241 Chem

CH-6

Aldehydes and ketones

Learning Objectives

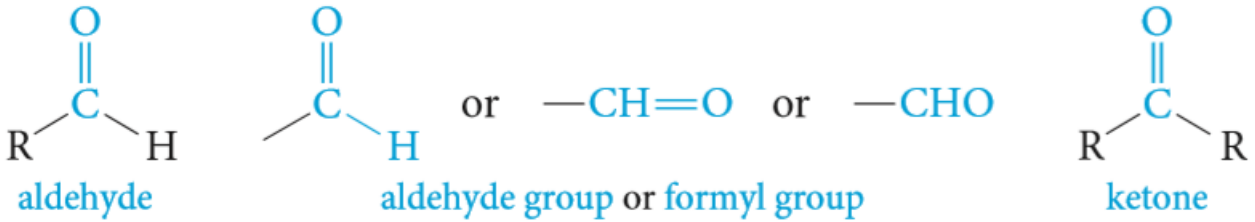
By the end of this chapter the student will:

- Know the structure of aldehyde and ketone.
- Know the nomenclature of aldehyde and ketone.
- Know the physical Properties of aldehyde and ketone.
- Know the different methods of preparation of aldehyde and ketone.
- Know the chemical reactions of aldehyde and ketone.

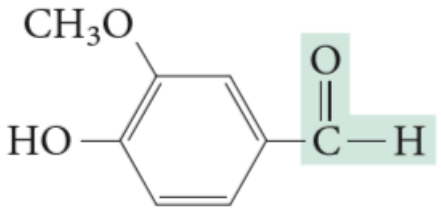
Structural Characteristic of Aldehydes and ketones

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

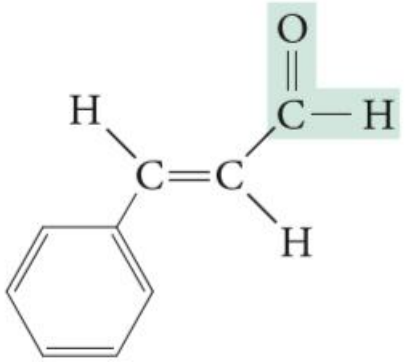
- The functional group of an aldehyde is a carbonyl group bonded least one hydrogen atom attached and The remaining group may be another hydrogen atom or any aliphatic or aromatic organic group.
- The functional group of a ketone is a carbonyl group bonded to two carbon atoms.



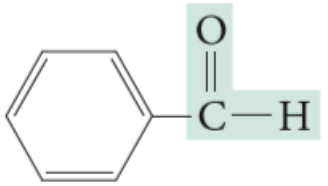
Aldehydes and ketones in Nature



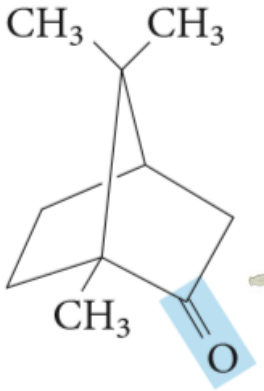
vanillin
(vanilla bean)
mp 80°C, bp 285°C



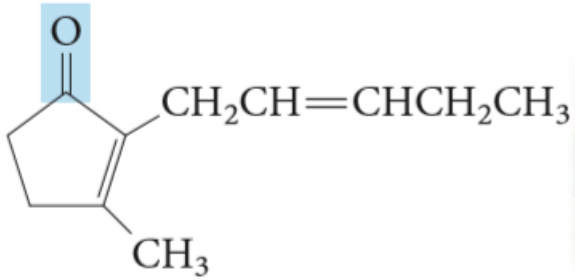
cinnamaldehyde
(cinnamon)
bp 253°C



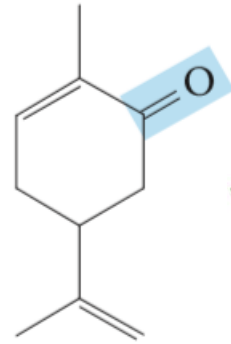
benzaldehyde
(oil of almonds)
bp 178.1°C



camphor
mp 179°C



jasmone
(from oil of jasmine)



carvone
(spearmint oil)
bp 231°C

Nomenclature of aldehydes

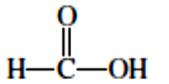
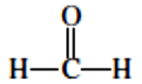
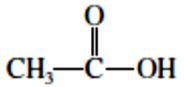
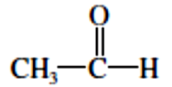
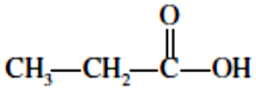
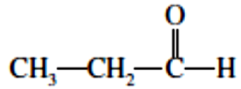
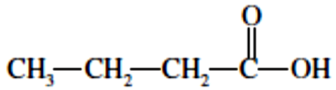
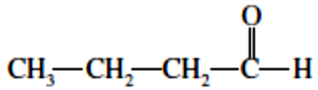
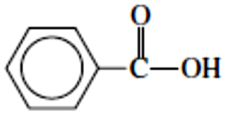
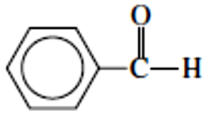
The IUPAC:

- Select the longest chain of carbon atoms that contains the functional group.
- Changing the suffix *-e* of the parent alkane to *-al.*
- Number must start with carbonyl group of an aldehyde as carbon-1.
- For unsaturated aldehydes, the presence of a carbon-carbon double or triple bond is indicated by the infix *-en-* or *-yn-*. As with other molecules with both an infix and a suffix, the location of the group corresponding to the suffix determines the numbering pattern.
- For cyclic molecules in which -CHO is bonded directly to the ring, the molecule is named by adding the suffix *-carbaldehyde* to the name of the ring. The atom of the ring to which the aldehyde group is bonded is numbered 1
- If an aldehyde has a second functional group of higher naming priority, the aldehyde oxygen is indicated by the prefix '*oxo-* or *formyl-*'.
- If carbon of CHO is included in the parent chain, then write *oxo*, if not included in parent chain write *formyl*.

