ALDEHYDES AND KETONES

Aldehydes And Ketones

- Aldehydes and ketones are characterized by the carbonyl functional group (C=O).
- The compounds occur widely in nature as intermediates in metabolism and biosynthesis.
- They are also common as chemicals, as solvents, monomers, adhesives, agrichemicals and pharmaceuticals.

The carbonyl group :

In this and several following chapters we study the physical and chemical properties of classes of compounds containing the carbonyl group, (C=O)

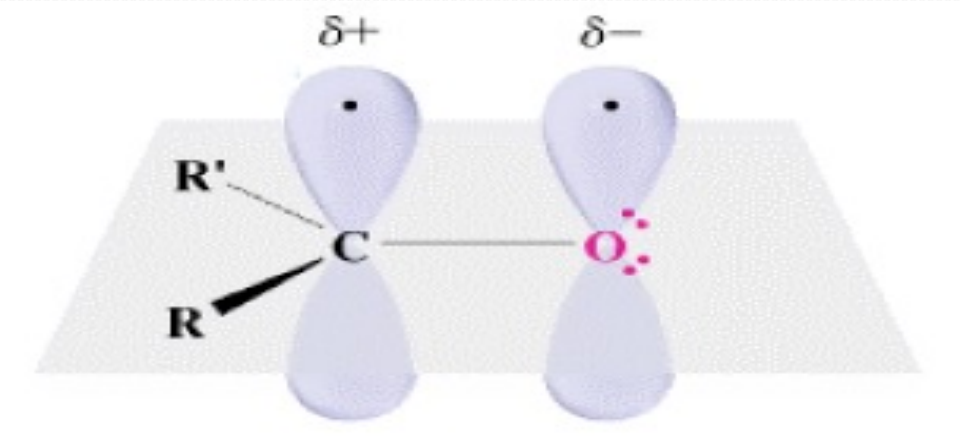
- aldehydes and ketones.
- carboxylic acids.
- acid halides, acid anhydrides, esters, amides.
- enolate anions.

Structure Of Carbonyl Group

The carbonyl group consists of;

- Three σ bonds formed by the overlap of sp^2 hybrid orbitals.
- One π bond formed by the overlap of parallel 2p orbitals.

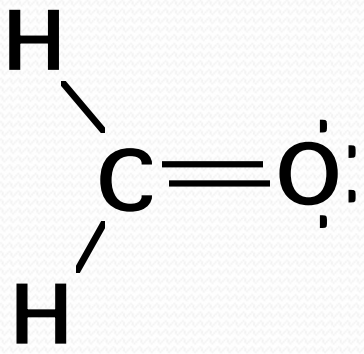
- The carbonyl carbon atom is sp^2 hybridized and forms three σ bonds and a π bond.
- The carbonyl compounds are planar about the double bond and have bond angles of approximately 120°.
- Carbon-oxygen double bonds are polarized because of the high electronegativity of oxygen relative to carbon.



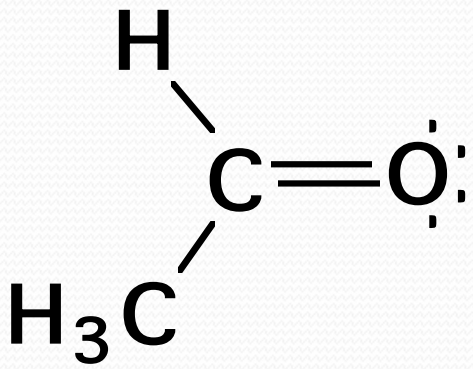
ALDEHYDES

The functional group of an aldehyde is a carbonyl group bonded to a H atom (RCHO)

- in methanal, it is bonded to two H atoms (HCHO).
- in all other aldehydes it is bonded to one H and one carbon atom (RCHO).



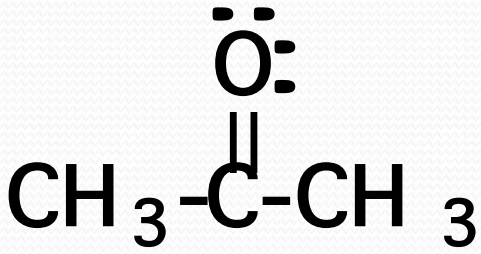
Methanal (formaldehyde)



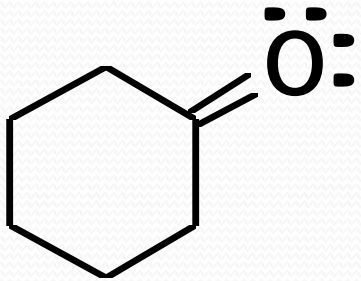
Ethanal (acetaldehyde)

KETONES

The functional group of a ketone is a carbonyl group bonded to two carbon atoms (R -CO -R).



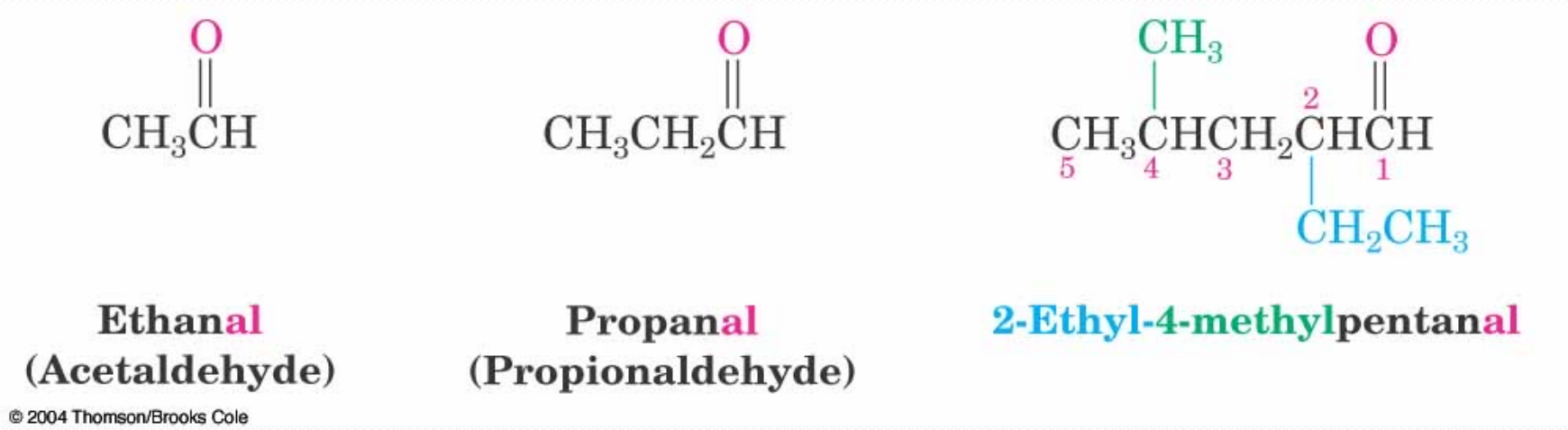
Propanone (Acetone)



