Fundamentals of Organic Chemistry

CHEM 108

King Saud University

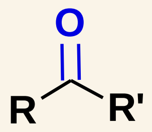
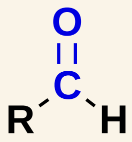
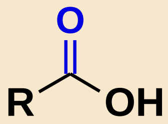
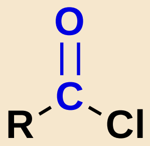
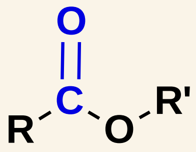
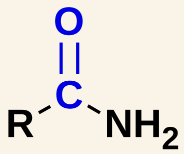
College of Science, Chemistry Department

CHEM 108

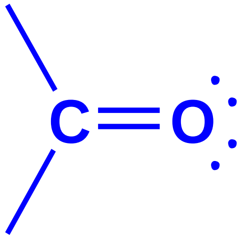
CHAPTER 5. ALDEHYDES & KETONES

Aldehydes & Ketones

Common Classes of Carbonyl Compounds

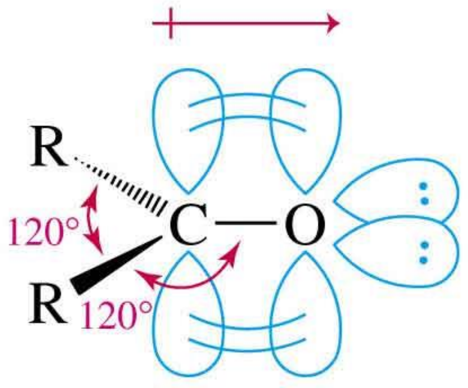
Class	General Formula	Class	General Formula
Ketones		Aldehydes	
Carboxylic acids		Acid Chlorides	
Esters		Amides	

Aldehydes & Ketones



The carbonyl group

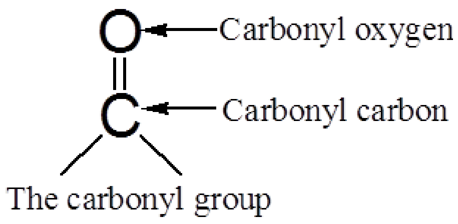
- Carbon is ***sp***^{2} **hybridized**.
- **C=O bond** is shorter, stronger, and more polar than C=C bond in alkenes.



	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)

Structure of Aldehydes and Ketones

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

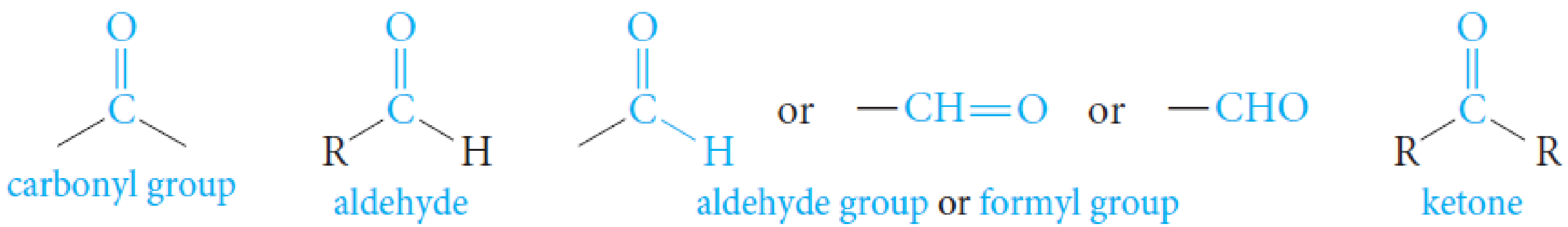


- **Aldehydes** have at least one hydrogen atom attached to the carbonyl carbon atom.

  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.

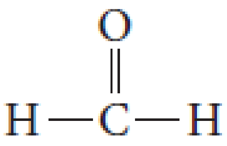


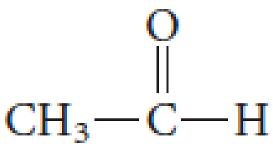
Nomenclature of Aldehydes

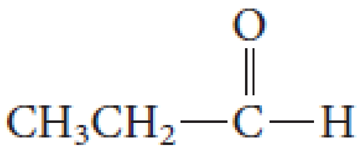
IUPAC System

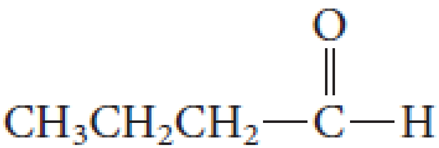
- *Aliphatic aldehydes* ***are named by dropping the suffix -e from the name of the hydrocarbon that has the same carbon skeleton as the aldehyde and replacing it with the suffix -al.***

Alkane - e+ *al = Alkanal*


methanal
(formaldehyde)


ethanal
(acetaldehyde)

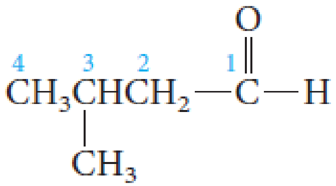

propanal
(propionaldehyde)


butanal
(*n*-butyraldehyde)

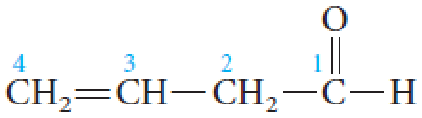
Nomenclature of Aldehydes

IUPAC System

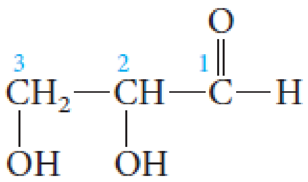
- ***Substituted aldehydes,*** *we number the chain starting with the aldehyde carbon.*
  - *-CH=O group is assigned the number 1 position.*
  - *Aldehyde group has priority over a double bond or hydroxyl group.*