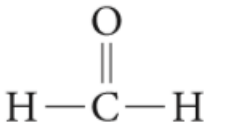
Nomenclature of aldehydes

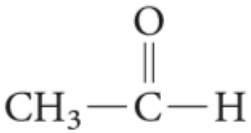
The Common name:

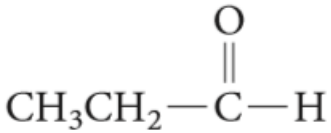
- The common name for an aldehyde is derived from the common name of the corresponding carboxylic acid by dropping the word *acid* and changing the suffix *-ic* or *–oic* to *-aldehyde*.
- In common names carbon atoms near the carbonyl group are often designated using Greek letters (α, β, ɣ , δ…..) beginning with carbon next the carbonyl group.

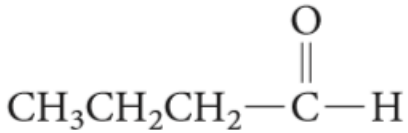
Carboxylic Acid	Derivation	Aldehyde
 formic acid (methanoic acid)	*formica*, ''ants''	 formaldehyde (methanal)
 acetic acid (ethanoic acid)	*acetum*, ''sour''	 acetaldehyde (ethanal)
 propionic acid (propanoic acid)	*protos pion*, ''first fat''	 propionaldehyde (propanal)
 butyric acid (butanoic acid)	*butyrum*, ''butter''	 butyraldehyde (butanal)
 benzoic acid	*gum benzoin*, ''blending''	 benzaldehyde

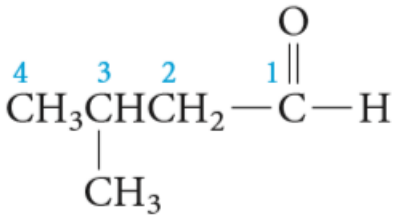
IUPAC name:
Common name:

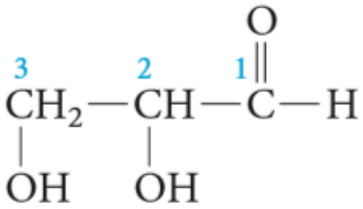

methanal
(formaldehyde)

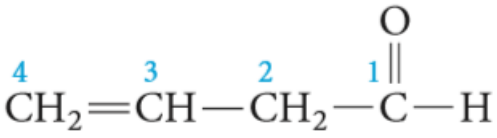

ethanal
(acetaldehyde)

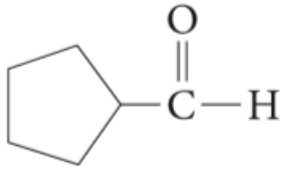

propanal
(propionaldehyde)

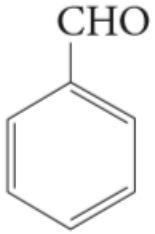

butanal
(*n*-butyraldehyde)

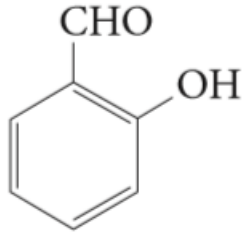

3-methylbutanal

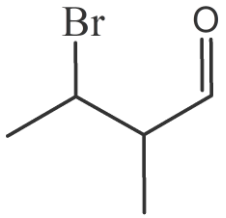

2,3-dihydroxypropanal
(glyceraldehyde)

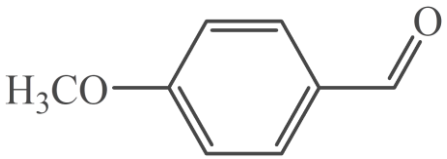

3-butenal

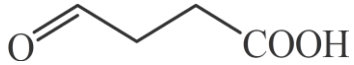

cyclopentanecarbaldehyde
(formylcyclopentane)

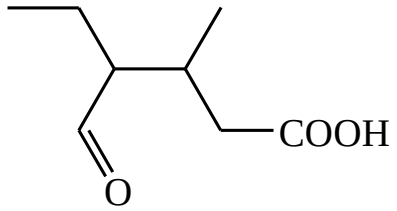

benzaldehyde
(benzenecarbaldehyde)

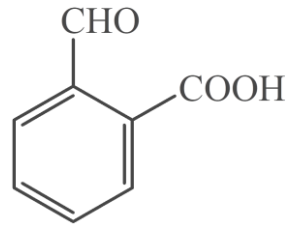

salicylaldehyde
(2-hydroxybenzenecarbaldehyde)


3-Bromo-2-methyl-butanal
(β-Bromo- α-methyl butyraldehyde)


4-Methoxybenzaldehyde
p-Methoxybenzaldehyde


4-Oxobutanoic acid


4-Formyl-3-methylhexanoic acid


2-Formylbenzoic acid

Nomenclature of Ketones

The IUPAC:

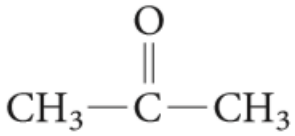
- Select the longest chain of carbon atoms that contains the functional group.
- Changing the suffix *-e* of the parent alkane to *-one*
- The parent chain is numbered from the direction that gives the carbonyl carbon the smaller number.
- If a ketone has a second functional group of higher naming priority, the ketone oxygen is indicated by the prefix "*oxo-*."

The Common names:

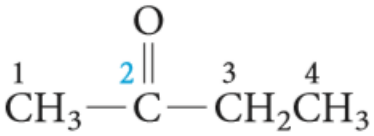
- The common name for ketones are derived by naming the two alkyl or aryl groups bonded to the carbonyl group as separate words followed by the word *ketone*.