Cyclohexanone

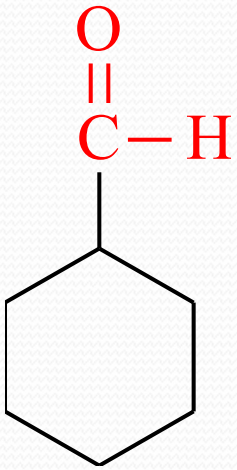
Naming Aldehydes

- Aldehydes are named by replacing the terminal -*e* of the corresponding alkane name with –*al*
- The parent chain must contain the —CHO group.
- The —CHO carbon is numbered as C1.

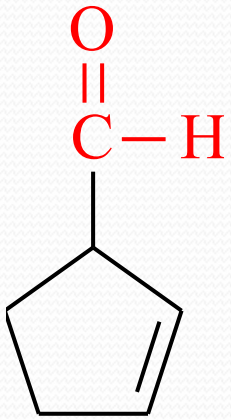


Naming Aldehydes

For cyclic molecules in which the -CHO group is attached to the ring, the name is derived by adding the suffix -carbaldehyde to the name of the ring.



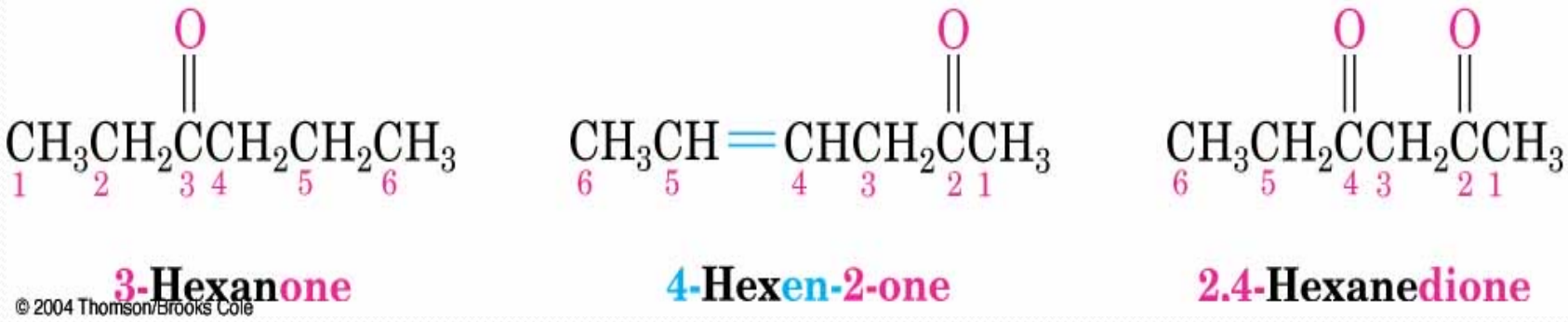
Cyclohexane carbaldehyde



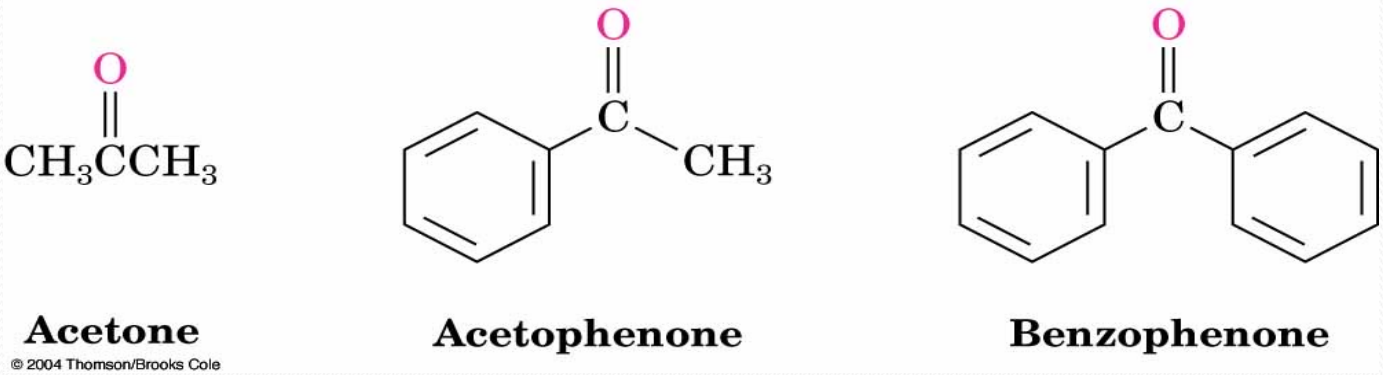
2-cyclopentenecarbaldehyde

Naming Ketones

- Replace the terminal -*e* of the alkane name with –*one.*
- Parent chain is the longest one that contains the ketone group.
- Numbering begins at the end nearer the carbonyl carbon.