3-methylbutanal

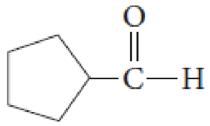


3-butenal

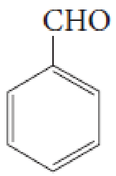


2,3-dihydroxypropanal
(glyceraldehyde)

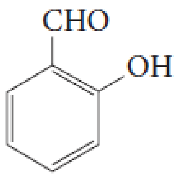
- ***Cyclic aldehydes,*** *the suffix –carbaldehyde is used.*



cyclopentanecarbaldehyde
(formylcyclopentane)



benzaldehyde
(benzenecarbaldehyde)

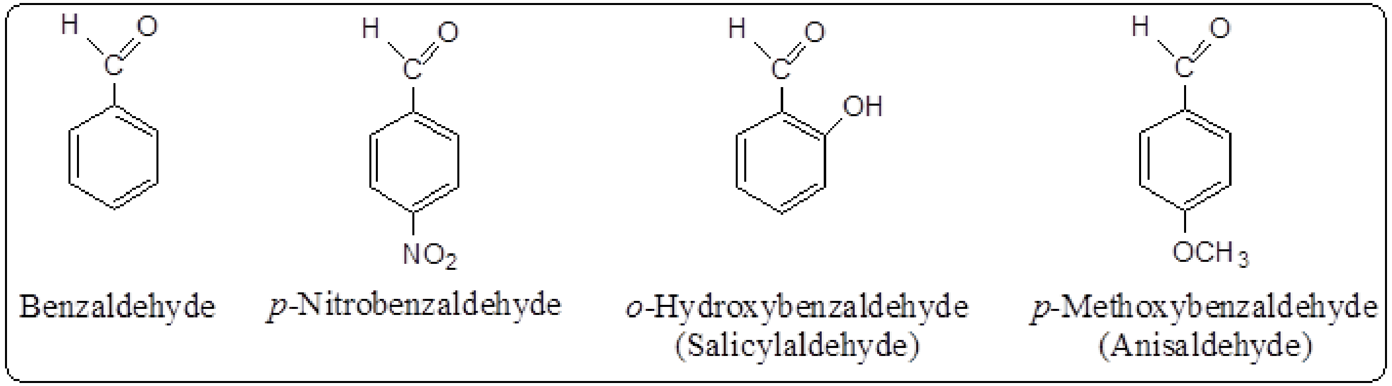


salicylaldehyde
(2-hydroxybenzenecarbaldehyde)

Nomenclature of Aldehydes

IUPAC System

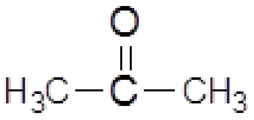
- ***Aromatic aldehydes*** *are usually designated as derivatives of the simplest aromatic aldehyde,* *benzaldehyde*.



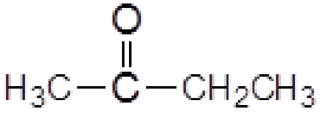
Nomenclature of Aldehydes

Common Names

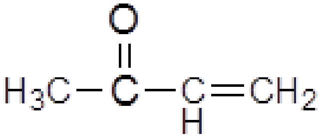
- Common names of ketones are formed by adding the word *ketone* to the names of the alkyl or aryl groups attached to the carbonyl carbon. Alkyl ketone.
- In still other cases, traditional names are used.



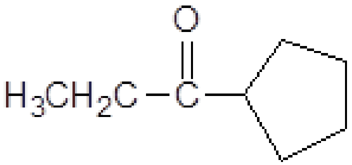
Acetone
(Dimethyl ketone)



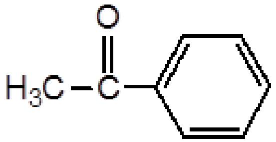
Methyl ethyl ketone



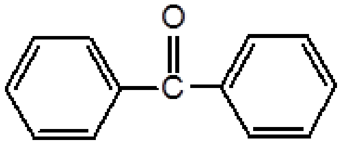
Methyl vinyl ketone



Ethyl cyclopentyl ketone



Methyl phenyl ketone
(Acetophenone)

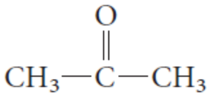


Diphenyl ketone
(Benzophenone)

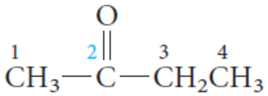
Nomenclature of Ketones

IUPAC System

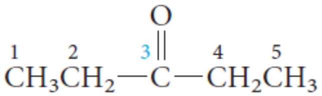
- In the IUPAC system, the ending for ketones is -one.
- The chain is numbered so that the carbonyl carbon has the lowest possible number.
- For cyclic ketones, numbering always starts from the C=O group.
- The prefix "oxo" is used when the ketone is not the principal functional group.



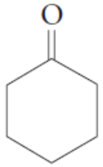
propanone
(acetone)



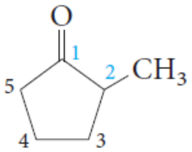
2-butanone
(ethyl methyl ketone)



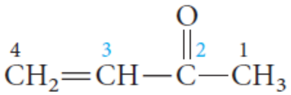
3-pentanone
(diethyl ketone)



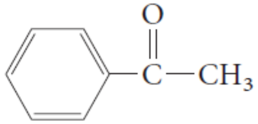
cyclohexanone



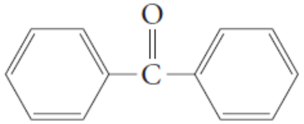
2-methylcyclopentanone



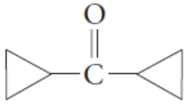
3-buten-2-one
(methyl vinyl ketone)