IUPAC name:

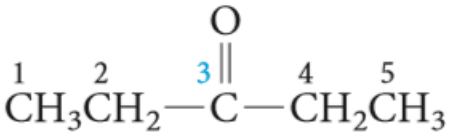
Common name:



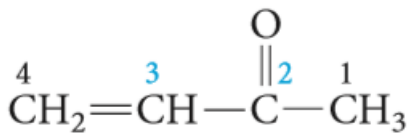
propanone
(acetone)



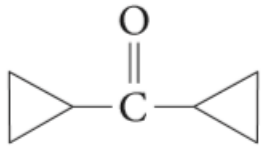
2-butanone
(ethyl methyl ketone)



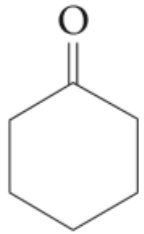
3-pentanone
(diethyl ketone)



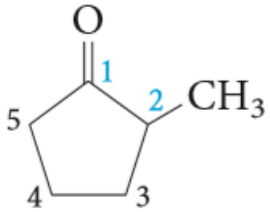
3-buten-2-one
(methyl vinyl ketone)



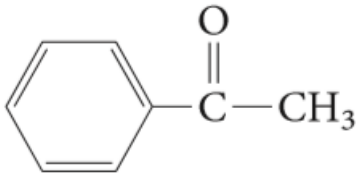
Dicyclopropylmethanone
Dicyclopropyl ketone



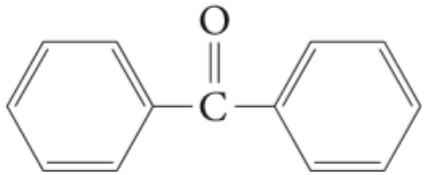
cyclohexanone



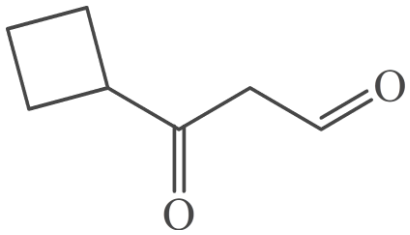
2-methylcyclopentanone



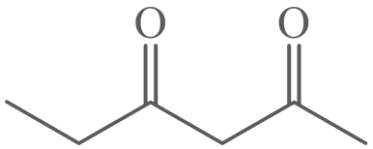
acetophenone
1-phenylethanone
(methyl phenyl ketone)



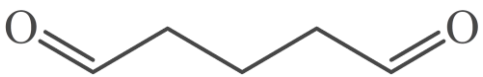
benzophenone
diphenylmethanone
(diphenyl ketone)



3-Cyclobutyl-3-oxopropanal



Hexane-2,4-dione



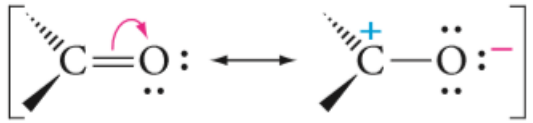
Pentanedial

Priority Order in Nomenclature System

Class	Suffix name	Prefix name
Carboxylic acid	-oic acid	Carboxy
Ester	-oate	Alkoxycarbonyl
Amide	-amide	Amido
Nitrile	-nitrile	Cyano
Aldehyde	-al	Oxo (=O)
Aldehyde	-al	Formyl (CH=O)
Ketone	-one	Oxo (=O)
Alcohol	-ol	Hydroxy
Amine	-amine	Amino
Alkene	-ene	Alkenyl
Alkyne	-yne	Alkynyl
Alkane	-ane	Alkyl
Ether	—	Alkoxy
Alkyl halide	—	Halo

Physical Properties of aldehydes and ketones

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

Boiling points

In general, aldehydes and ketones have **higher boiling points than alkenes** because they are more polar and the dipole–dipole attractive forces between molecules are stronger. But they have **lower boiling points than alcohols** because, unlike alcohols, two carbonyl groups can't form hydrogen bonds to each other.

Solubility:

Aldehydes and ketones can form hydrogen bonds with the protons of OH groups. This makes them more soluble in water than alkenes, but less soluble than alcohols.

	$CH_3CH_2CH{=}CH_2$	$CH_3CH_2CH{=}O$	CH_3CCH_3 (O)	$CH_3CH_2CH_2OH$
	1-Butene	Propanal	Propanone	1-Propanol
bp (1 atm)	−6°C	49°C	56.1°C	97°C
Solubility in water (g/100 mL)	Negligible	20	∞	Miscible in all proportions

Preparation of Aldehyde and Ketone

- Oxidation of Primary and Secondary Alcohols
- Ozonolysis of Alkenes
- Friedel–Crafts Acylation
- Hydration of Alkynes

1. Oxidation of Primary and Secondary Alcohols

Strong oxidizing agent

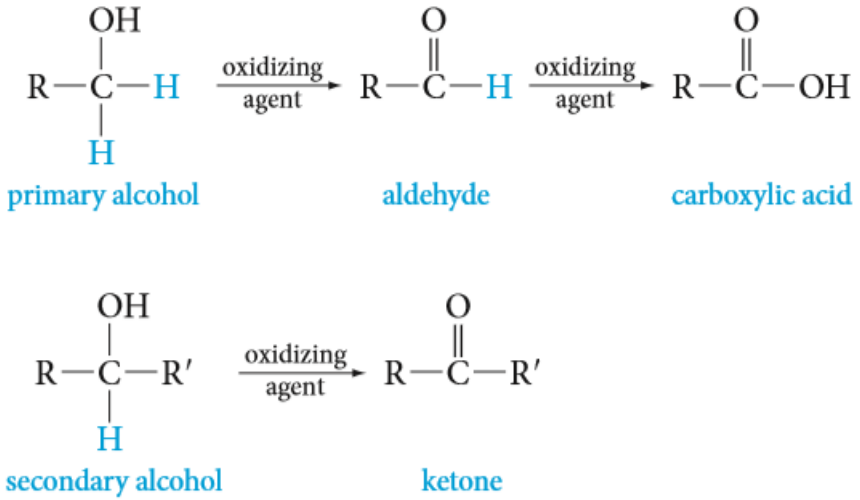
Potassium permanganate $KMnO_4$,OH^-/ H_3O^+

Chromic oxide CrO_3 / H_2SO_4 (H_2CrO_4 Jones' reagent)