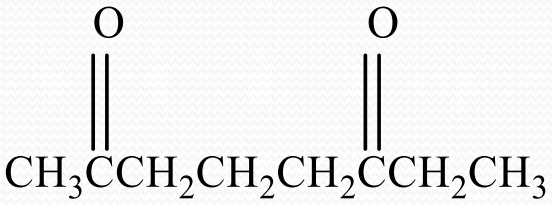
- Ketones having common names:

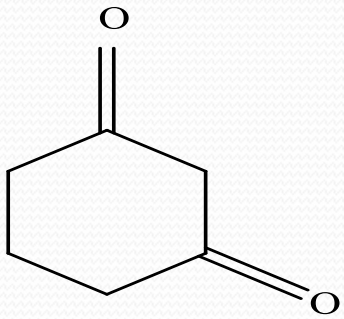


Naming Ketones

- The R–C=O as a substituent is an acyl group is used with the suffix -yl from the root of the carboxylic acid.
- CH_3CO: acetyl; CHO: formyl; C_6H_5CO: benzoyl
- The prefix *oxo*- is used if other functional groups are present and the doubly bonded oxygen is labeled as a substituent on a parent chain.

Examples:





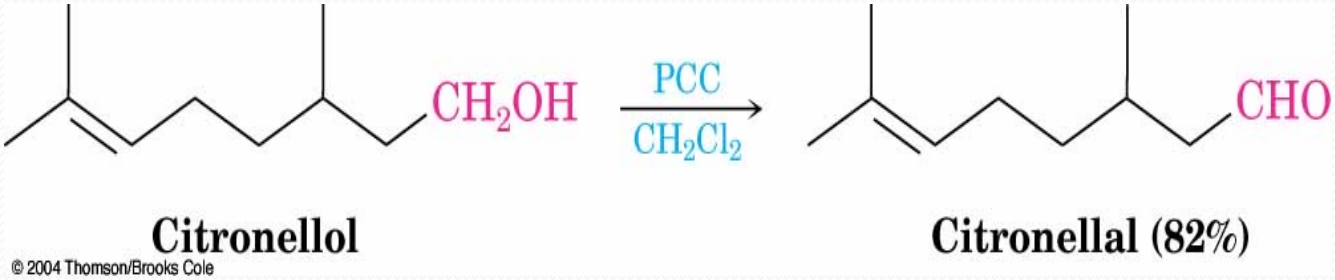
Order Of Functional Groups

For compounds that contain more than one functional group indicated by a suffix.

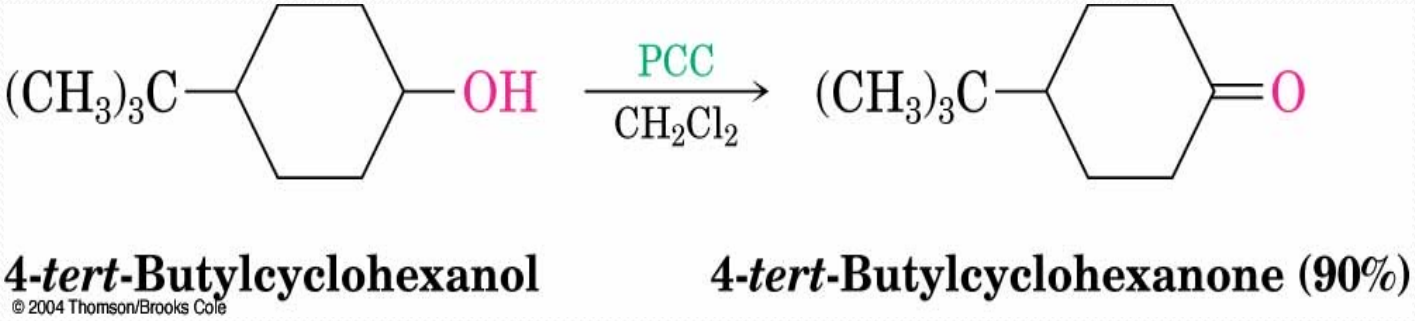
	Suffix if Higher	Prefix if Lower
-COOH	-oic acid	
-CHO	-al	oxo-
-C=O	-one	oxo-
-OH	-ol	hydroxy

Preparation Of Aldehydes And Ketones

- Oxidation of primary alcohols in presence of PCC/CH_2Cl_2 give aldehydes.

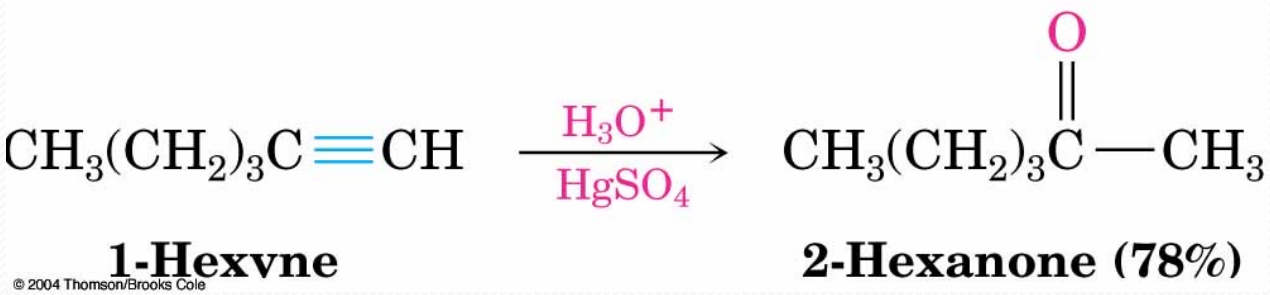


- Oxidation of secondary alcohols in presence of PCC or CrO_3 or $Na_2Cr_2O_7$ yield Ketone.