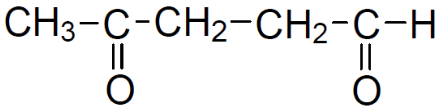
acetophenone
(methyl phenyl ketone)



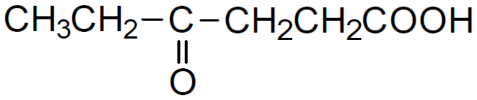
benzophenone
(diphenyl ketone)



dicyclopropyl ketone



4-oxopentanal

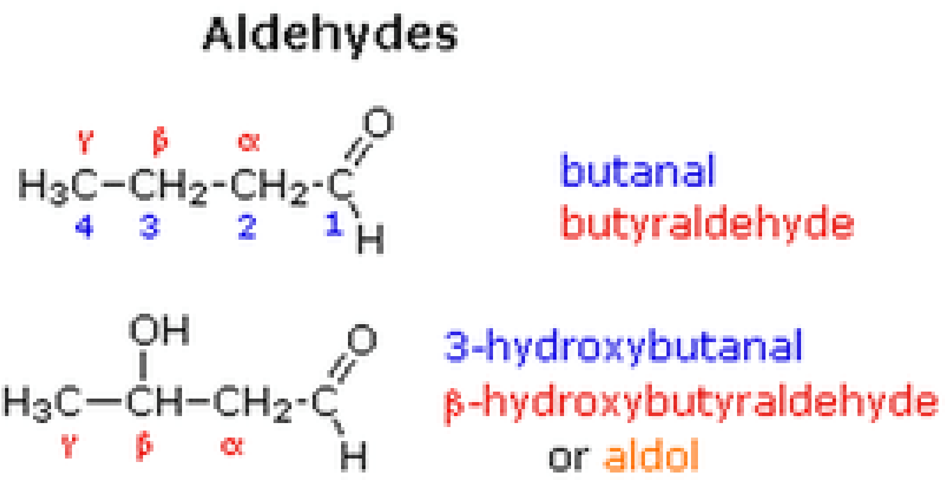


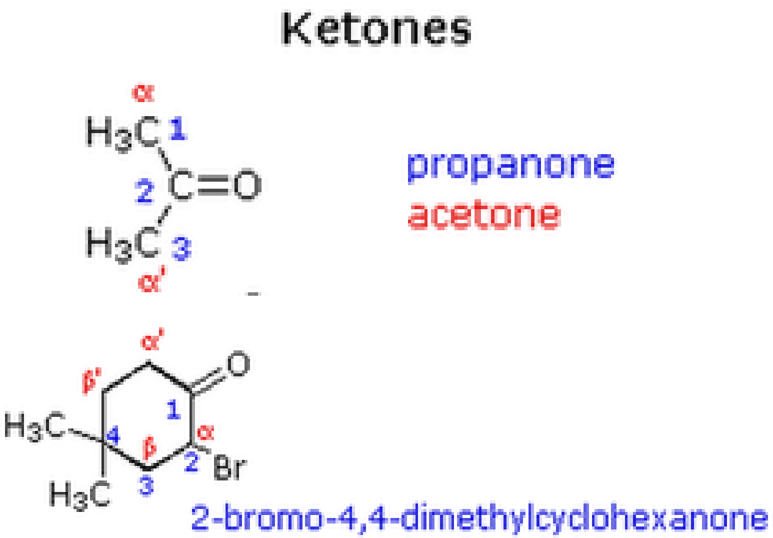
4-oxohexanoic acid

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.



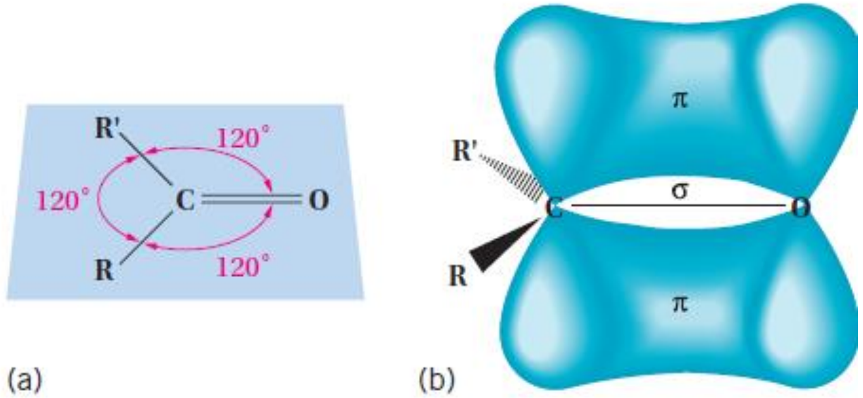


- **The functional group priority order in nomenclature system** is as following:

  Acid and derivatives >aldehyde> ketone> alcoho > amine > alkene > alkyne > ether

The Carbonyl Group

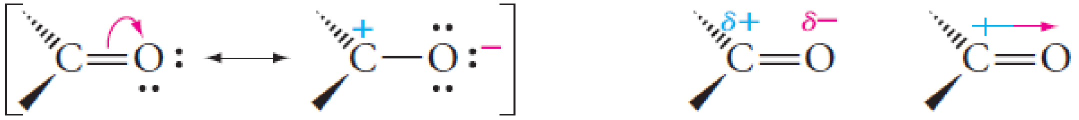
- **The structure and properties of the carbonyl group.**
  - The carbon–oxygen double bond consists of a sigma bond and a pi bond.
  - The carbon atom is sp^2-hybridized. The three atoms attached to the carbonyl carbon lie in a plane with bond angles of 120°.
  - The pi bond is formed by overlap of 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) .



