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Chemistry Department

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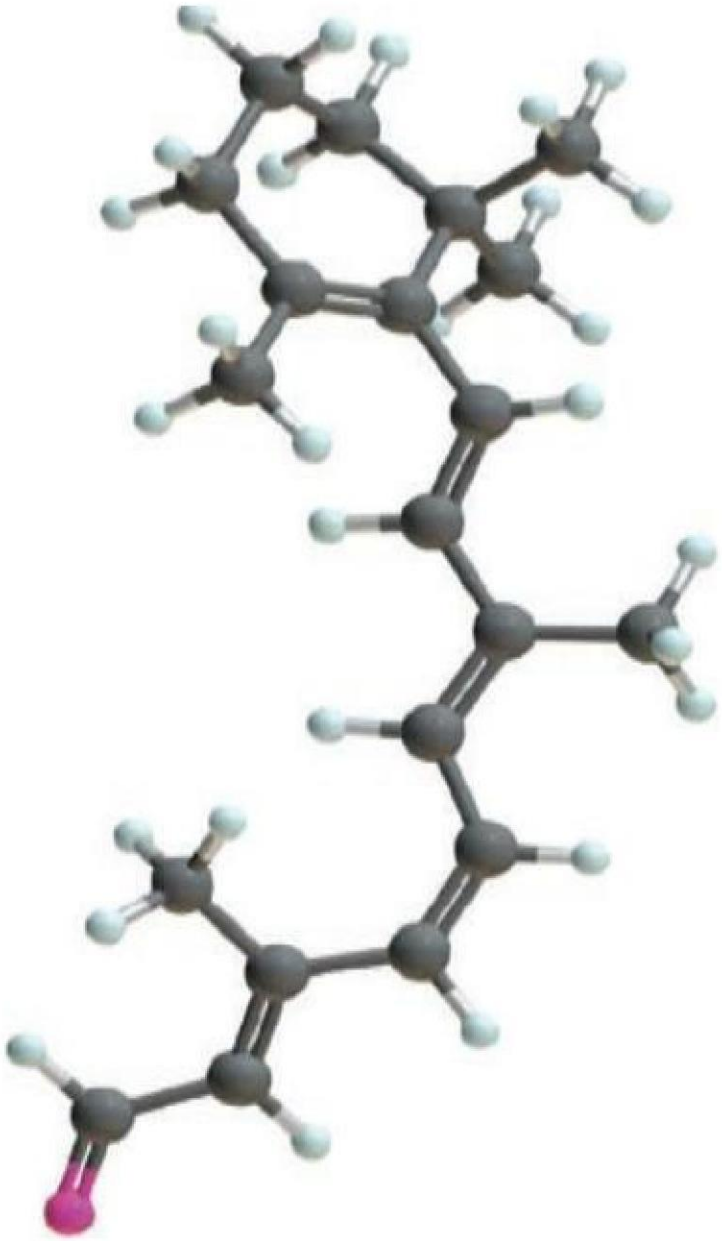
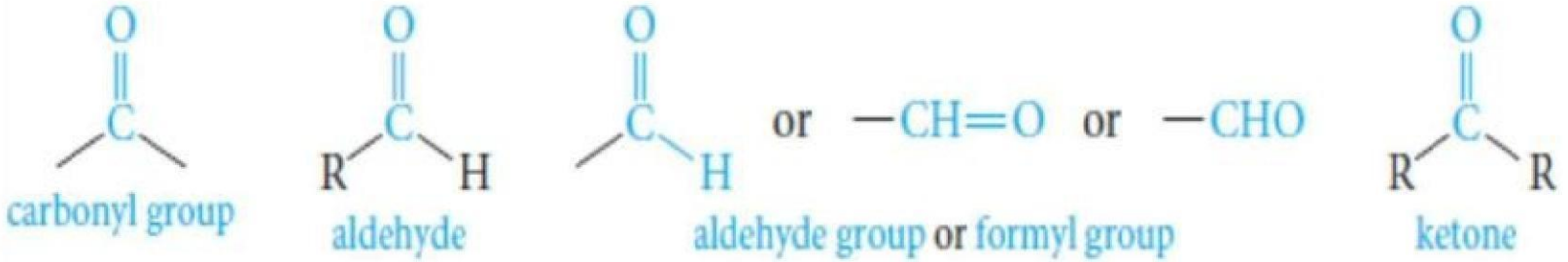
Aldehyde and ketones

Lec.10



Introduction

- Aldehydes and ketones are characterized by the presence of the **carbonyl group**, perhaps the most important functional group in organic chemistry.
- 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.



