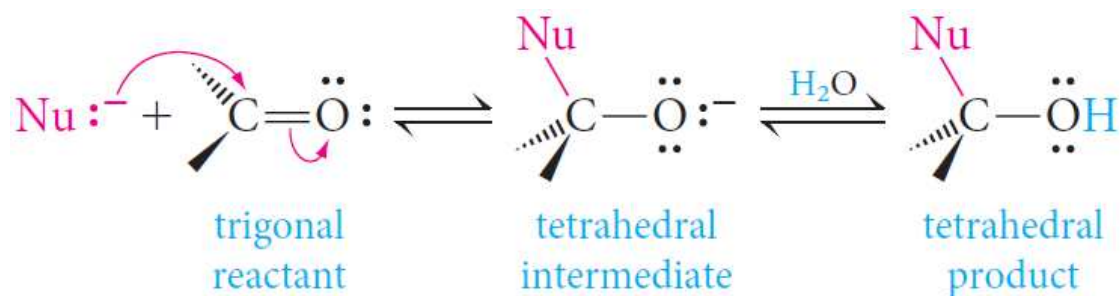




## C) Nucleophilic Addition Reactions

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- 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).

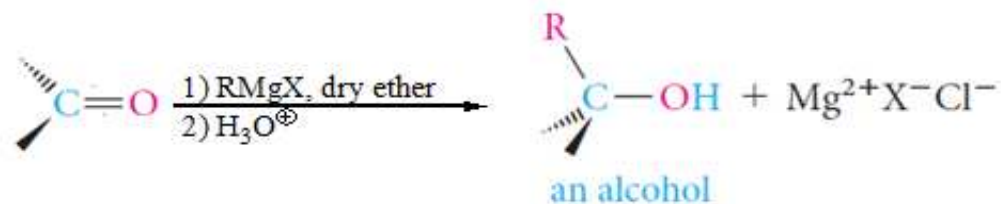
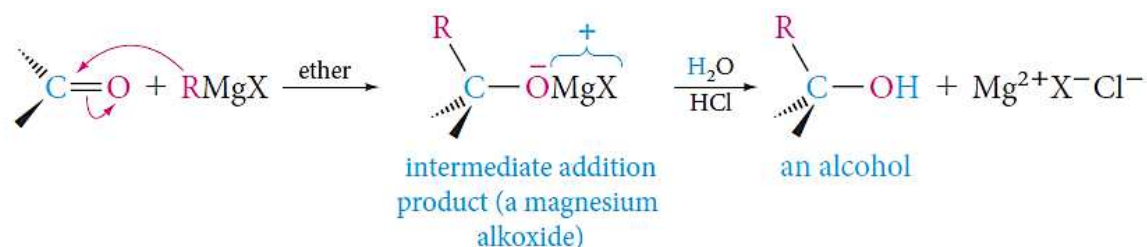


## C) Nucleophilic Addition Reactions

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### 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.



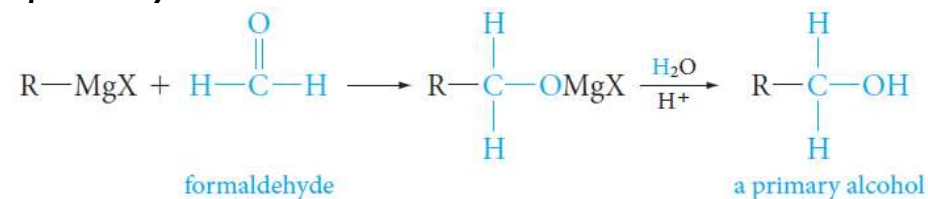
- The type of carbonyl compound chosen determines the class of alcohol produced.