(a) (b)

The Carbonyl Group

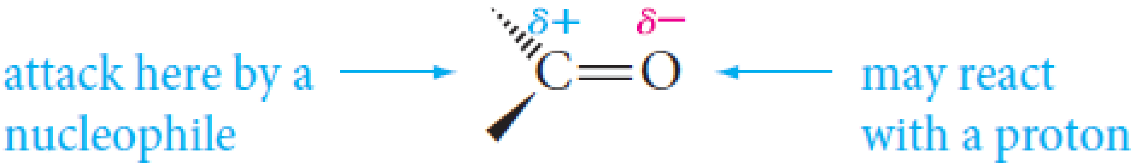
- Oxygen is much more electronegative than carbon. Therefore, the electrons in the C=O bond are attracted to the oxygen, producing a highly polarized bond.



resonance contributors to the carbonyl group

polarization of the carbonyl group

- 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).



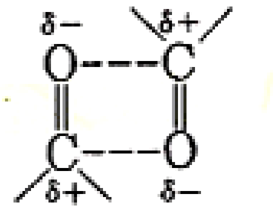
Physical Properties of Aldehydes and Ketones

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.

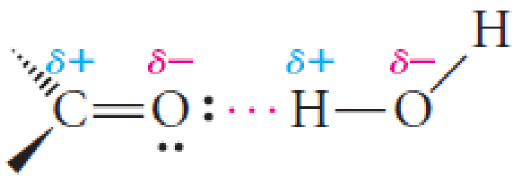


Dipole-dipole attractions among carbonyl compounds

Physical Properties of Aldehydes and Ketones

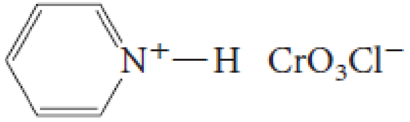
Solubility

- 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.



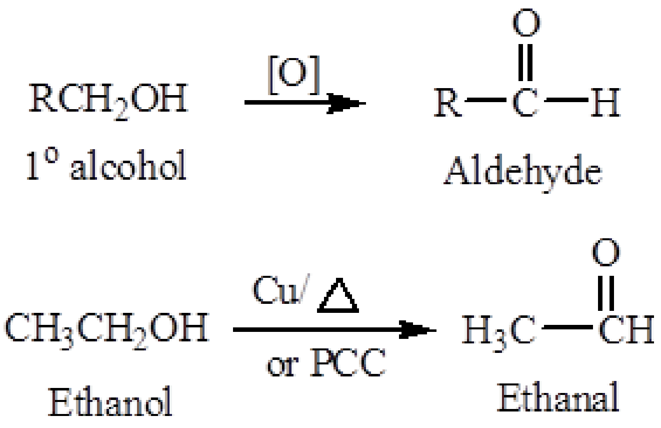
1) Oxidation of Primary and Secondary Alcohols

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



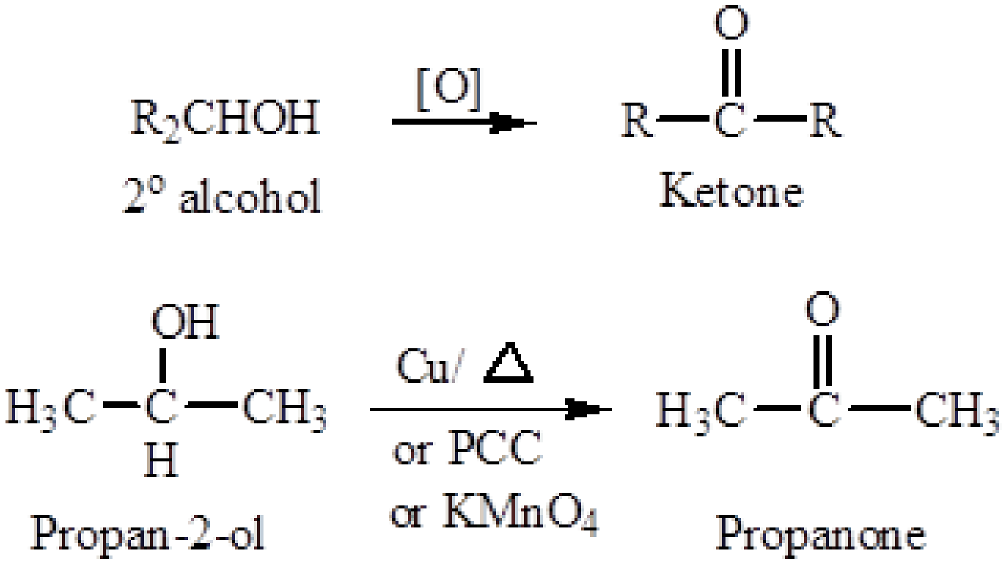
pyridinium chlorochromate
(PCC)

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



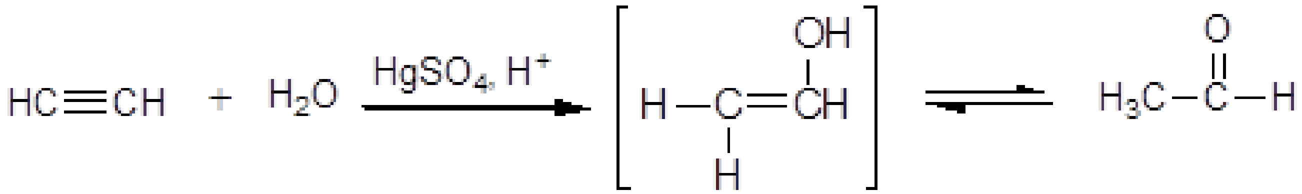
1) Oxidation of Primary and Secondary Alcohols