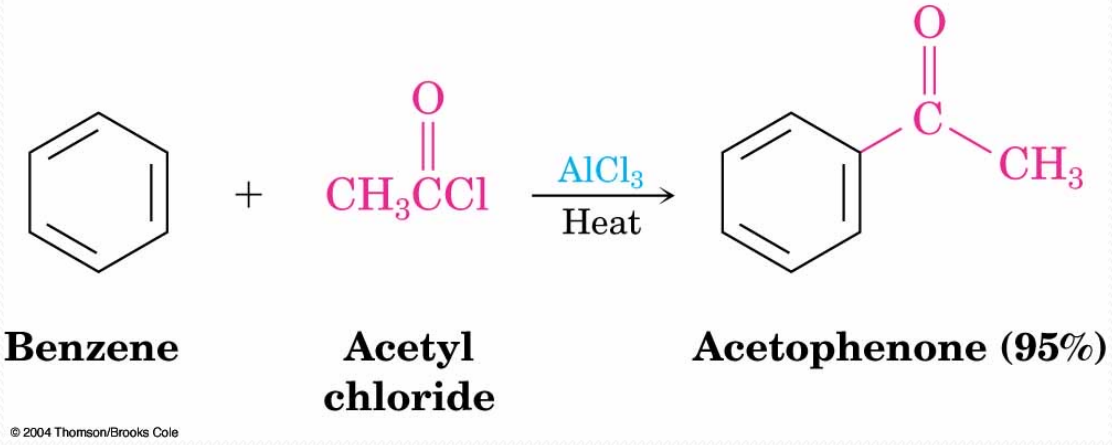


Preparation Of Ketones

- Hydration of terminal alkynes yield methyl ketones in presence of $HgSO_4$.



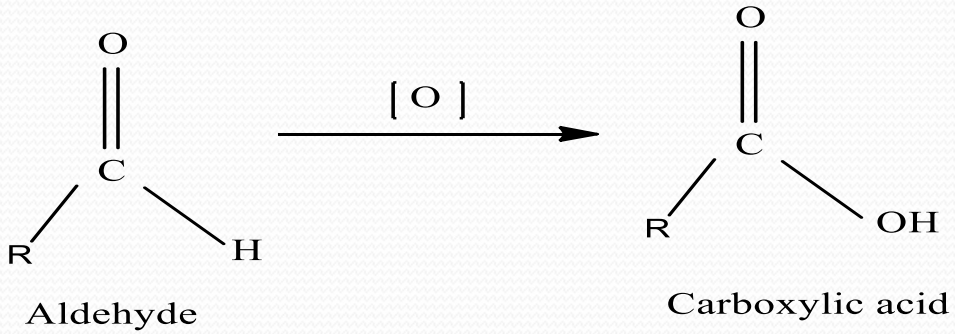
- Friedal crafts acylation of benzene yields acetophenone.



Oxidation Of Aldehydes And Ketones

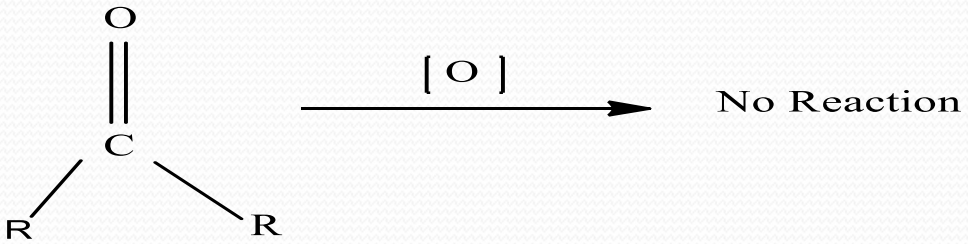
Oxidizing agents

- $KMnO_4/HNO_3$
- CrO_3
- Ag_2O/NH_3
- Tollen's reagent.



Aldehyde

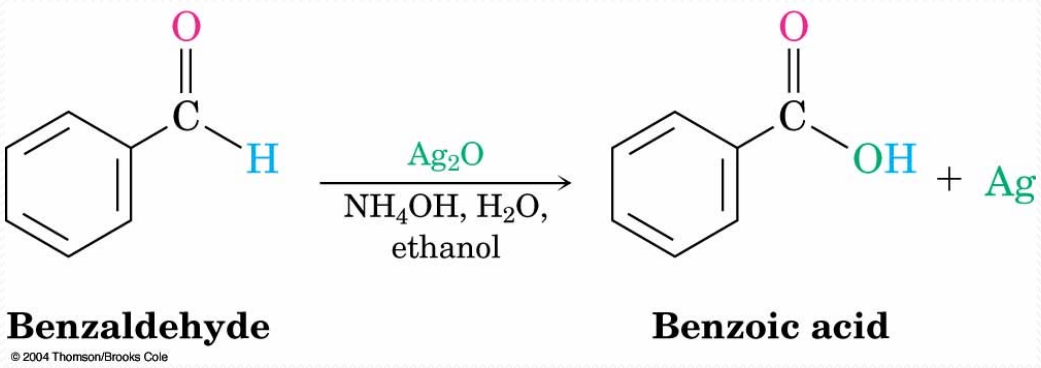
Carboxylic acid



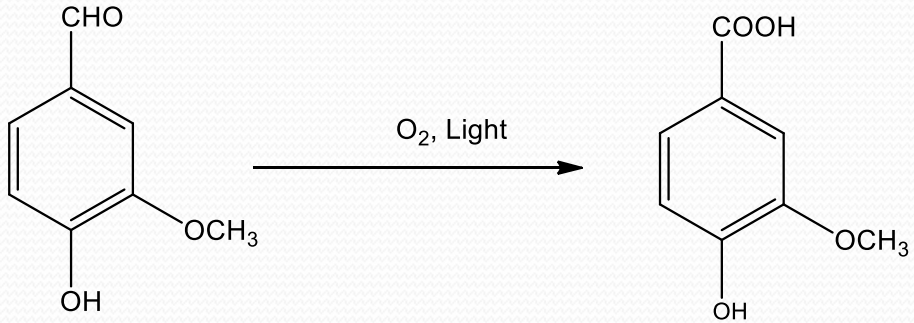
Ketone

Oxidation Of Aldehydes

Silver oxide, Ag_2O, in aqueous ammonia (Tollen's' reagent) oxidizes aldehydes to carboxylic acids.



Oxygen, O_2, in air can also convert aldehydes into carboxylic acids.