❖ The simplest aldehyde, the carbonyl group is bonded to two hydrogen atoms. methanal (always called formaldehyde).

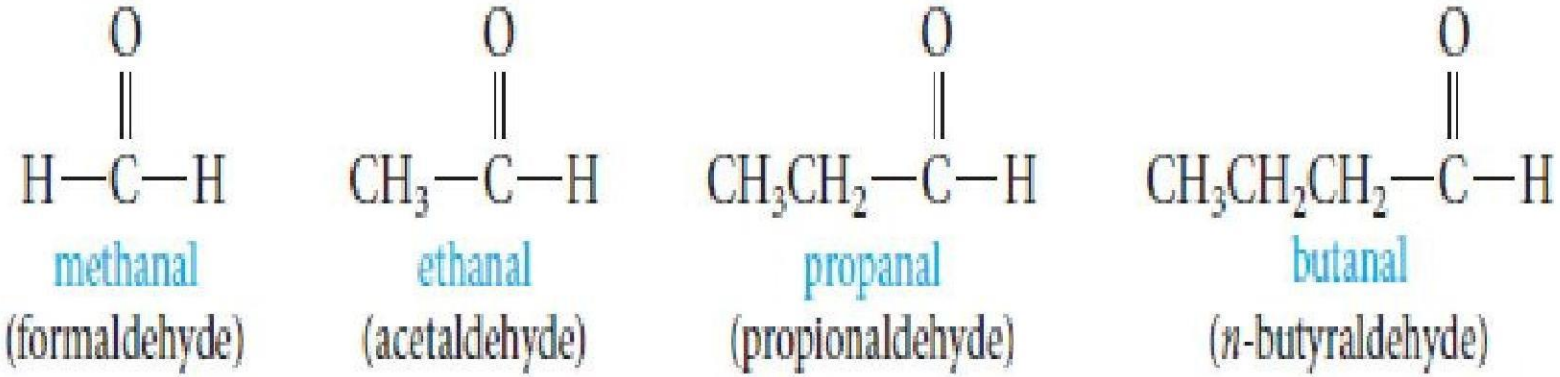
❖ The simplest ketone is propanone, which is always called acetone.

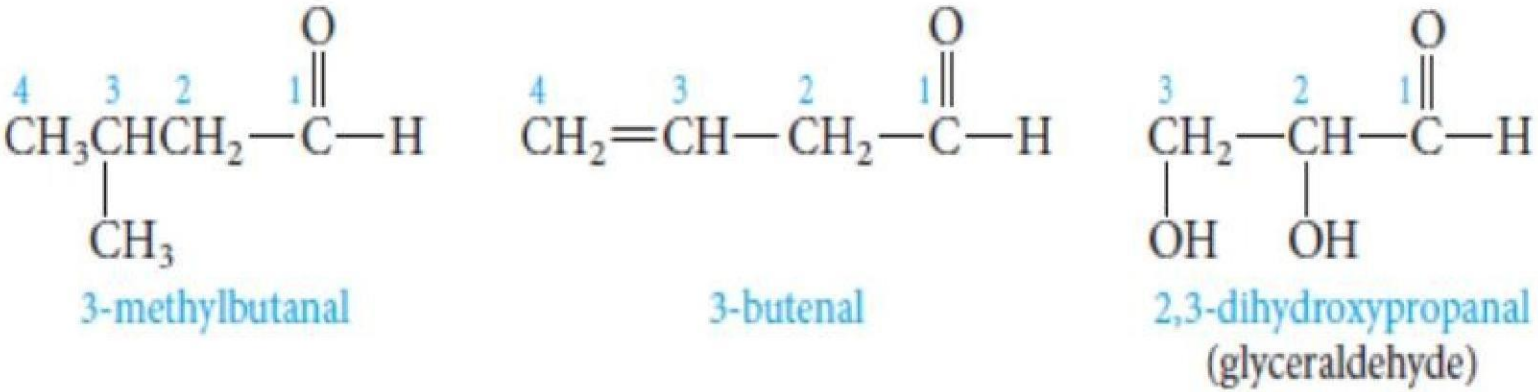
I. Nomenclature

IUPAC Nomenclature

✓ The characteristic ending for aldehydes **is –al,** we number the chain starting with the aldehyde carbon,

for example:



