Fundamentals of Organic Chemistry

CHEM 109

For Students of Health Colleges

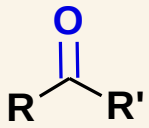
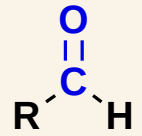
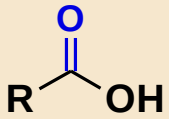
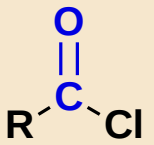
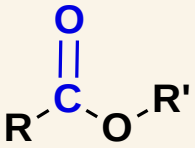
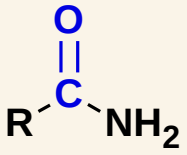
Credit hrs.: (2+1)

King Saud University

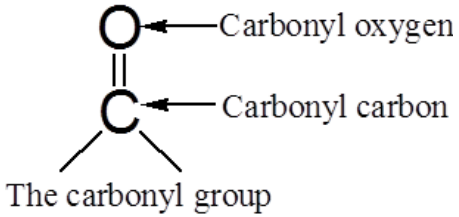
College of Science, Chemistry Department

CHAPTER 5. ALDEHYDES & KETONES

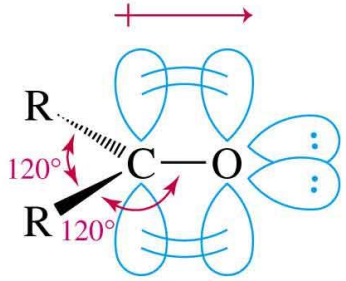
Common Classes of Carbonyl Compounds

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

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).



	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)

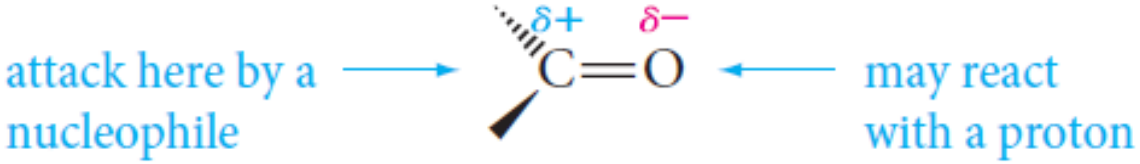
The Carbonyl Group

- 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).



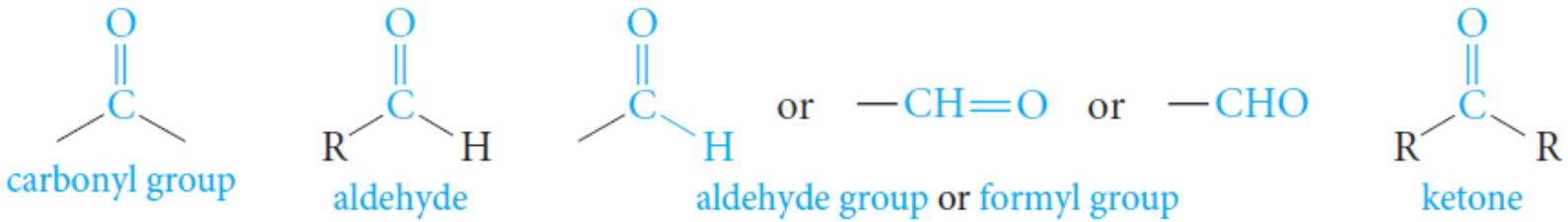
Structure of Aldehydes and Ketones

- **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.