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



2) Hydration of Alkynes

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

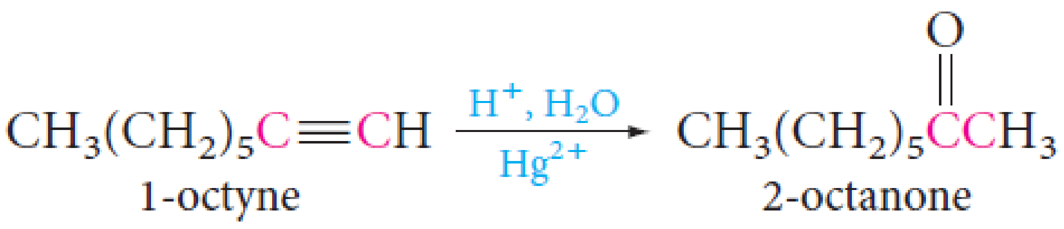


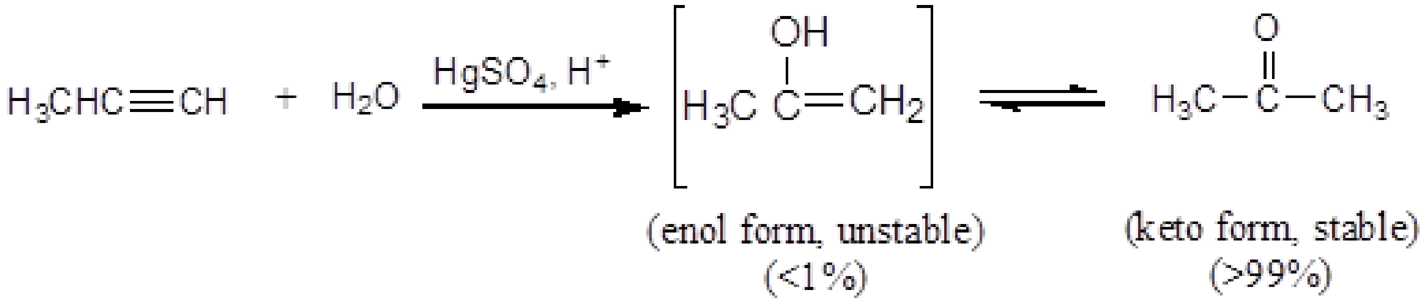
Vinyl alcohol
(enol form of acetaldehyde, unstable) (<1%)

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

2) Hydration of Alkynes

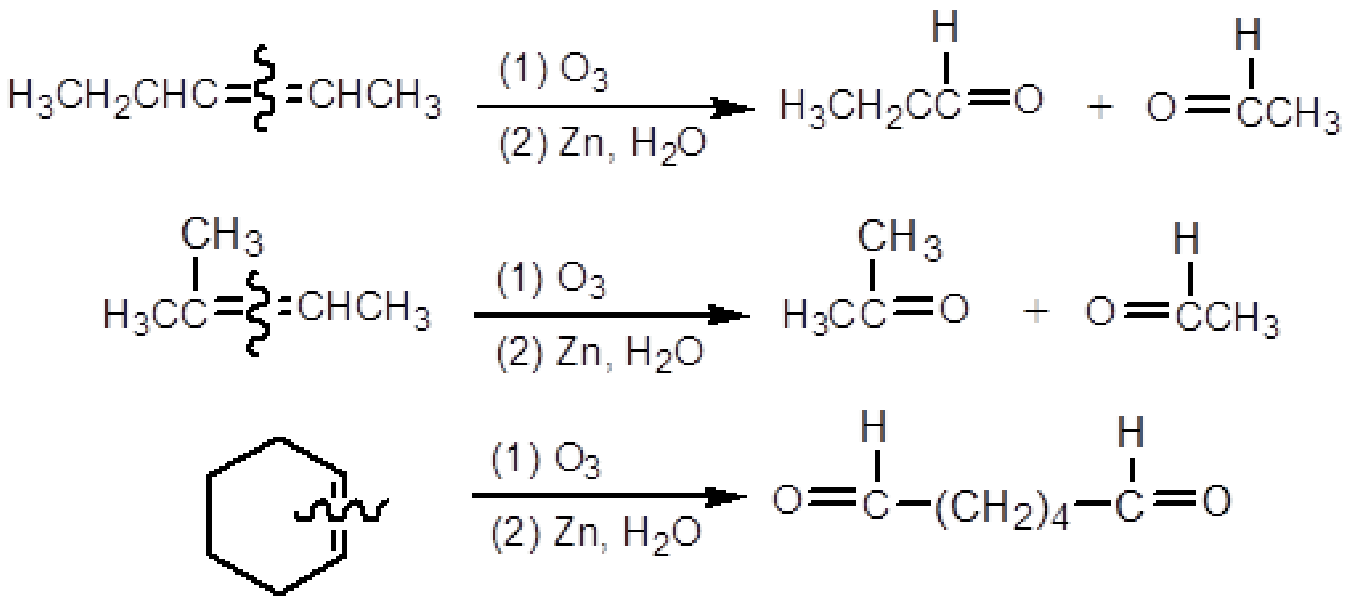
- Hydration of terminal alkynes EXCEPT acetylene yields ketones (catalyzed by acid and mercuric).





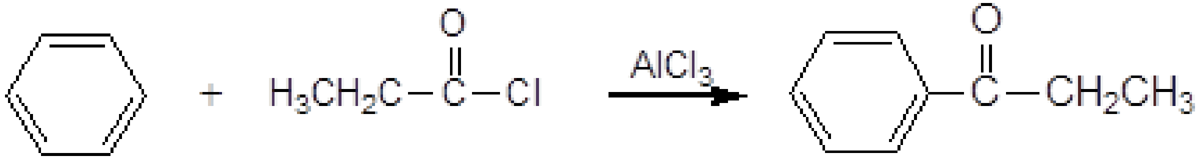
3) Ozonolysis of Alkenes

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



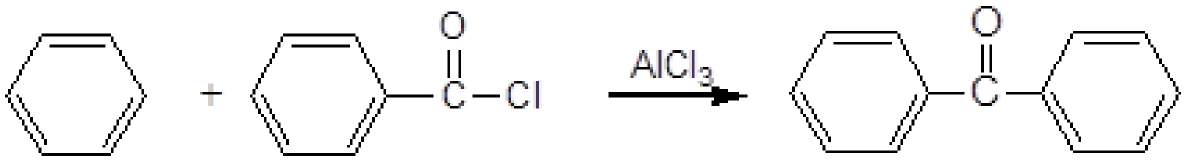
4) Friedel-Crafts Acylation

Preparing ketones that contain an aromatic ring.