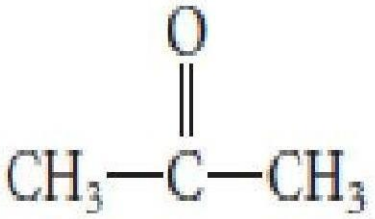


Notice from the last two examples that an aldehyde group has priority over a double bond or a hydroxyl group, not only in numbering but also in parent chain naming(suffix)

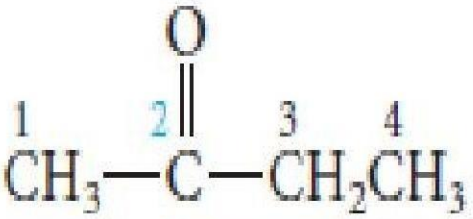
- ✓ The ending for ketones **is -one** (from the last syllable of ketone). The chain is numbered so that the carbonyl carbon has the lowest possible number.

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

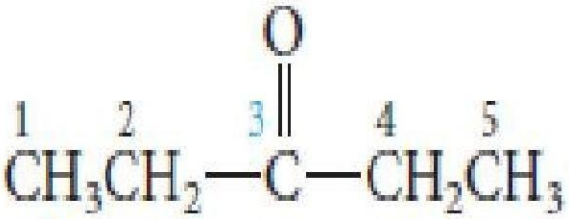
For example:



propanone
(acetone)



2-butanone
(ethyl methyl ketone)



3-pentanone
(diethyl ketone)

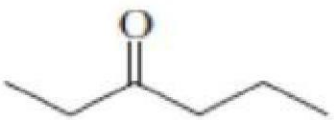
Example (1):

Write structural formulas for all ketones with the molecular formula $C_6H_{12}O$ and give each its IUPAC name.

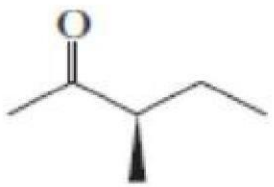
Solution

Following are line-angle formulas and IUPAC names for the six ketones with this molecular formula.

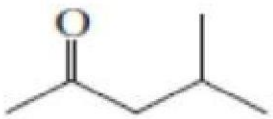
2-Hexanone



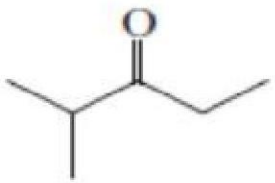
3-Hexanone



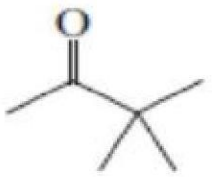
3-Methyl-2-pentanone



4-Methyl-2-pentanone



2-Methyl-3-pentanone



3,3-Dimethyl-2-butanone

II. Physical Properties

- *Aldehydes and ketones are polar compounds that engage in dipole-dipole interactions in pure liquid*

Note: 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.

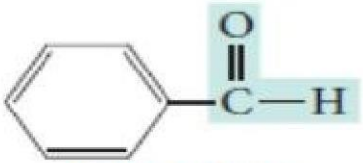
Polarity of a carbonyl group

- *They have higher boiling points than nonpolar compounds of comparable molecular weight.*

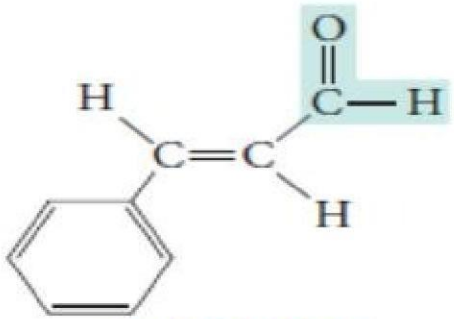
Important Notes:

✓*The positive part of one molecule is attracted to the negative part of another molecule.* These intermolecular forces of attraction, called **dipole–dipole interactions**, are generally stronger than van der Waals attractions but not as strong as hydrogen bonds.