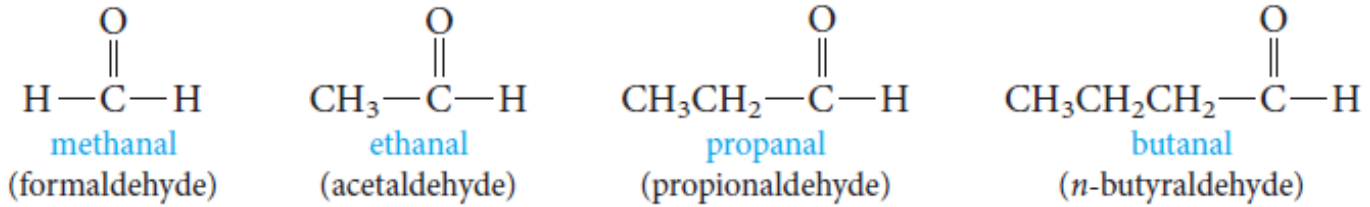


Nomenclature of Aldehydes

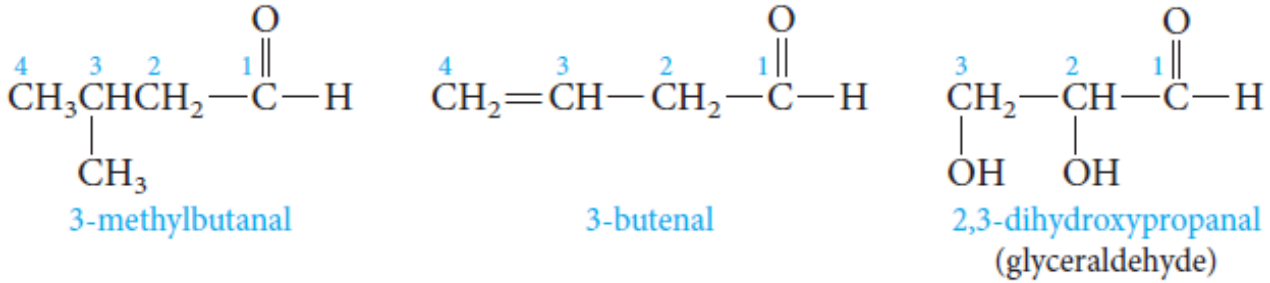
IUPAC System

- ***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*



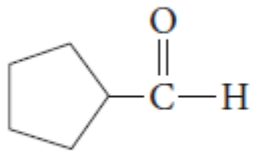
- ***Substituted aldehydes,*** *we number the chain starting with the aldehyde carbon.*
  - *-CH=O group is assigned the number 1 position.*
  - *Aldehyde group has priority over a double bond or hydroxyl group.*



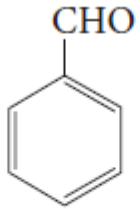
Nomenclature of Aldehydes

IUPAC System

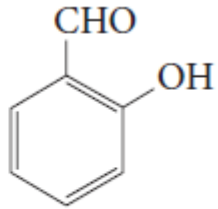
- ***Cyclic aldehydes,*** *the suffix –carbaldehyde is used.*



cyclopentanecarbaldehyde
(formylcyclopentane)

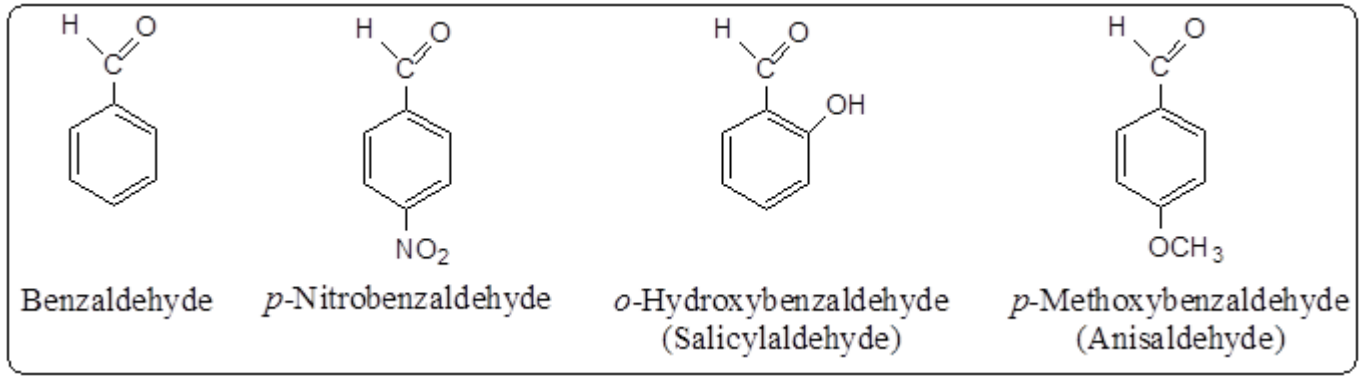


benzaldehyde
(benzenecarbaldehyde)



salicylaldehyde
(2-hydroxybenzenecarbaldehyde)