Weak oxidizing agent

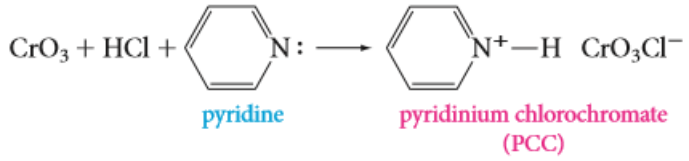
Chromic oxide CrO_3 / pyridine

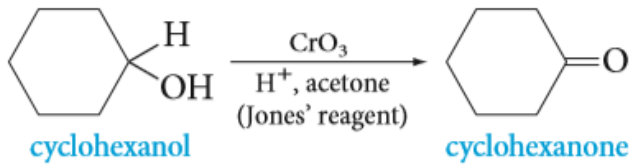
Pyridinium chlorochromate PCC / methylene chloride CH_2Cl_2



Hint:

PCC is prepared by dissolving CrO_3 in hydrochloric acid and then adding pyridine:





$CH_3(CH_2)_6CH_2OH \xrightarrow[\text{reagent}]{\text{Jones'}} CH_3(CH_2)_6CO_2H$

1-octanol — octanoic acid

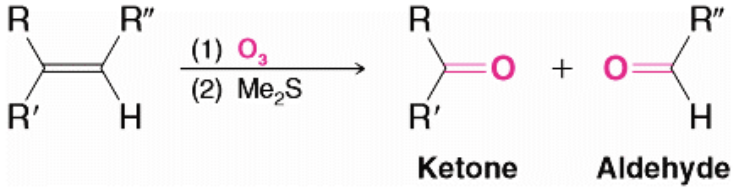
$CH_3(CH_2)_6CH_2OH \xrightarrow[CH_2Cl_2,\ 25^\circ C]{PCC} CH_3(CH_2)_6C(=O)H$

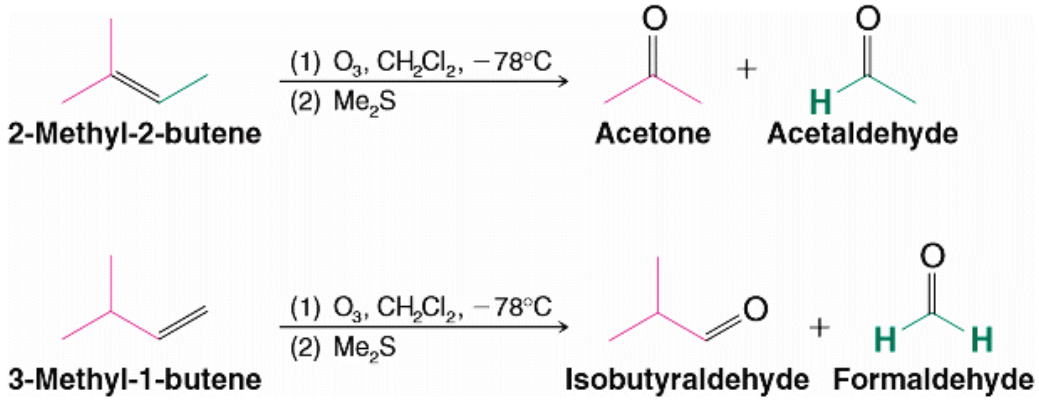
1-octanol — octanal

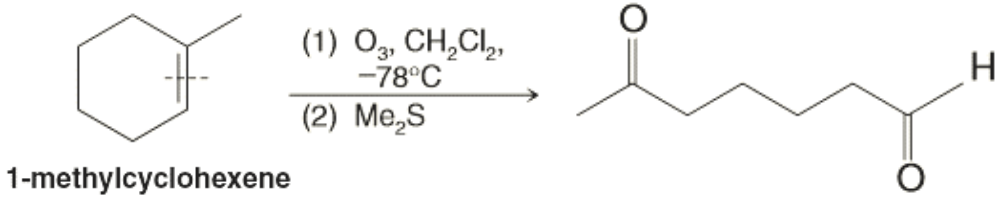
Preparation of Aldehyde and Ketone

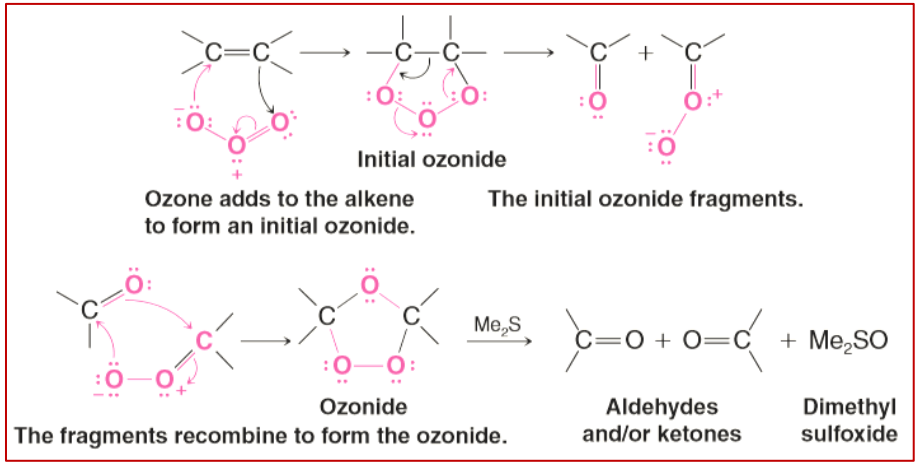
2- Ozonolysis of Alkenes

Ozonolysis consists of bubbling ozone into a very cold (-78°C) solution of the alkene in CH_2Cl_2, followed by treatment of the solution with dimethyl sulfide (or zinc and acetic acid).