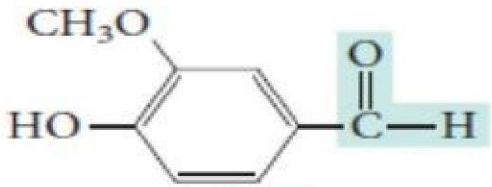
- *carbonyl compounds with low molecular weights are soluble in water.* The polarity of the carbonyl group also affects the solubility properties of aldehydes and ketones.
- Examples of aldehydes and ketones in nature:



benzaldehyde
(oil of almonds)
bp 178.1°C



cinnamaldehyde
(cinnamon)
bp 253°C



vanillin
(vanilla bean)
mp 80°C, bp 285°C

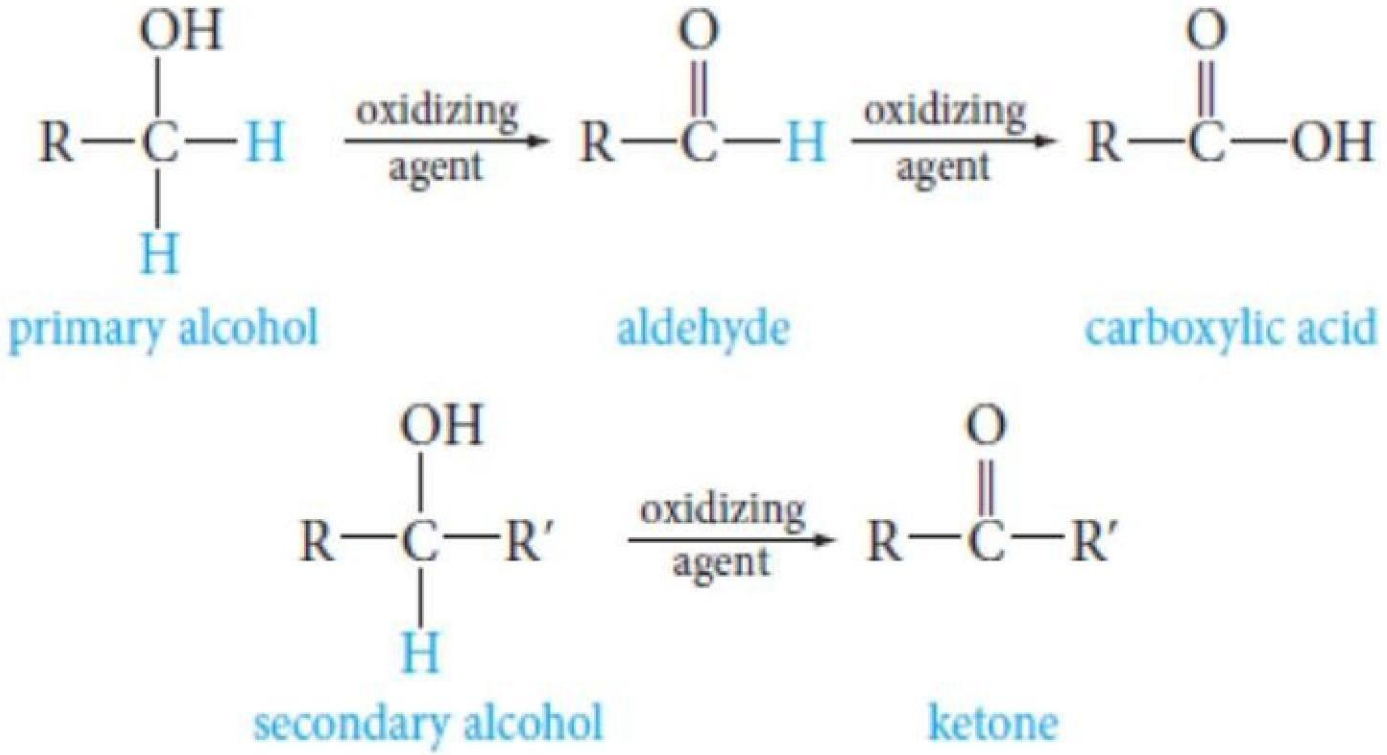
Table 16.3 Physical Properties of Selected Aldehydes and Ketones