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



Benzaldehyde

p-Nitrobenzaldehyde

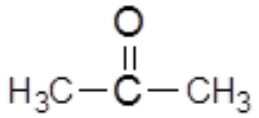
o-Hydroxybenzaldehyde
(Salicylaldehyde)

p-Methoxybenzaldehyde
(Anisaldehyde)

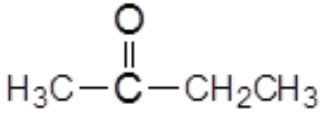
Nomenclature of Aldehydes

Common Names

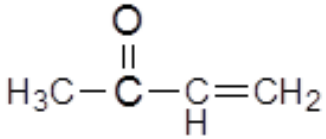
- Common names of ketones are formed by adding the word *ketone* to the names of the alkyl or aryl groups attached to the carbonyl carbon. Alkyl ketone.
- In still other cases, traditional names are used.



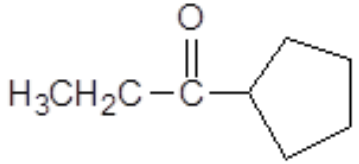
Acetone
(Dimethyl ketone)



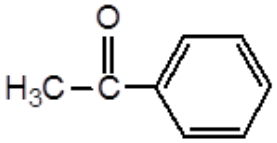
Ethyl methyl ketone



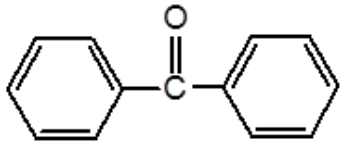
Methyl vinyl ketone



Cyclopentyl ethyl ketone



Methyl phenyl ketone
(Acetophenone)

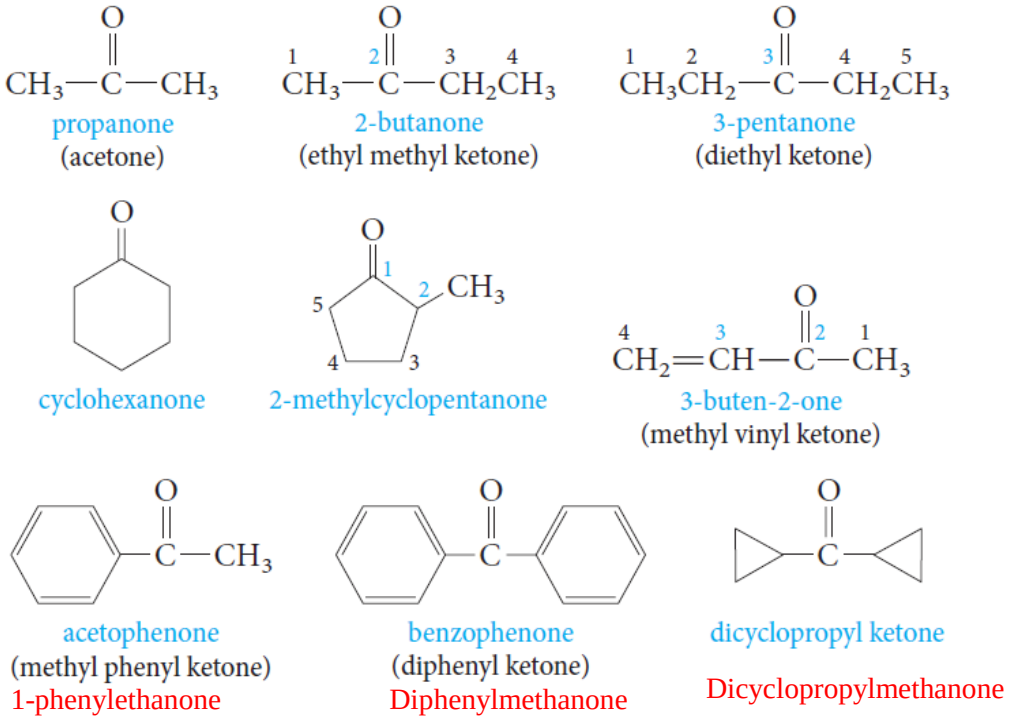


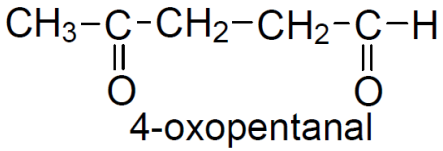
Diphenyl ketone
(Benzophenone)

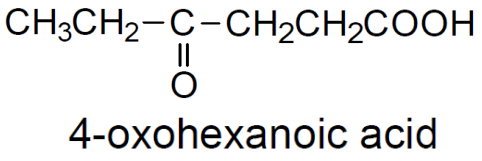
Nomenclature of Ketones

IUPAC Names

- 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.