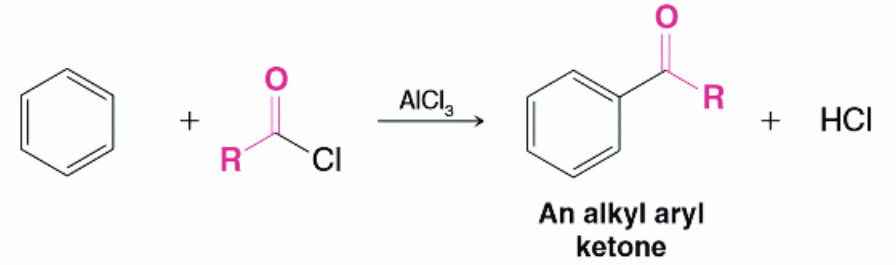






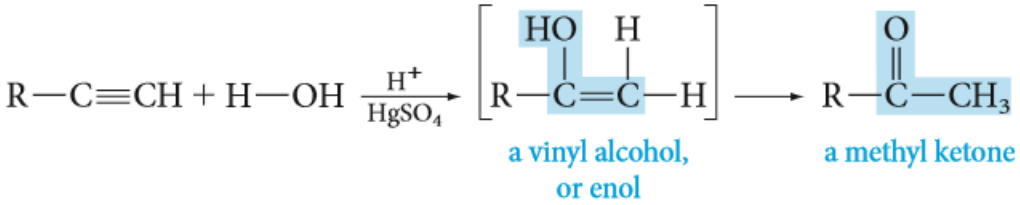
Preparation of Aldehyde and Ketone

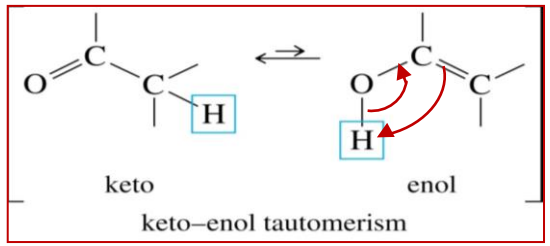
3- Friedel–Crafts Acylation: Preparation of Aromatic ketones

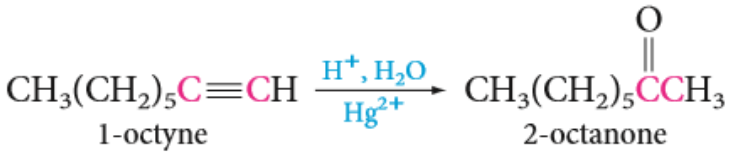


4- Hydration of Alkynes

Addition of water to terminal alkynes requires not only an acid catalyst but mercuric ion as well.

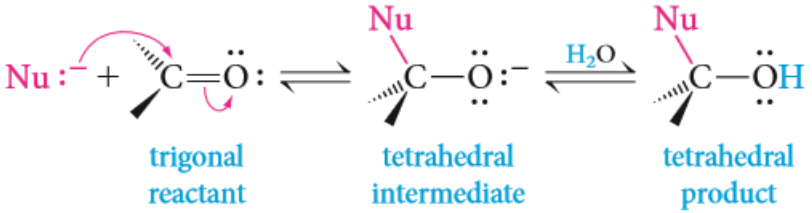






Reaction of Aldehyde and Ketone

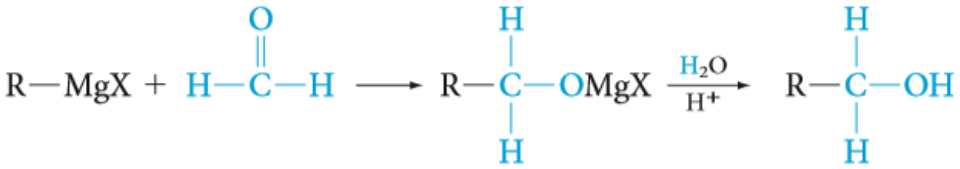
1. Nucleophilic addition to carbonyl groups
    - Addition of Grignard Reagents to aldehyde and ketone
    - Reduction of carbonyl group
    - The Addition of Alcohols: Hemiacetals and Acetals
    - Addition of Hydrogen Cyanide: Formation of cynohydrins
    - Addition of Ammonia and Ammonia Derivatives
2. Aldol condensation
3. Oxidation of Aldehydes



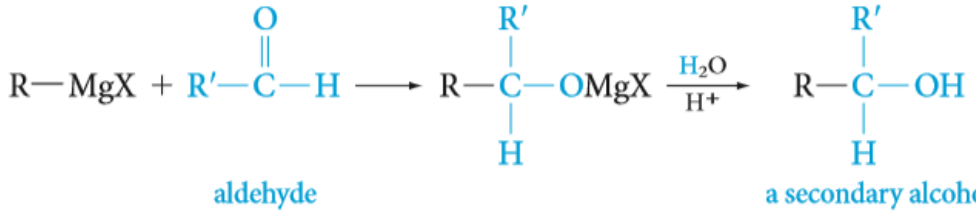
Reaction of Aldehyde and Ketone

1- Nucleophilic addition to carbonyl groups:

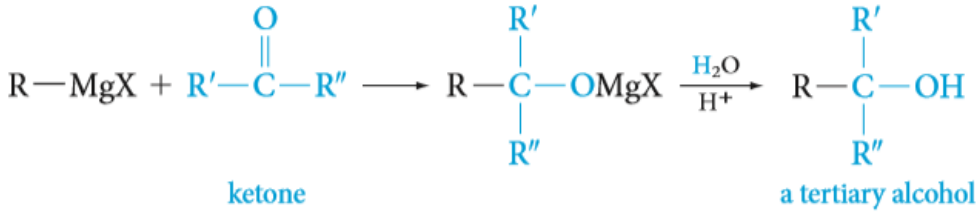
a) Addition of Grignard Reagents to aldehyde and ketone: formation of alcohol