Propionyl chloride

Ethyl phenyl ketone (Prpiophenone)

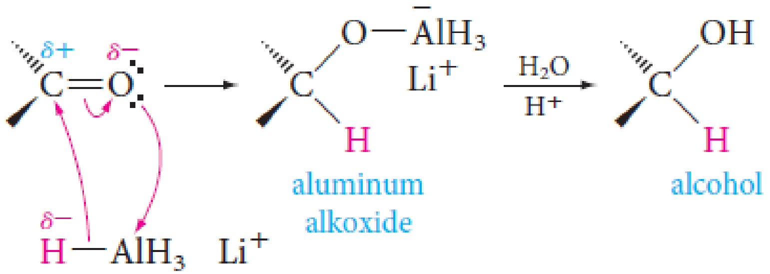


Benzoyl chloride

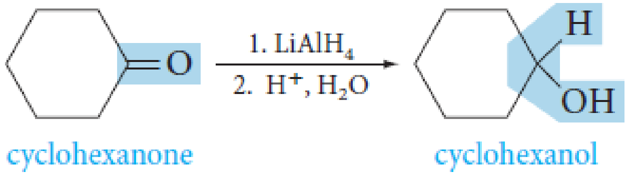
Diphenyl ketone (Benzophenone)

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 ($NaBH_4$).

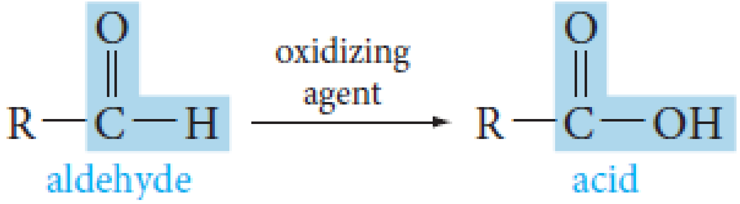


- **Example:**



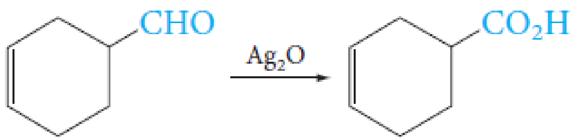
B) Oxidation of Carbonyl Compounds

- 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.