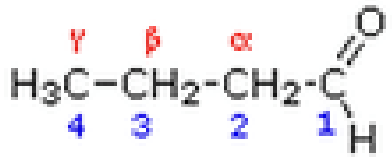


Nomenclature of Aldehydes and Ketones

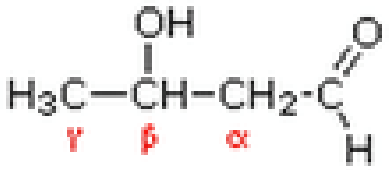
NOTES

- **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

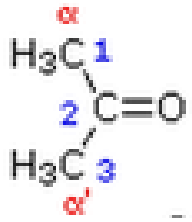


butanal
butyraldehyde

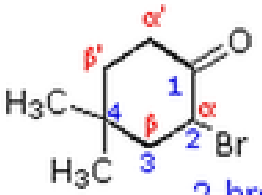


3-hydroxybutanal
β-hydroxybutyraldehyde
or aldol

Ketones



propanone
acetone



2-bromo-4,4-dimethylcyclohexanone

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

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

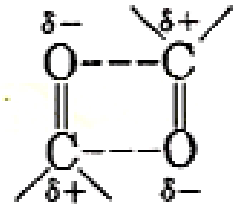
Physical Properties of Aldehydes and Ketones

Boiling Points

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

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

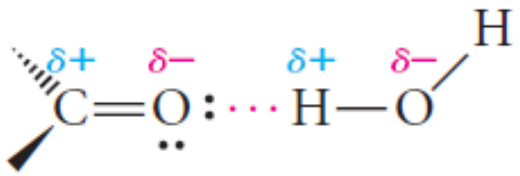


Dipole-dipole attractions among carbonyl compounds

Physical Properties of Aldehydes and Ketones

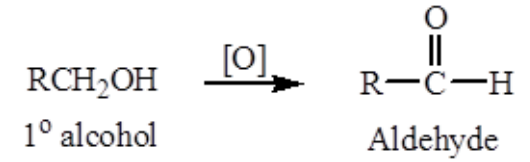
Solubility

- 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.