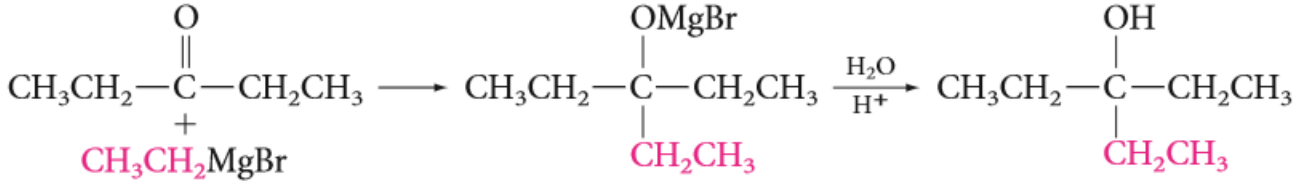


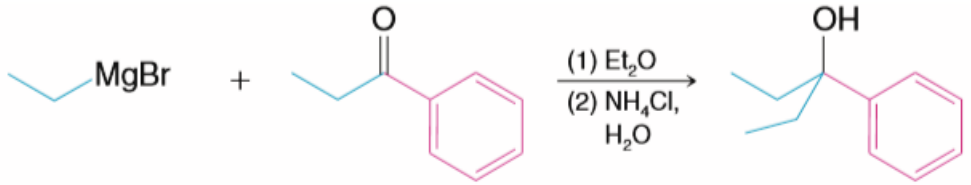
Other aldehydes give secondary alcohols.



Ketones give tertiary alcohols.

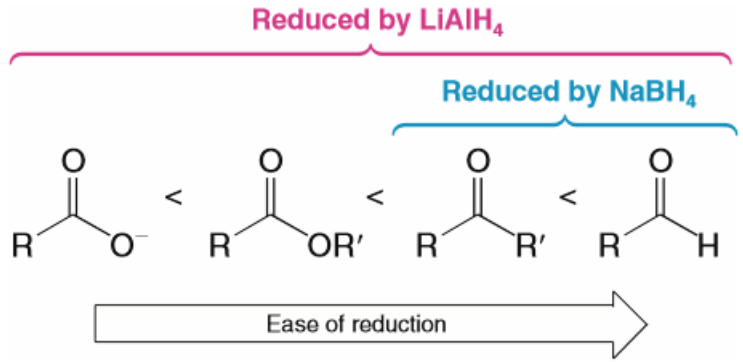


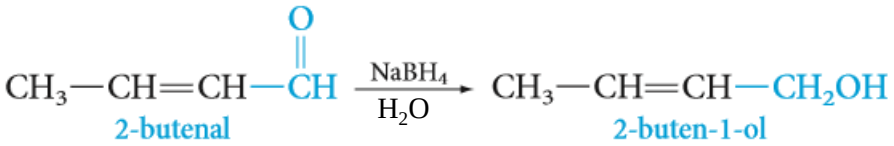


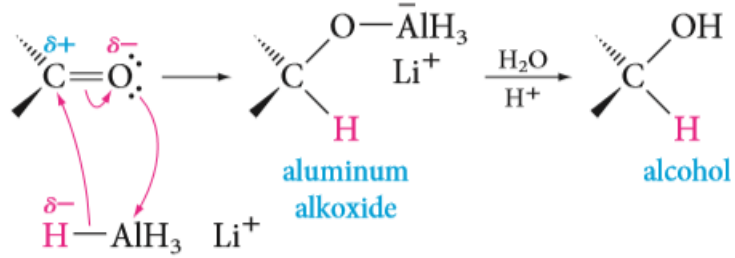


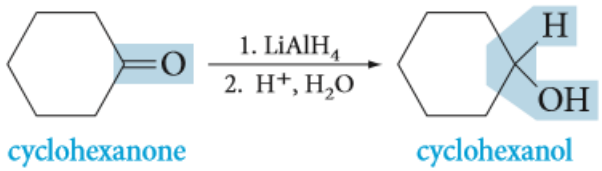
Reaction of Aldehyde and Ketone

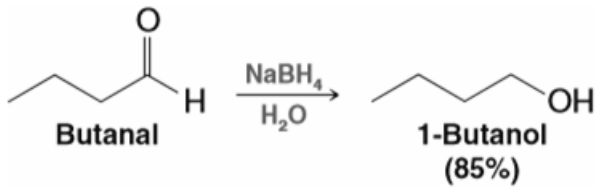
b) Reduction of carbonyl group: Addition of metal hydrides (formation of alcohol)