## C) Nucleophilic Addition Reactions

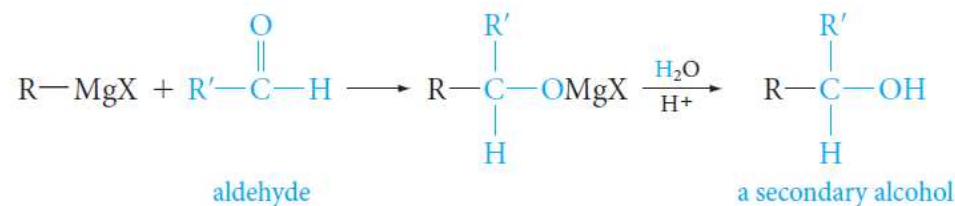
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### 1) Addition of Grignard Reagents: Formation of Alcohols

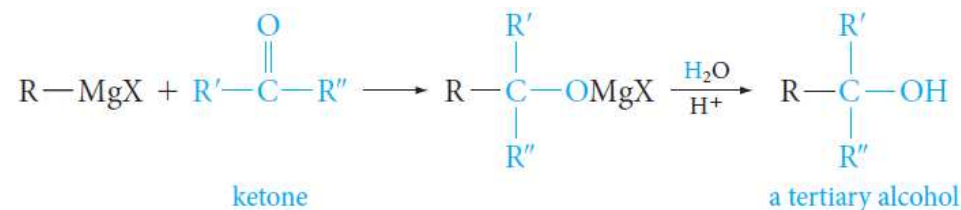
- Formaldehyde gives primary alcohols.



- Other aldehydes give secondary alcohols



- Ketones give tertiary alcohols.





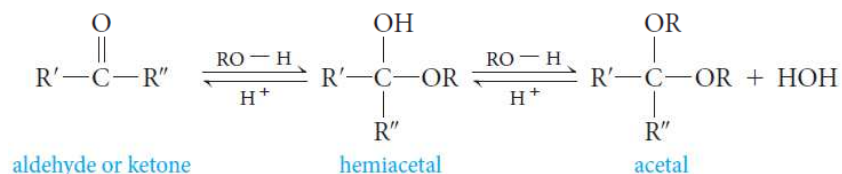


## C) Nucleophilic Addition Reactions

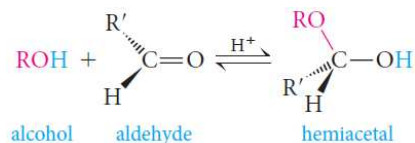
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### 3) Addition of Alcohols: Formation of Hemiacetals and Acetals

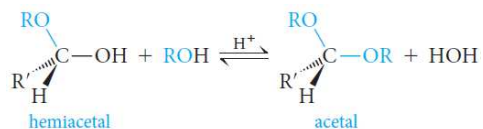
- Alcohols add to the C=O bond, the OR group becoming attached to the carbon and the proton becoming attached to the oxygen.
- Aldehydes and ketones react with alcohols to form, first, hemiacetals and then, if excess alcohol is present, acetals.



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



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



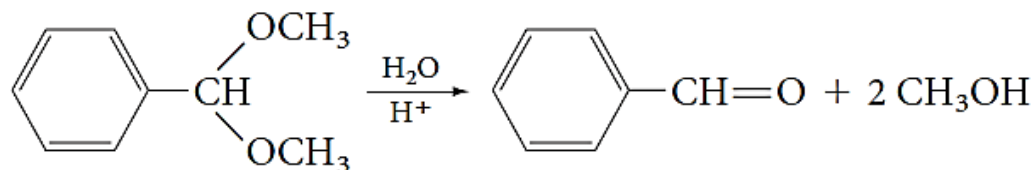
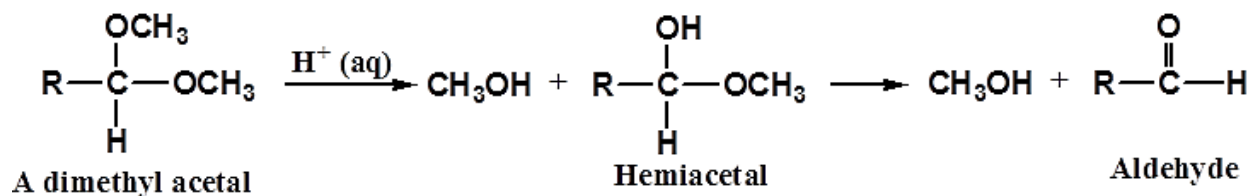


## C) Nucleophilic Addition Reactions

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### 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.



## C) Nucleophilic Addition Reactions

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### 4) Addition of Ammonia and Ammonia Derivatives

The addition of nitrogen nucleophile, such as ammonia ( $\text{NH}_3$ ) and substituted ammonia ( $\text{NH}_2\text{-Y}$ ).