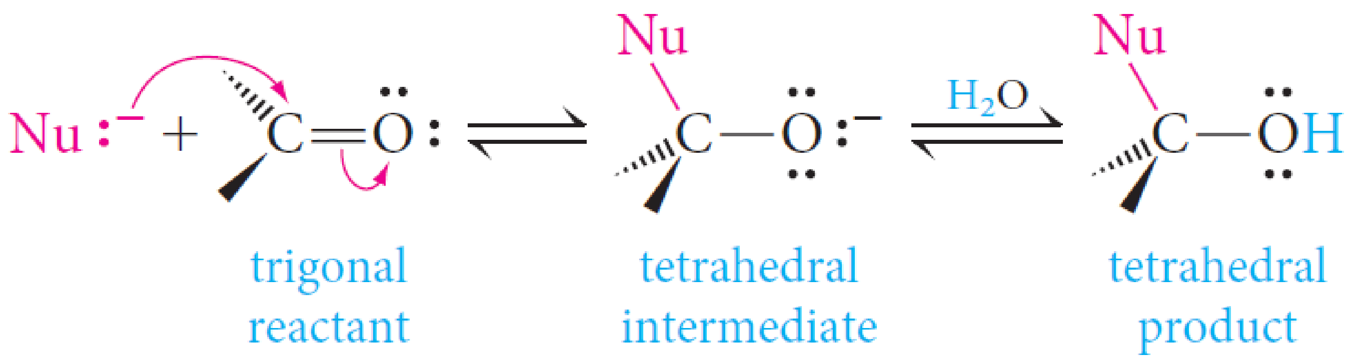
- **Example:**

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



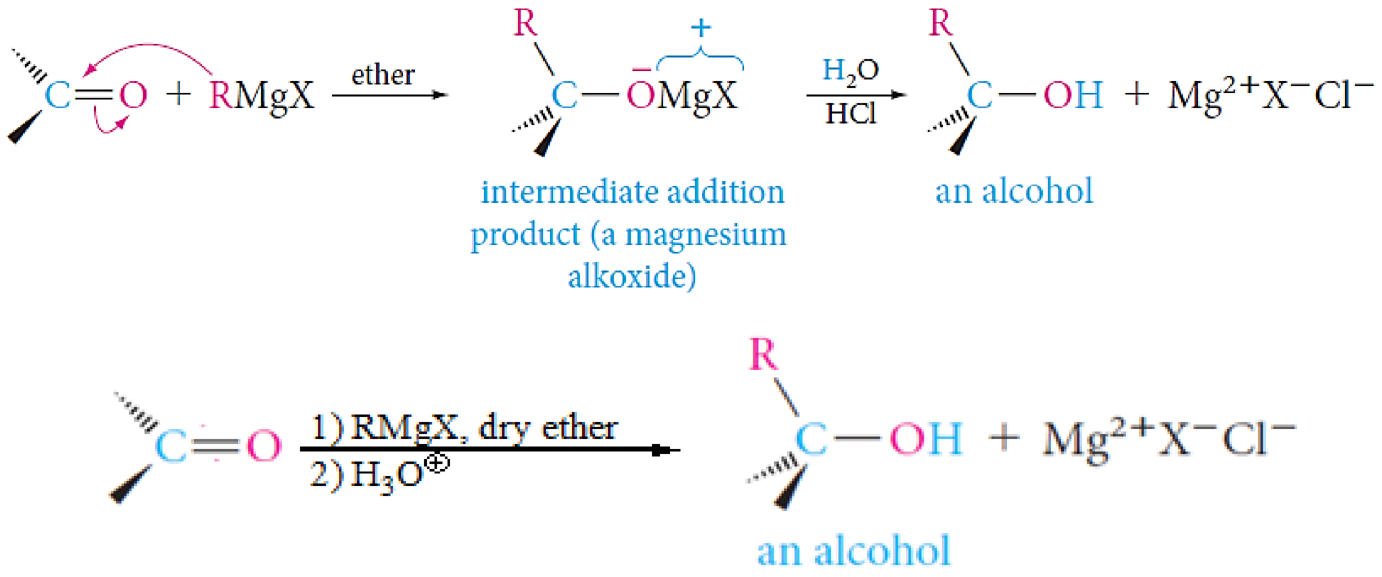
C) Nucleophilic Addition Reactions

- 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.

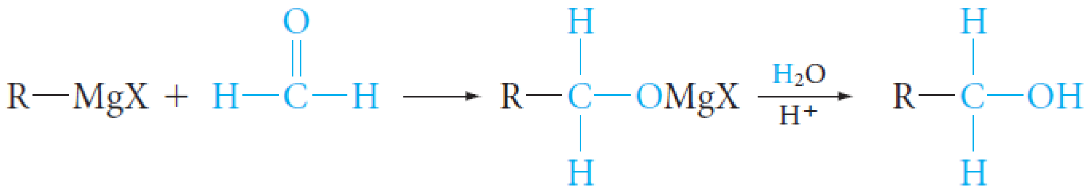


- The type of carbonyl compound chosen determines the class of alcohol produced.

C) Nucleophilic Addition Reactions

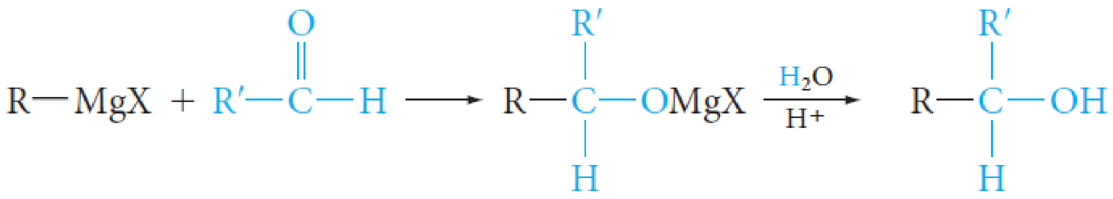
1) Addition of Grignard Reagents: Formation of Alcohols

- *Formaldehyde gives primary alcohols.*



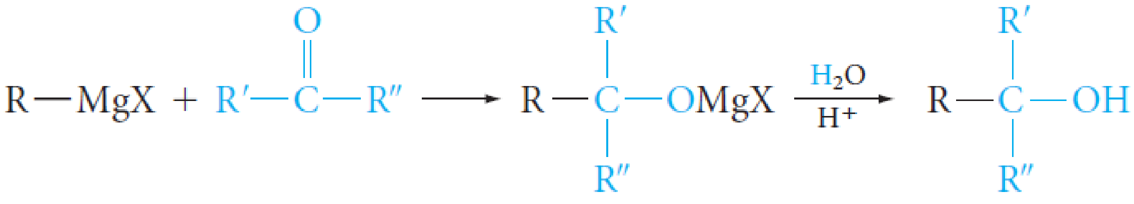
formaldehyde   a primary alcohol

- *Other aldehydes give secondary alcohols*



aldehyde   a secondary alcohol

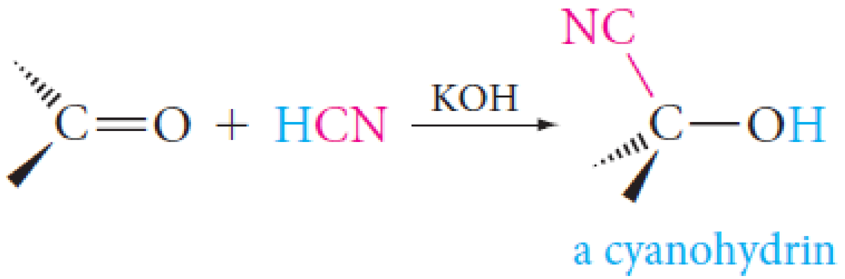
- *Ketones give tertiary alcohols.*



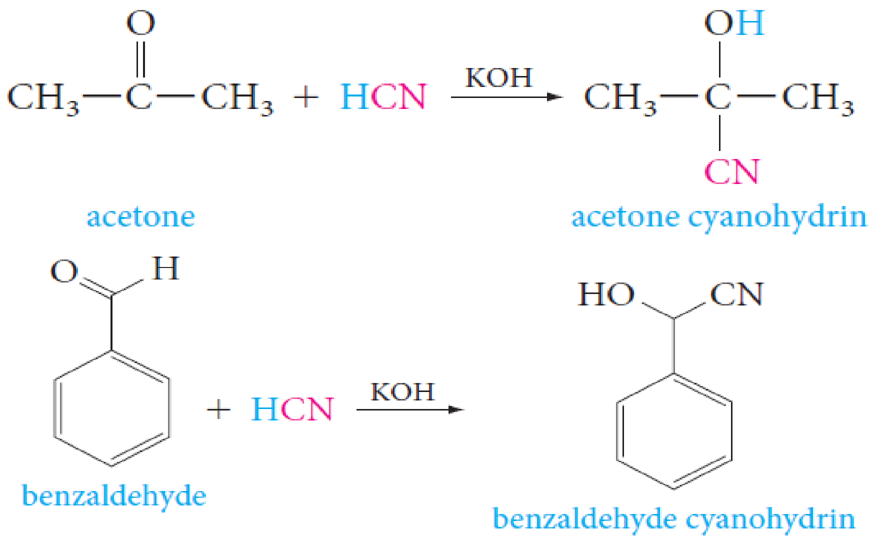
ketone   a tertiary alcohol

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.