Vanillin
An aldehyde

An oxidation product
a carboxylic acid

Nucleophilic Addition Reactions Of Aldehydes And Ketones

The nucleophilic addition reaction of aldehydes and ketones , the nucleophile adds to the electrophilic carbon of the carbonyl group.

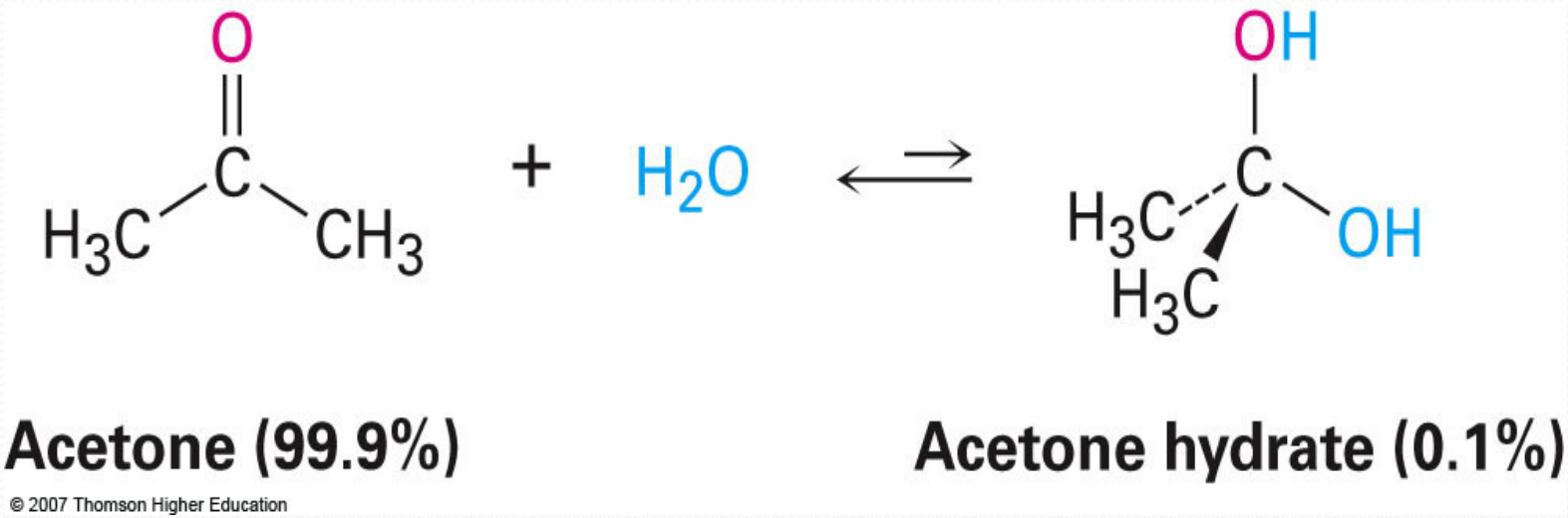
- Hydration with Water.
- Acetal formation with ROH.
- Grignard addition with RMgX.
- Imine formation with RNH_2.

Nucleophilic addition in acidic conditions, positively charged intermediates are favored.

Nucleophilic addition in basic conditions. negatively charged intermediates are favored.

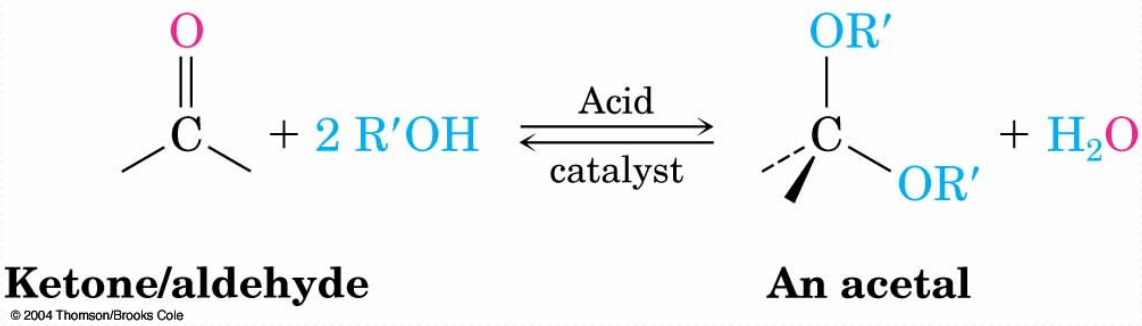
Nucleophilic Addition Of Water : Hydration

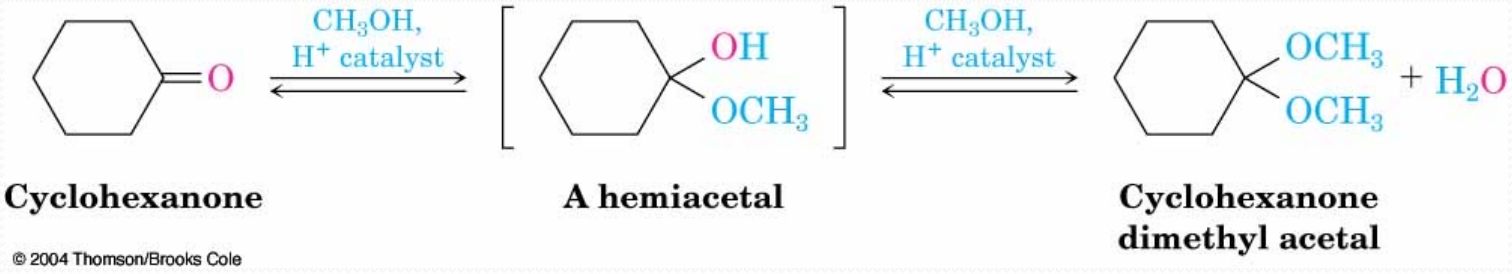
- Aldehydes and ketones react with water to yield 1,1-diols (**geminal (gem) diols).**
- Hydration is reversible: a gem diol can eliminate water.