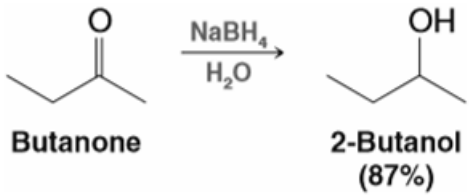






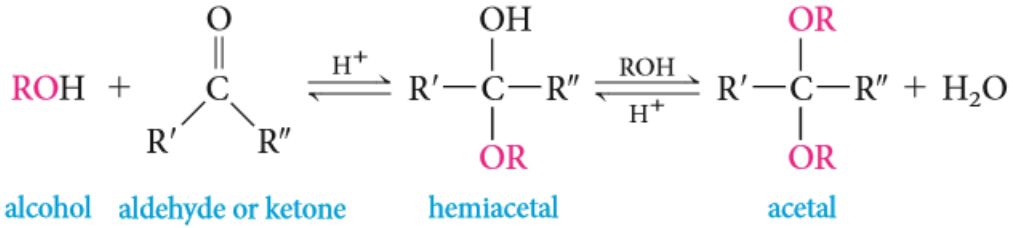


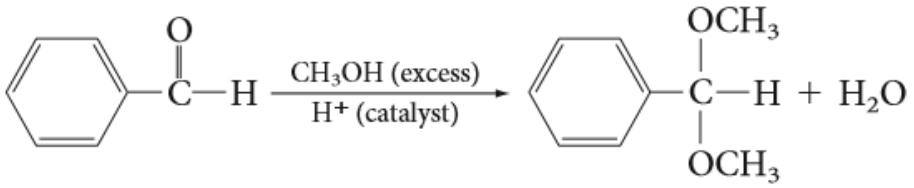


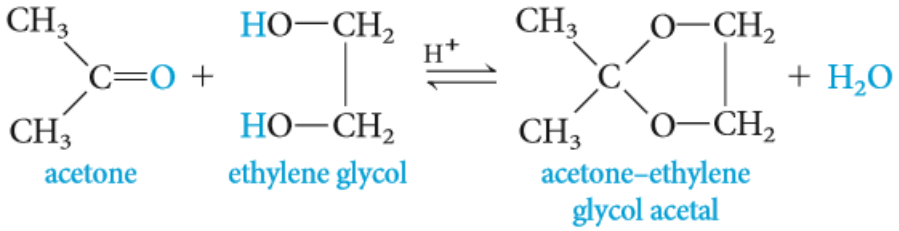


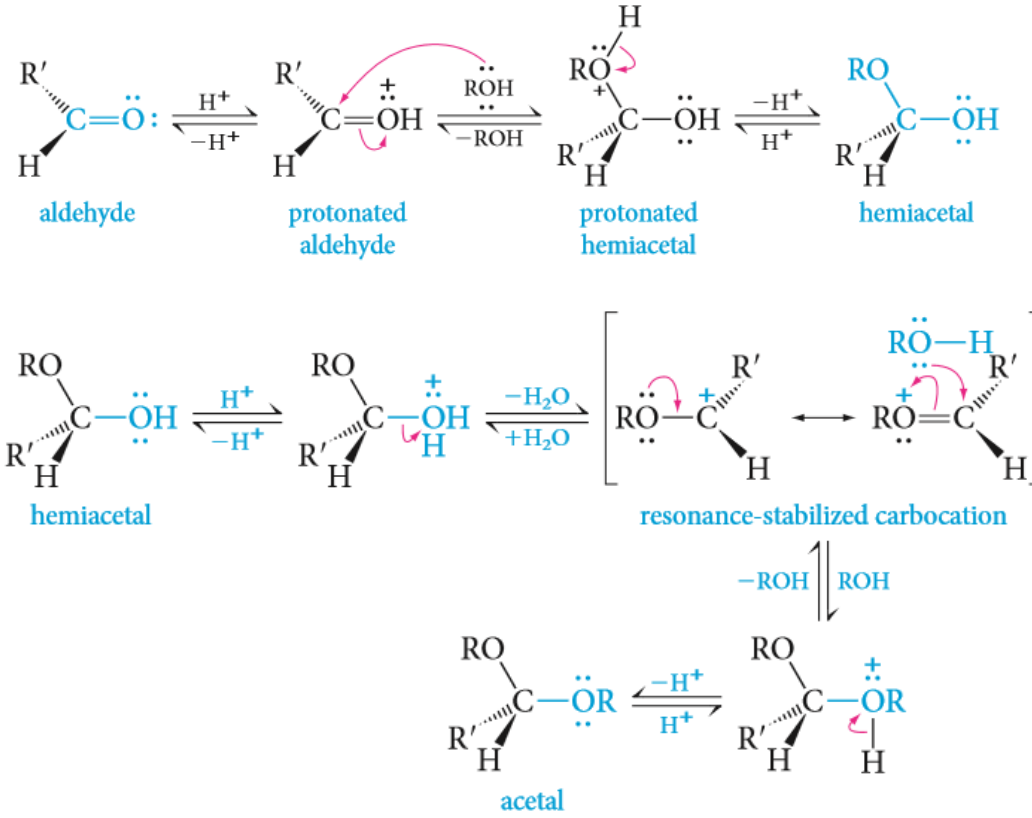
Reaction of Aldehyde and Ketone

c) The Addition of Alcohols: Hemiacetals and Acetals



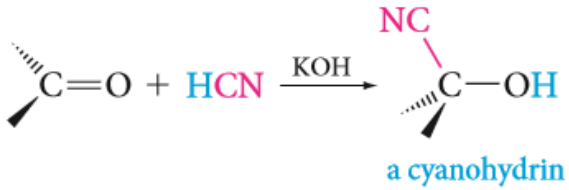


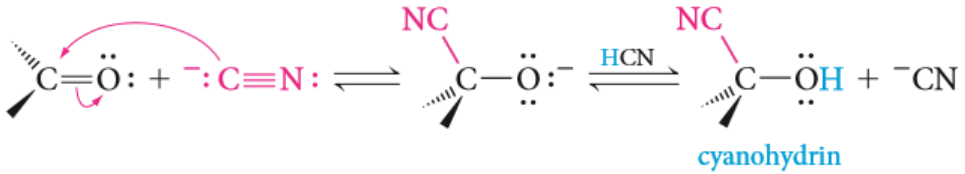


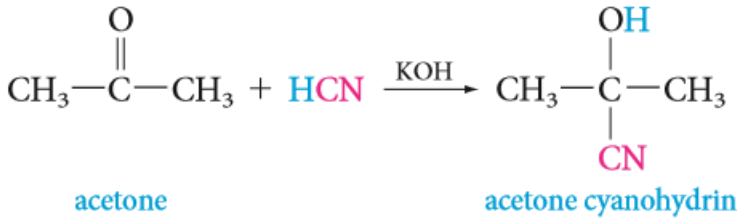


Reaction of Aldehyde and Ketone

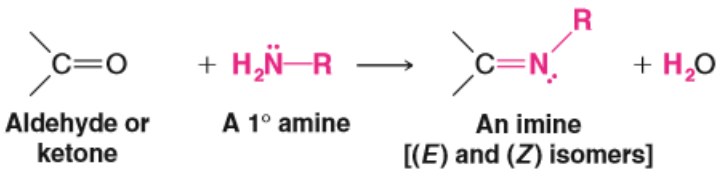
d) Addition of Hydrogen Cyanide: Formation of cynohydrins