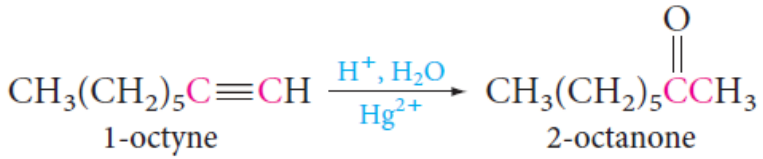
Preparation of Aldehydes and Ketones

1) Oxidation of Primary and Secondary Alcohols

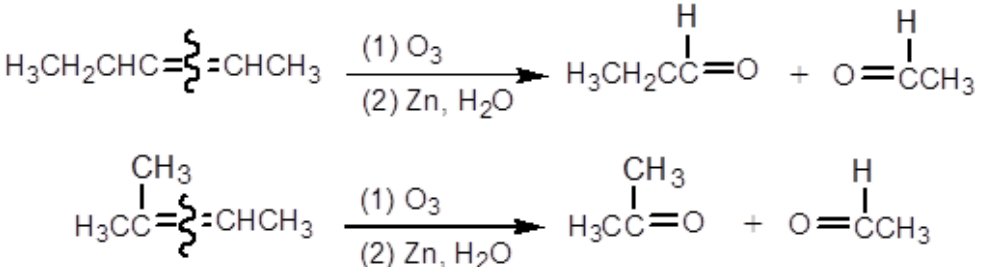


2) Hydration of Alkynes

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



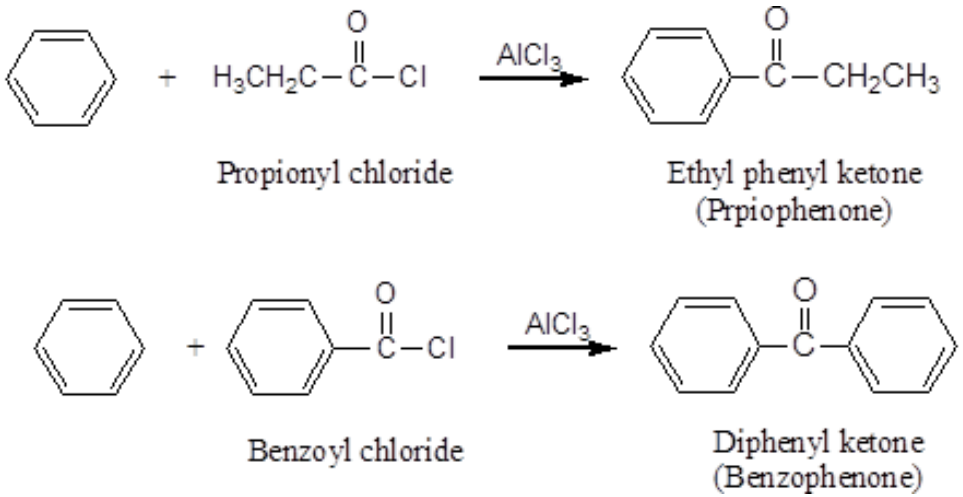
3) Ozonolysis of Alkenes



Preparation of Aldehydes and Ketones

4) Friedel-Crafts Acylation

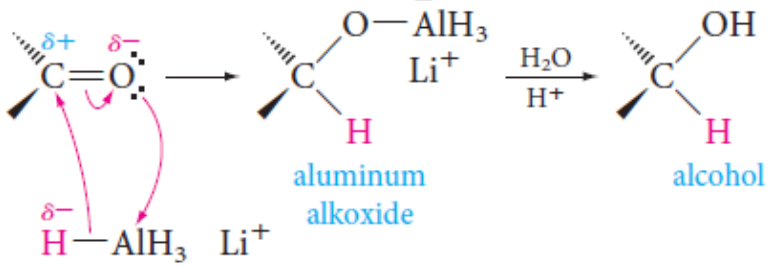
Preparing ketones that contain an aromatic ring.



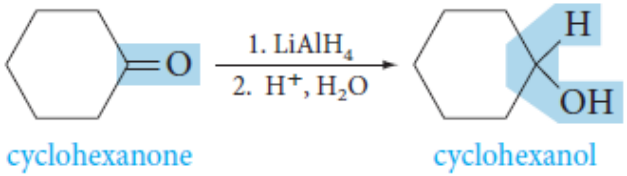
Reactions of Aldehydes and Ketones

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 ($NaBH_4$).



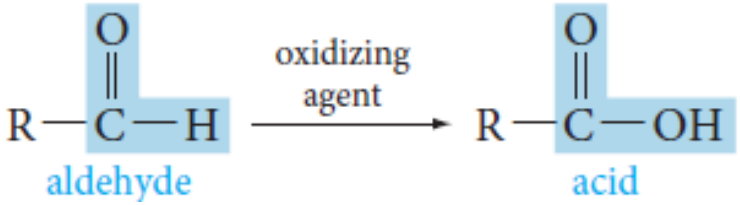
- **Example:**



Reactions of Aldehydes and Ketones

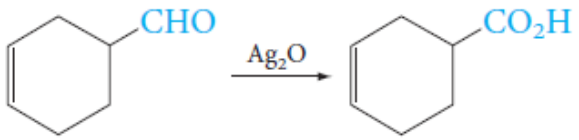
B) Oxidation of Carbonyl Compounds

- 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.