Nucleophilic Addition Of Alcohols: Acetal Formation

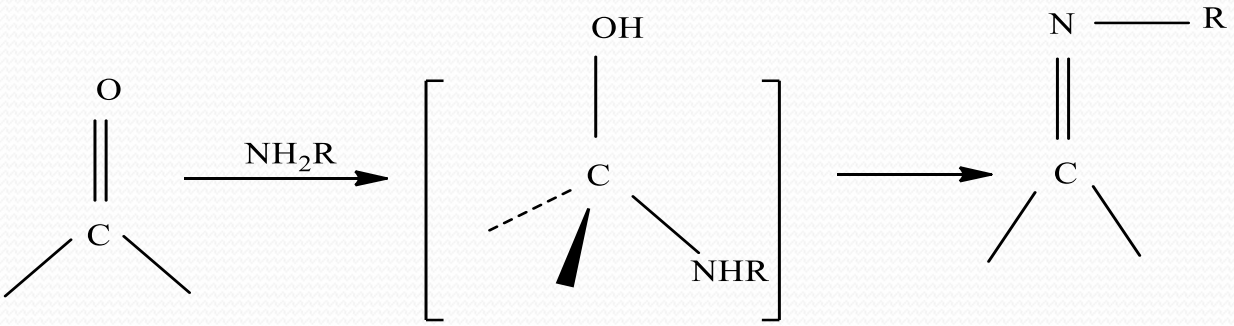
- Two equivalents of ROH in the presence of an acid catalyst add to C=O to yield acetals, $R_2C(OR')_2$
- These can be called *ketals* if derived from a ketone.





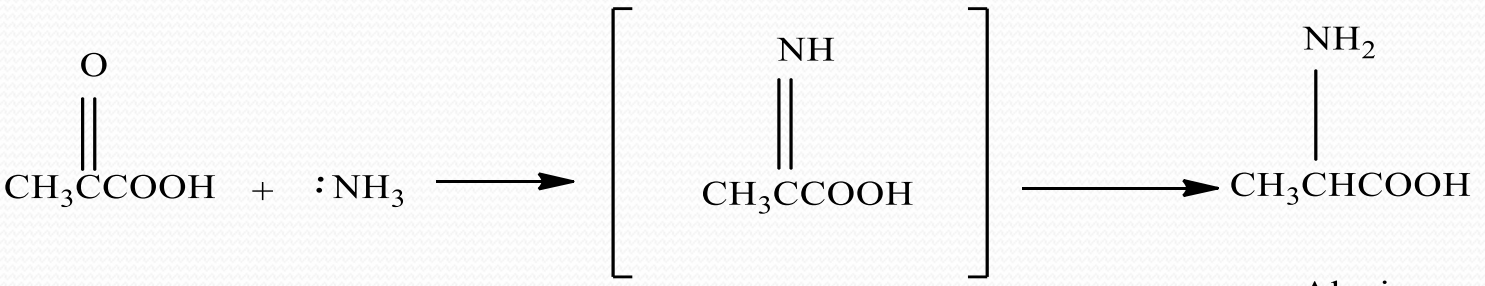
Nucleophilic Addition Of Amines: Imine Formation

- Ammonia and primary amines add to aldehydes and ketones to yield imines, $R_2C{=}NR'$.



A ketone or aldehyde | Amino alcohol intermediate | An Imine

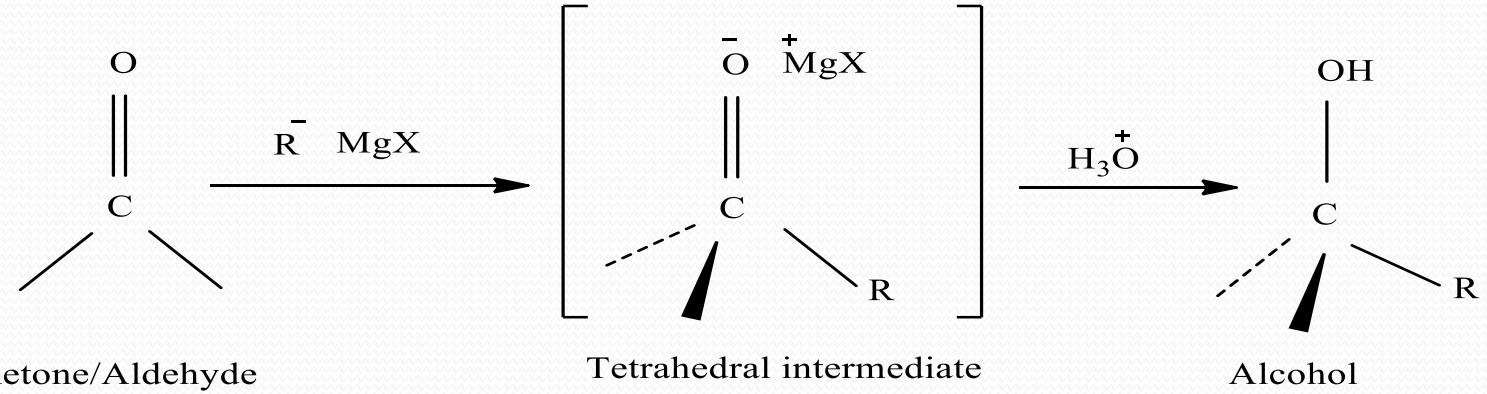
- Imines are common intermediates in biological pathways.
- Imine gets further reduced in presence of enzymes.