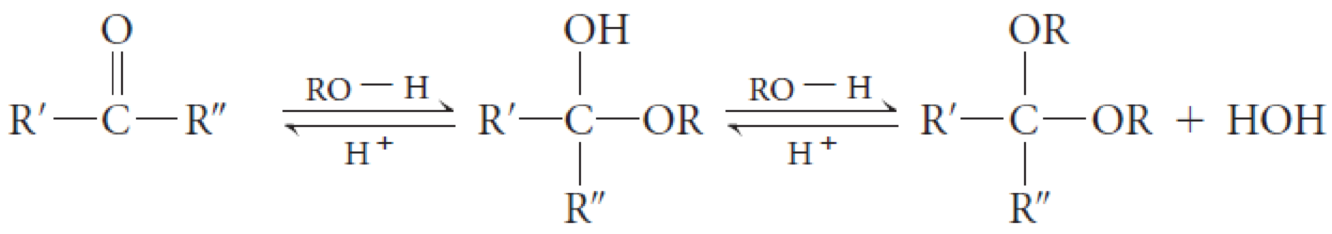
- **Example**



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.

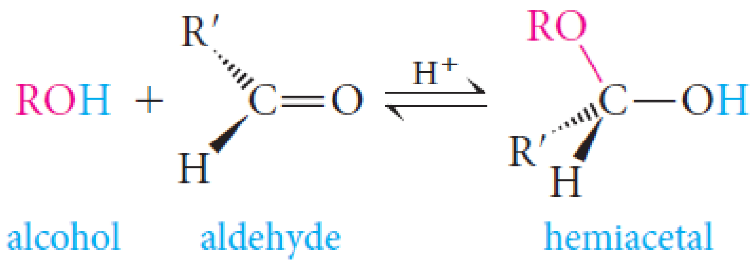


aldehyde or ketone — hemiacetal — acetal

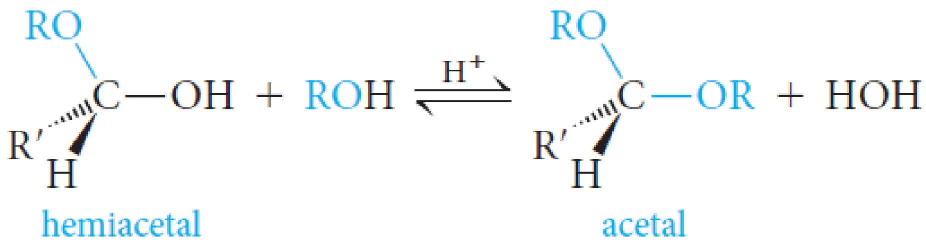
C) Nucleophilic Addition Reactions

3) Addition of Alcohols: Formation of Hemiacetals and Acetals

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

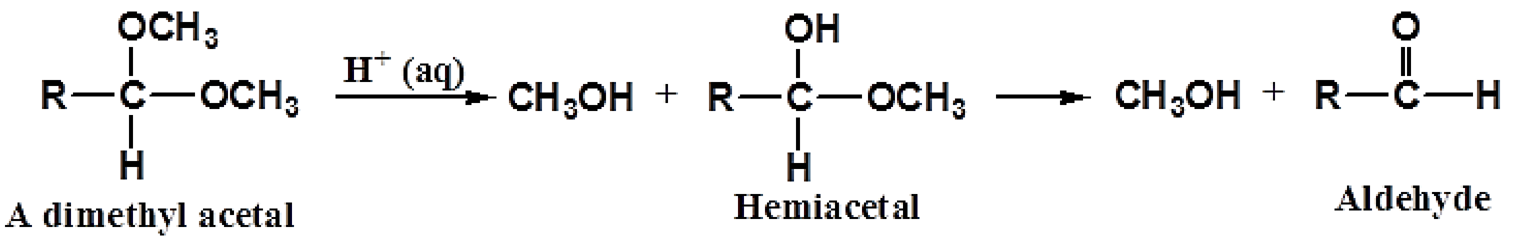


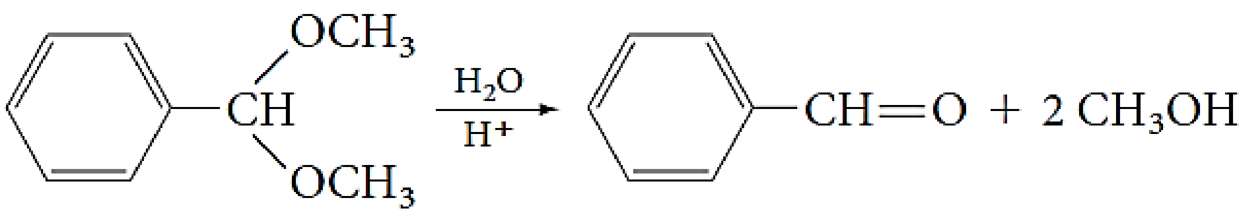
- **Acetals** have two ether functions at the same carbon atom.



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

4) Addition of Ammonia and Ammonia Derivatives

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