IUPAC Name	Common Name	Structural Formula	Boiling Point (°C)	Solubility (g/100 g water)
Methanal	Formaldehyde	$HCHO$	−21	Infinite
Ethanal	Acetaldehyde	CH_3CHO	20	Infinite
Propanal	Propionaldehyde	CH_3CH_2CHO	49	16
Butanal	Butyraldehyde	$CH_3CH_2CH_2CHO$	76	7
Hexanal	Caproaldehyde	$CH_3(CH_2)_4CHO$	129	Slight
Propanone	Acetone	CH_3COCH_3	56	Infinite
2-Butanone	Ethyl methyl ketone	$CH_3COCH_2CH_3$	80	26
3-Pentanone	Diethyl ketone	$CH_3CH_2COCH_2CH_3$	101	5

III. Preparation of Aldehydes and Ketones

1- By Oxidation of alcohols

- **Primary alcohols give aldehydes, which may be further oxidized to carboxylic acids.**
- **Secondary alcohols give ketones**

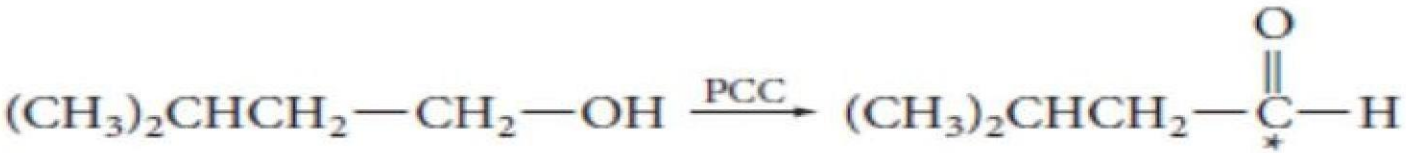


EXAMPLE:

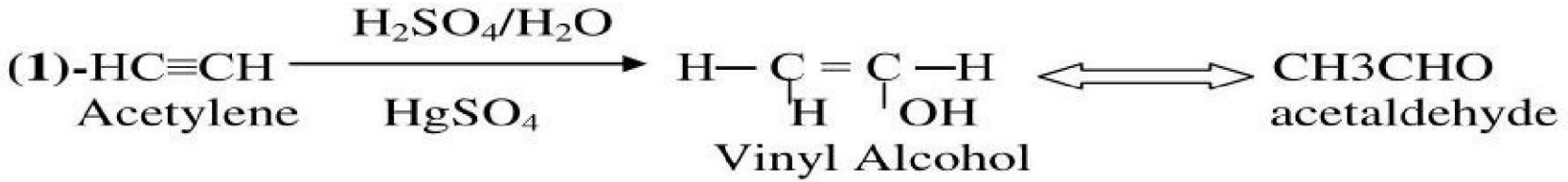
Write an equation for the oxidation of an appropriate alcohol to (CH3)2CHCH2CHO (3-methylbutanal).

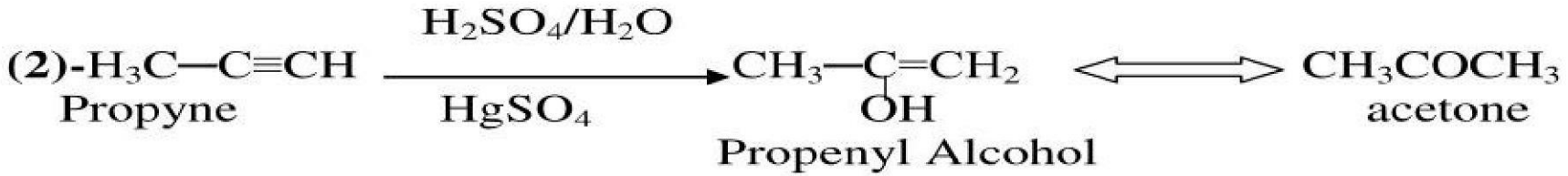
Solution :

Aldehydes are prepared by oxidation of 1° alcohols (RCH2OH) with an oxidizing agent(PCC) .First, find the carbonyl carbon in 3-methylbutanal .Convert this carbon to a primary alcohol. A proper equation is:



2- Hydration of alkynes:





IV. REACTIONS

The carbon-oxygen double bond is polar and may be attacked either by nucleophile or electrophile.