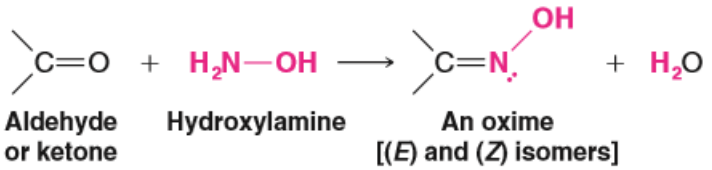


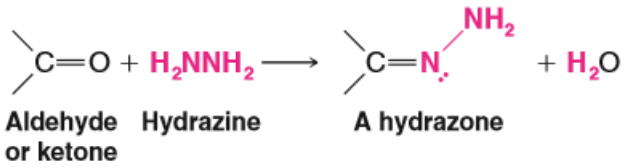


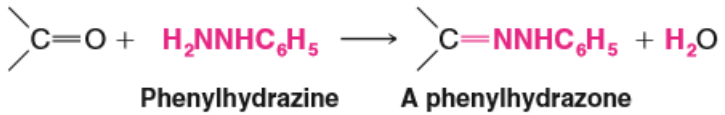


e) Addition of Ammonia and Ammonia Derivatives







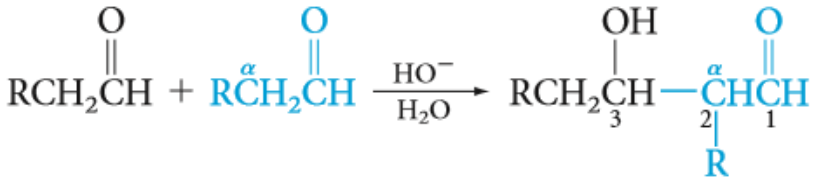


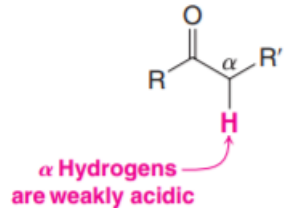
Formula of ammonia derivative	Name	Formula of carbonyl derivative	Name
RNH_2 or $ArNH_2$	primary amine	C=NR or C=NAr	imine
NH_2OH	hydroxylamine	C=NOH	oxime
NH_2NH_2	hydrazine	$C=NNH_2$	hydrazone
$NH_2NHC_6H_5$	phenylhydrazine	$C=NNHC_6H_5$	phenylhydrazone

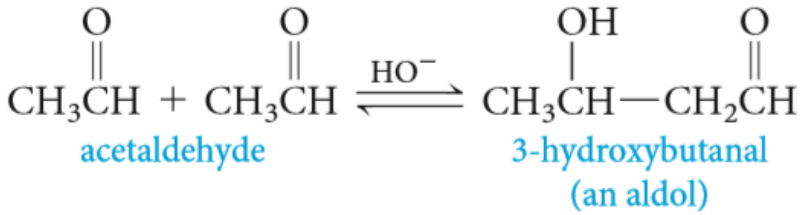
Reaction of Aldehyde and Ketone

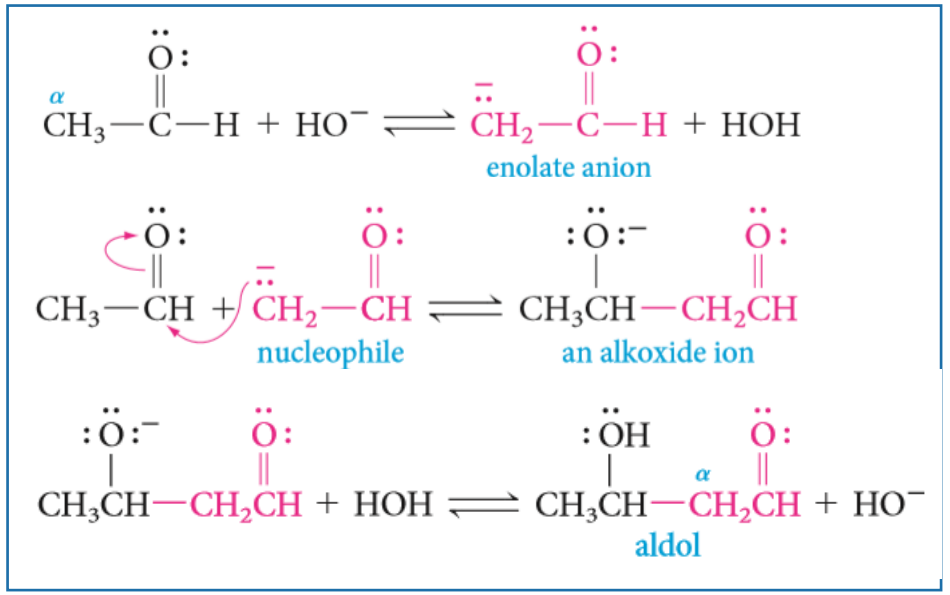
3- Aldol condensation:

Enolate anions may act as carbon nucleophiles. They add reversibly to the carbonyl group of another aldehyde or ketone molecule in a reaction called the aldol condensation, The product is called an aldol (so named because the product is both an aldehyde and an alcohol).

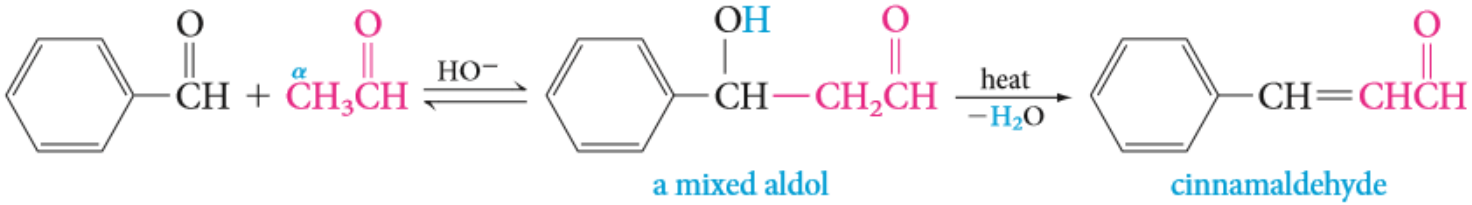






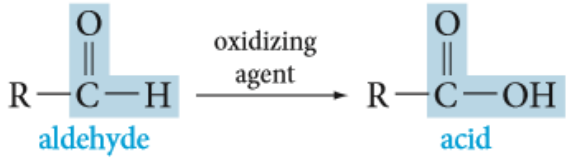


The mixed aldol condensation (crossed aldol reaction)



Reaction of Aldehyde and Ketone

4- Oxidation of Aldehydes



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