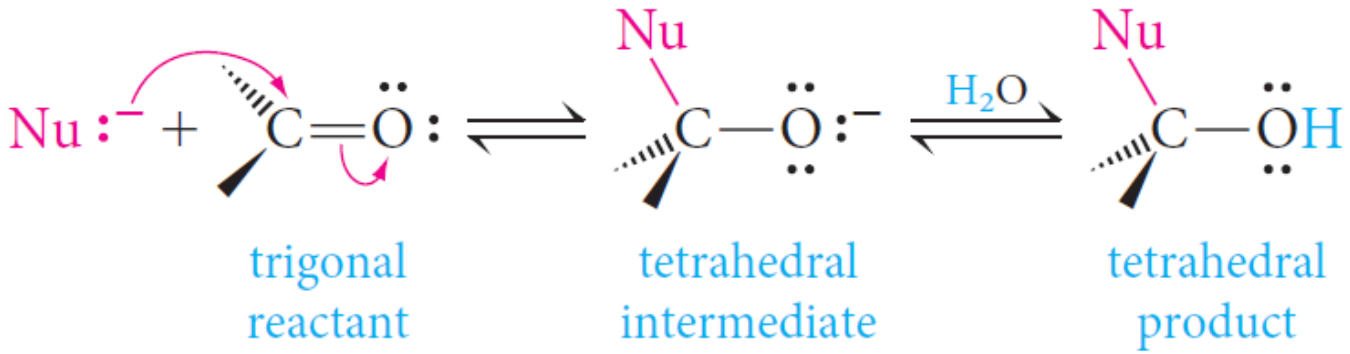
- **Example:**

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



C) Nucleophilic Addition Reactions

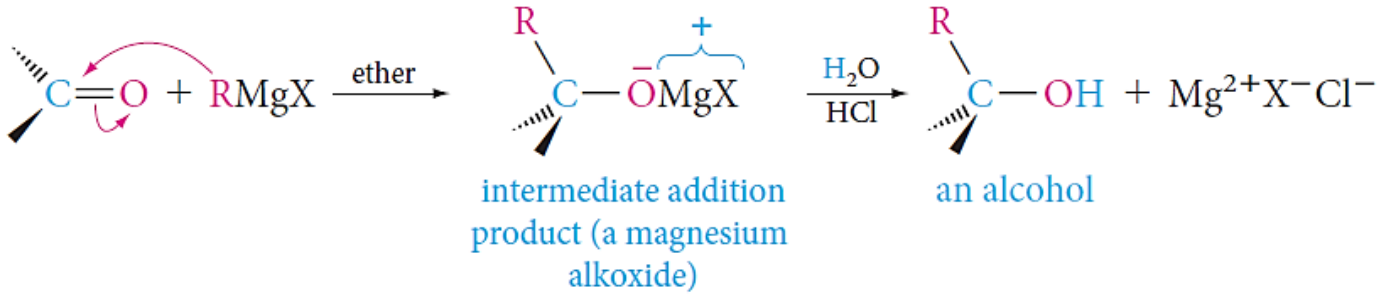
- Nucleophiles attack the carbon atom of a carbon-oxygen double bond because that carbon has a partial positive charge.
- The overall reaction involves addition of a nucleophile and a proton across the pi bond of the carbonyl group (when carried out in alcohol or water).

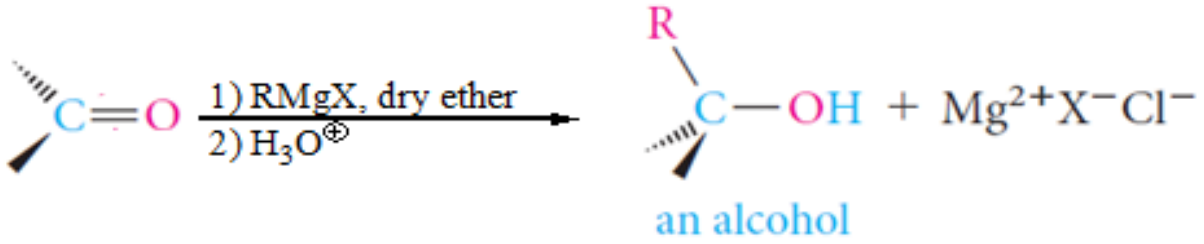


C) Nucleophilic Addition Reactions

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.