- The carbonyl group is stabilized by adjacent alkyl groups. Which are electron releasing. Ketone with two R groups more stable than an aldehyde with only one R.

Formaldehyde with no alkyl groups is the most reactive of the aldehydes and ketones.

RCOR ⟶ RCHO ⟶ HCHO

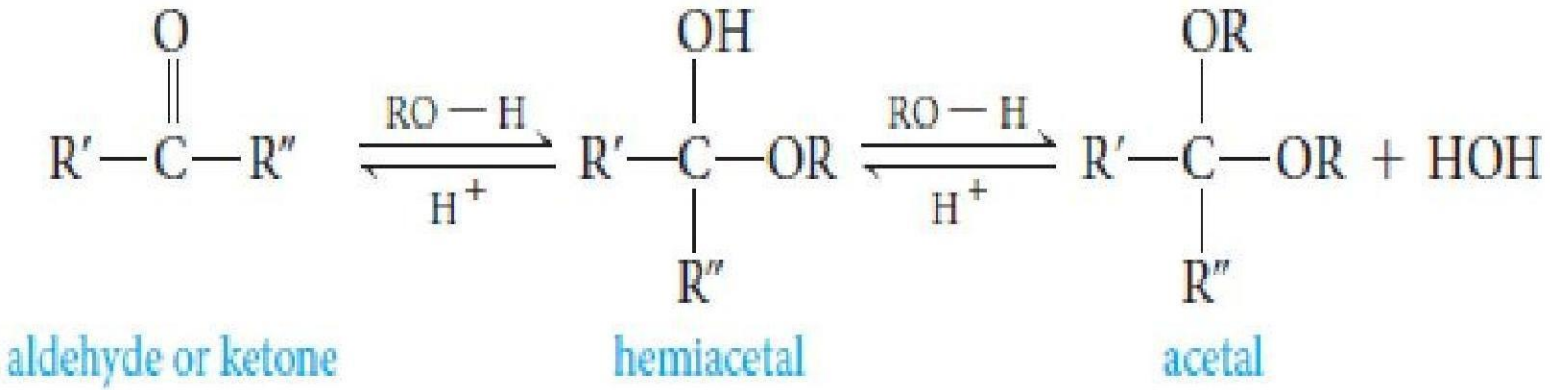
Ketone aldehyde formaldehyde

⟶

Increasing reactivity

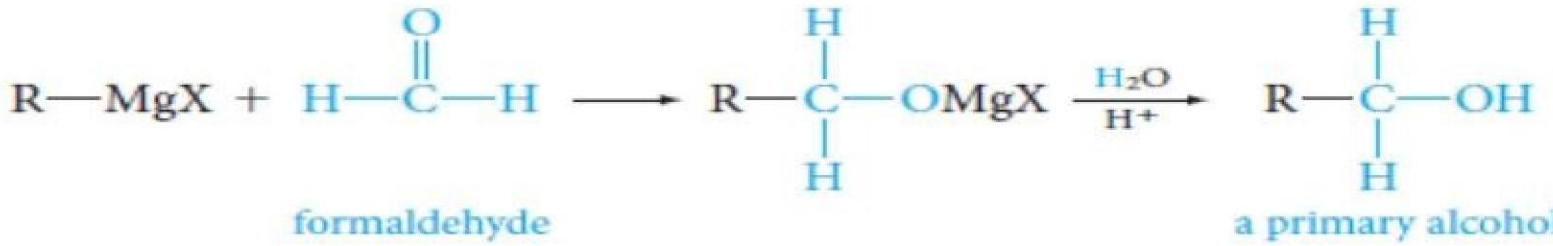
1-Addition of alcohols:

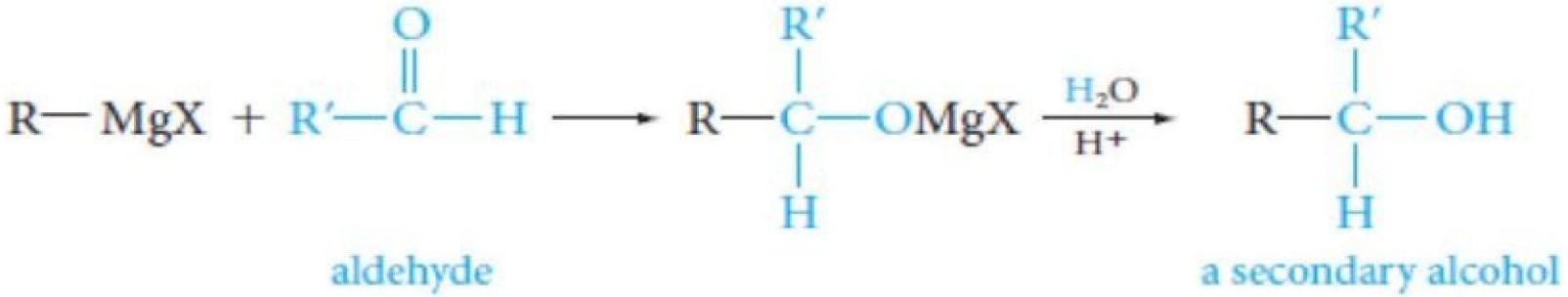
- Alcohols are oxygen nucleophiles. They add to the C=O bond, the OR group becoming attached to the carbon and the proton becoming attached to the oxygen. Because alcohols are *weak* nucleophiles, an acid catalyst is required.* The product is a **hemiacetal** [it contains both alcohol(OH) and ether(C=O) functional groups on the same carbon atom. The addition is reversible] if excess alcohol is present, acetals.

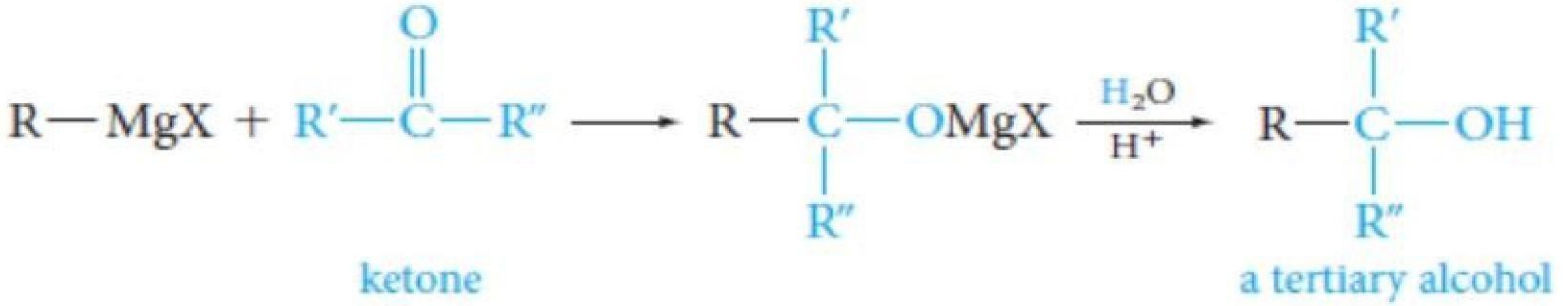


2-Addition of Grignard Reagents and Acetylides

- The R group of the Grignard reagent adds irreversibly to the carbonyl carbon, forming a new carbon–carbon bond.







PROBLEM:

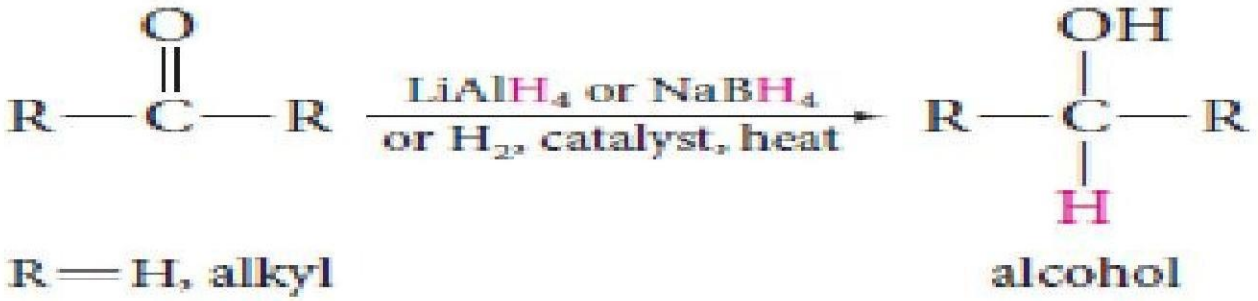
Provide the products expected from the reaction of

1- formaldehyde with ethyl magnesium bromide followed by hydrolysis.

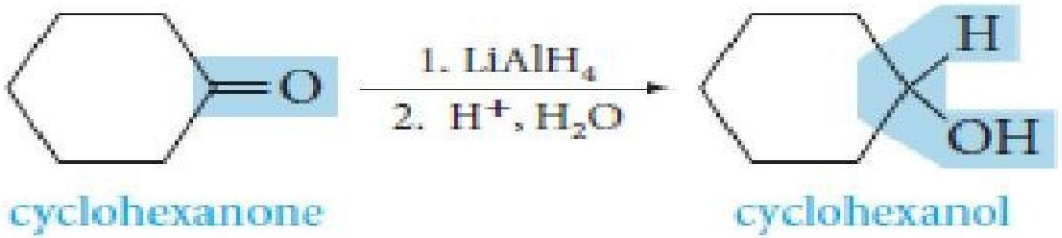
2- cyclohexanone with methyl magnesium bromide followed by hydrolysis

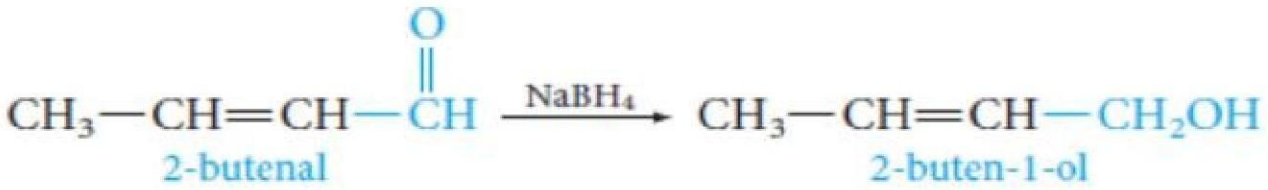
3-Reduction to Alcohols

The most common metal hydrides used to reduce carbonyl compounds are lithium aluminum hydride (LiAlH4) and sodium borohydride (NaBH4).



Examples:

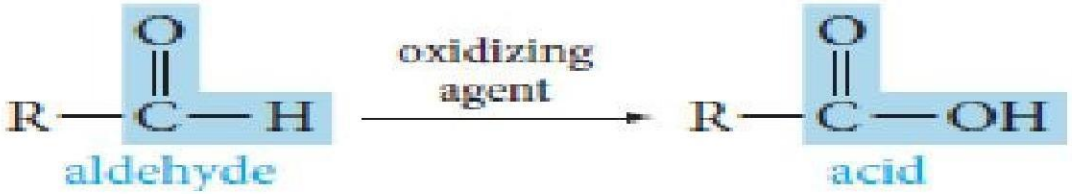




Because a carbon–carbon double bond is not readily attacked by nucleophiles, metal hydrides can be used to reduce a carbon–oxygen double bond to the corresponding alcohol without reducing a carbon–carbon double bond present in the same compound.

4-Oxidation of Carbonyl Compounds

Aldehydes are more easily oxidized than ketones. Oxidation of an aldehyde gives a carboxylic acid with the same number of carbon atoms but Ketones also can be oxidized, but require special oxidizing conditions



Because the reaction occurs easily, many oxidizing agents, such as KMnO4, CrO3, Ag2O

Note: A laboratory test that distinguishes aldehydes from ketones takes advantage of their different ease of oxidation. In the Tollens' silver mirror test, the silver–ammonia complex ion is reduced by aldehydes (but not by ketones) to metallic silver.