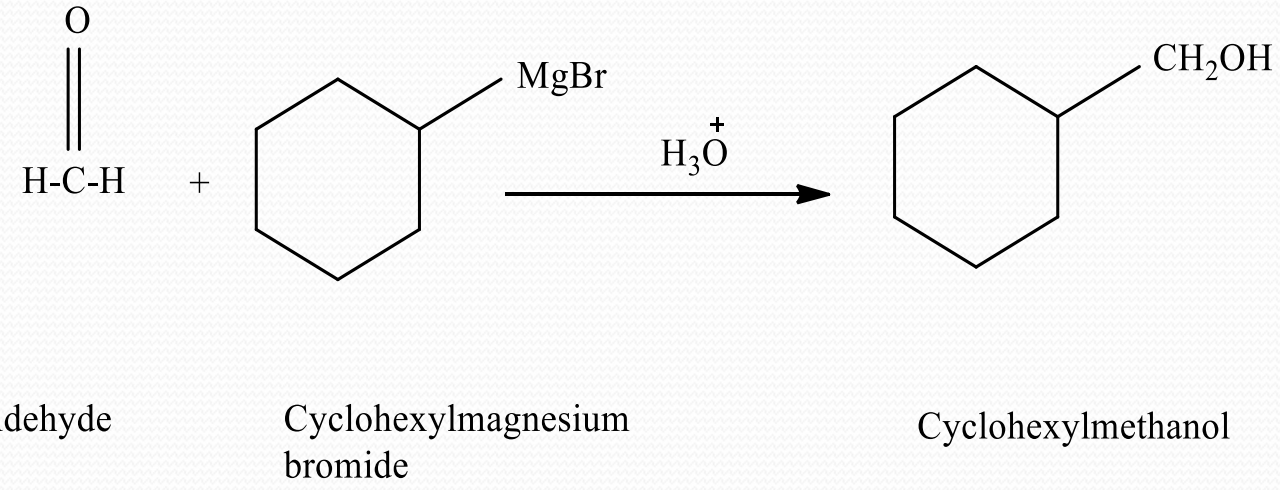
Pyruvic acid | An Imine | Alanine (Amino Acid)

Nucleophilic Addition Of Grignard Reagent: Alcohol Formation

The reaction of aldehydes and ketones with Grignard reagent yields alcohols.

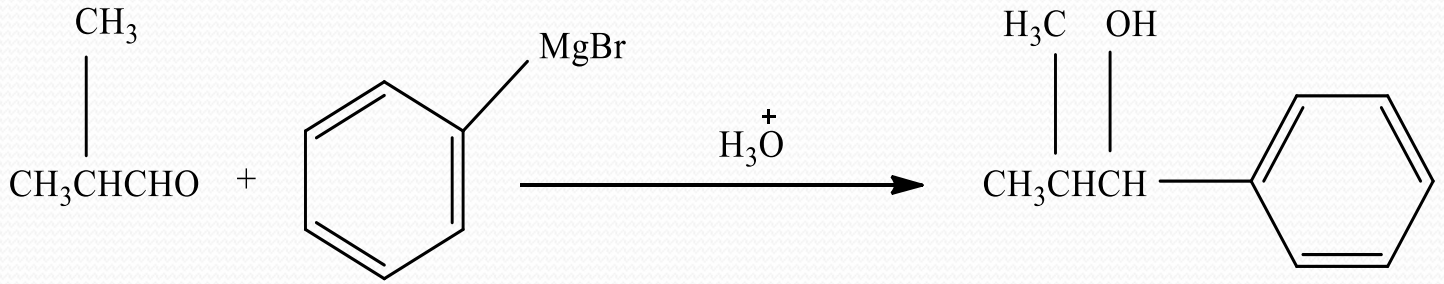


Example:



Nucleophilic Addition Of Grignard Reagent: Alcohol Formation

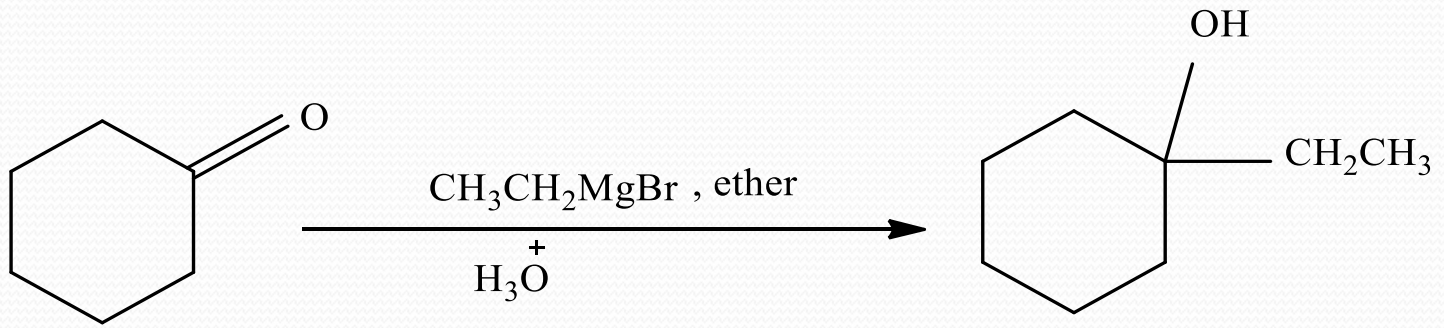
Examples



2-Methylpropanal

Cyclohexylmagnesium bromide

2-Methyl-1-phenylpropan-1-ol

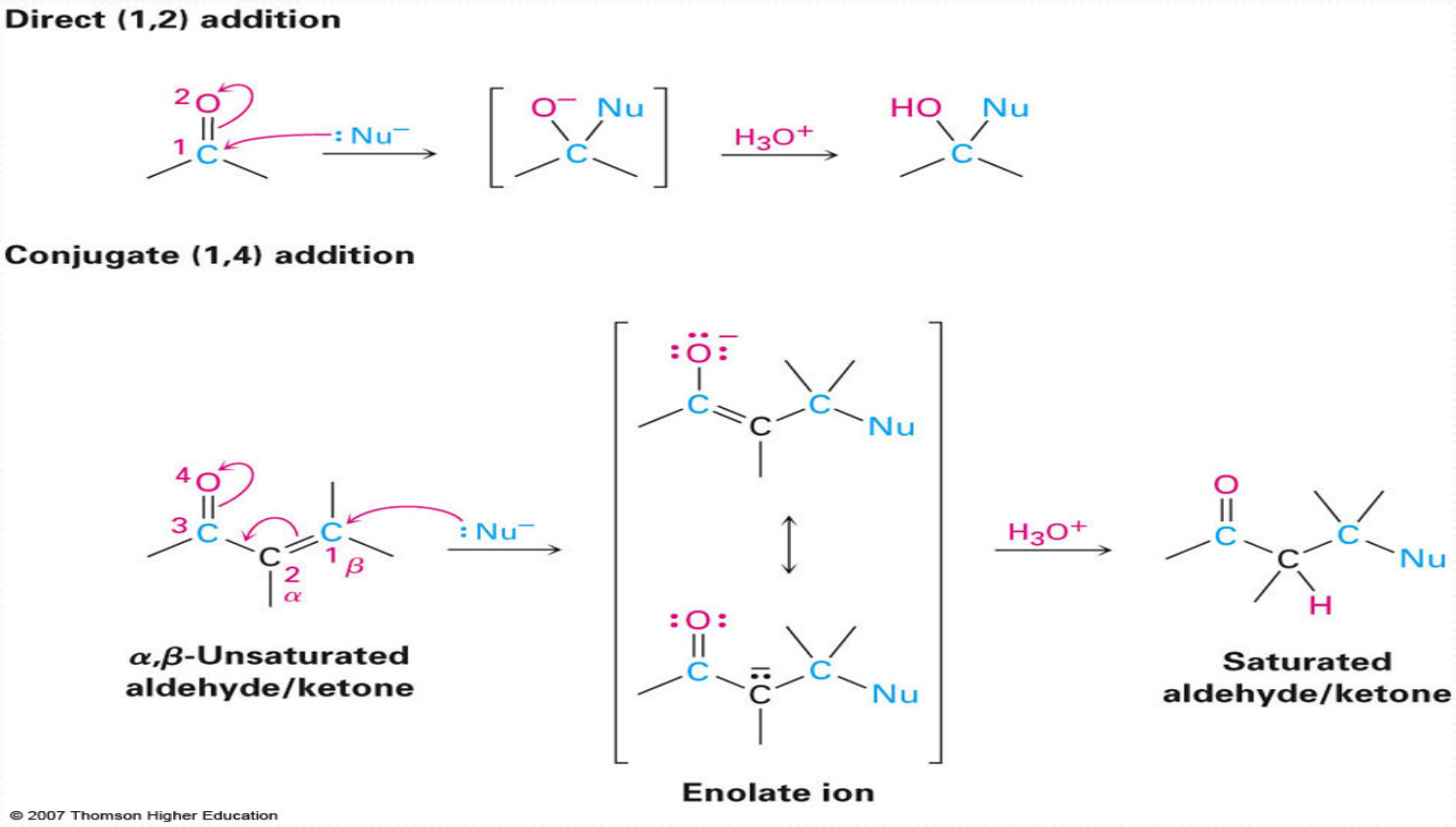


Cycloheaxanone

1-Ethylcyclohexanol

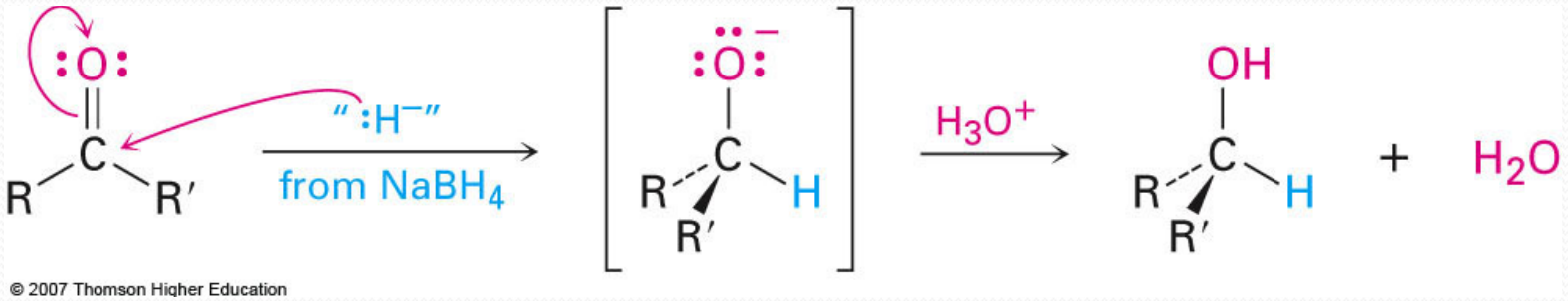
Conjugate (1,4) Nucleophilic Addition Reaction

α,β – Unsaturated aldehydes /ketones on nuclepphilic addition , the initial product formed is a resonance stabilized enolate ion, which undergoes protonation on the α-carbon to form a saturated aldehyde/ ketones.

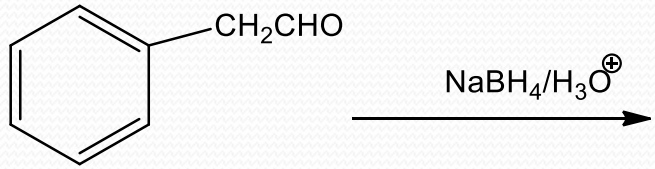


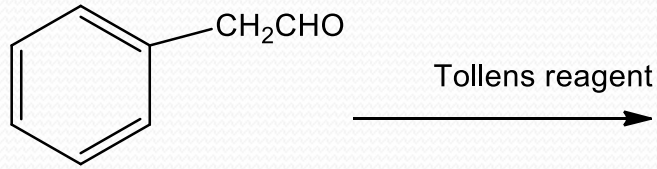
Hydride Addition

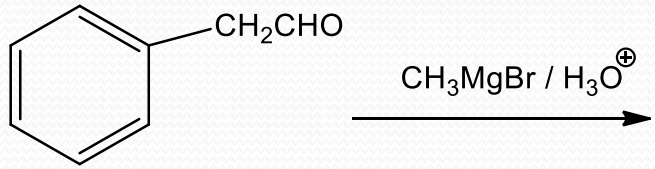
- Convert C=O to CH-OH
- $LiAlH_4$ and $NaBH_4$ react as donors of hydride ion.
- Protonation after addition yields the alcohol.



Practice Problems

1. 

2. 

3. 

4.