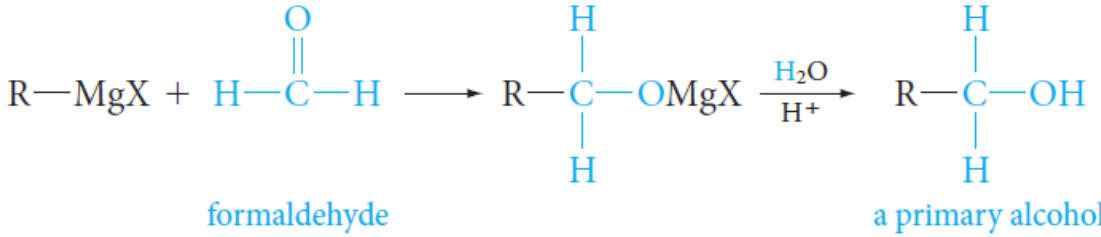


- The type of carbonyl compound chosen determines the class of alcohol produced.

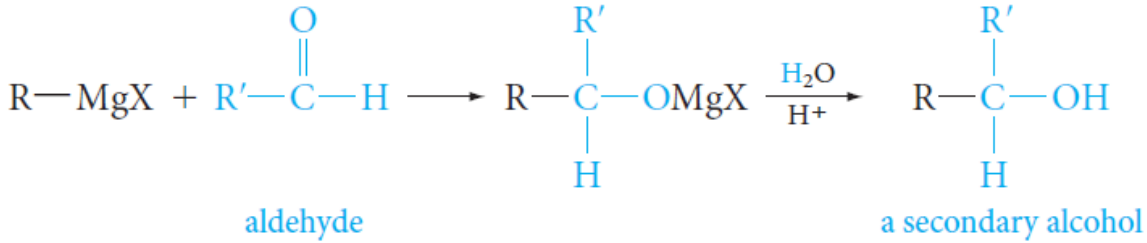
C) Nucleophilic Addition Reactions

1) Addition of Grignard Reagents: Formation of Alcohols

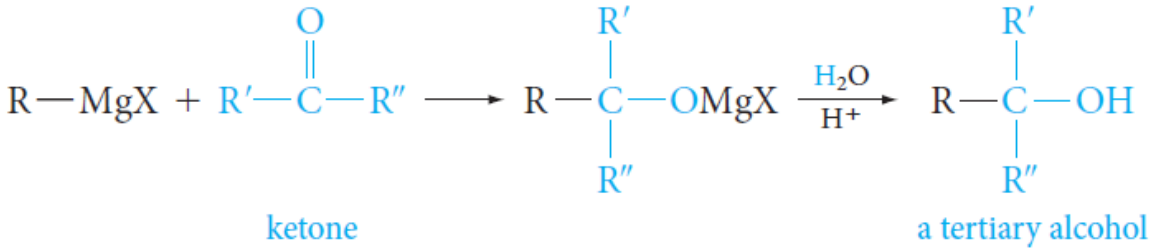
- *Formaldehyde gives primary alcohols.*



- *Other aldehydes give secondary alcohols*



- *Ketones give tertiary alcohols.*



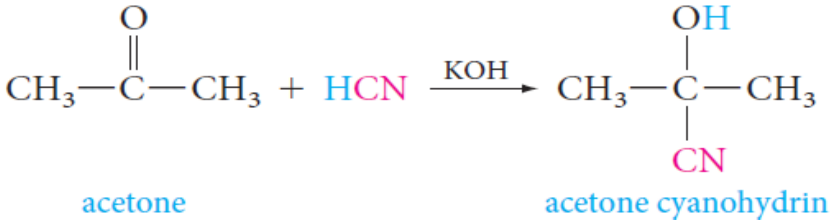
C) Nucleophilic Addition Reactions

2) Addition of Hydrogen Cyanide: Formation of Cyanohydrins

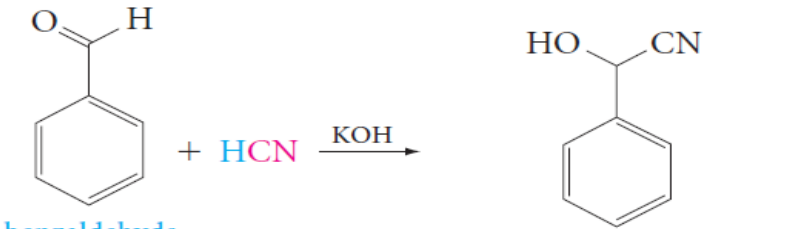
- Hydrogen cyanide adds to the carbonyl group of aldehydes and ketones to form cyanohydrins, compounds with a hydroxyl and a cyano group attached to the same carbon.

a cyanohydrin

- **Example**



acetone — acetone cyanohydrin

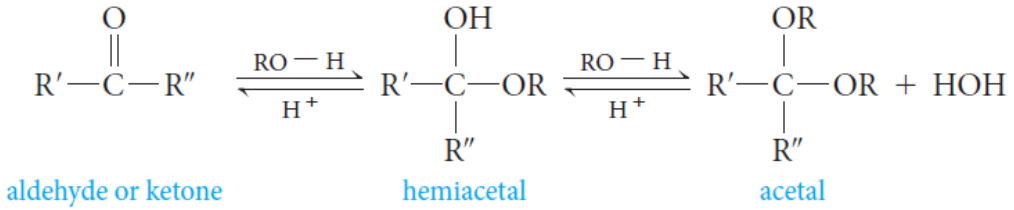


benzaldehyde — benzaldehyde cyanohydrin

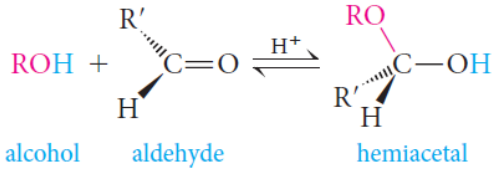
C) Nucleophilic Addition Reactions

3) Addition of Alcohols: Formation of Hemiacetals and Acetals

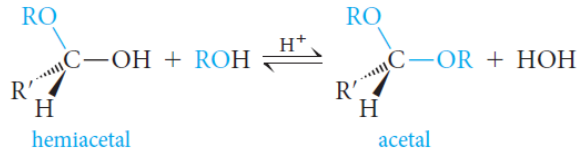
- *Alcohols add to the C=O bond, the OR group becoming attached to the carbon and the proton becoming attached to the oxygen.*
- Aldehydes and ketones react with alcohols to form, first, hemiacetals and then, if excess alcohol is present, acetals.



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



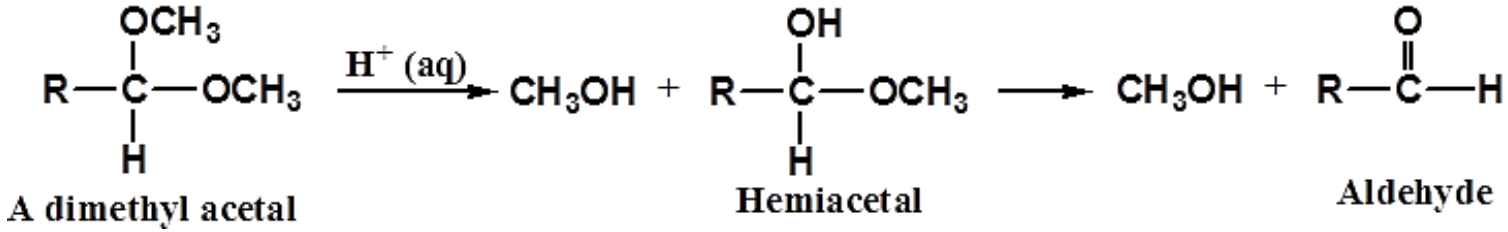
- Acetals have two ether functions at the same carbon atom.



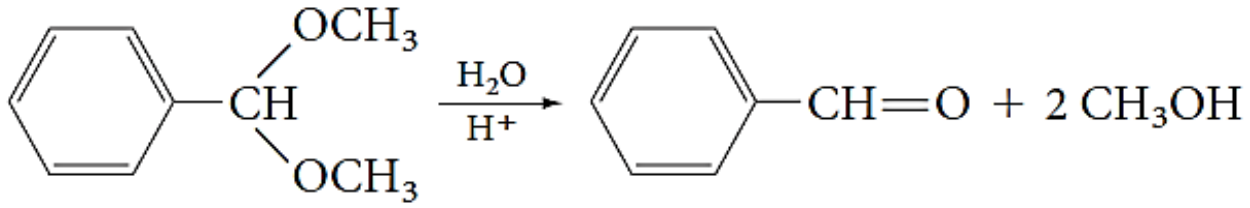
C) Nucleophilic Addition Reactions

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.



A dimethyl acetal — Hemiacetal — Aldehyde



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).