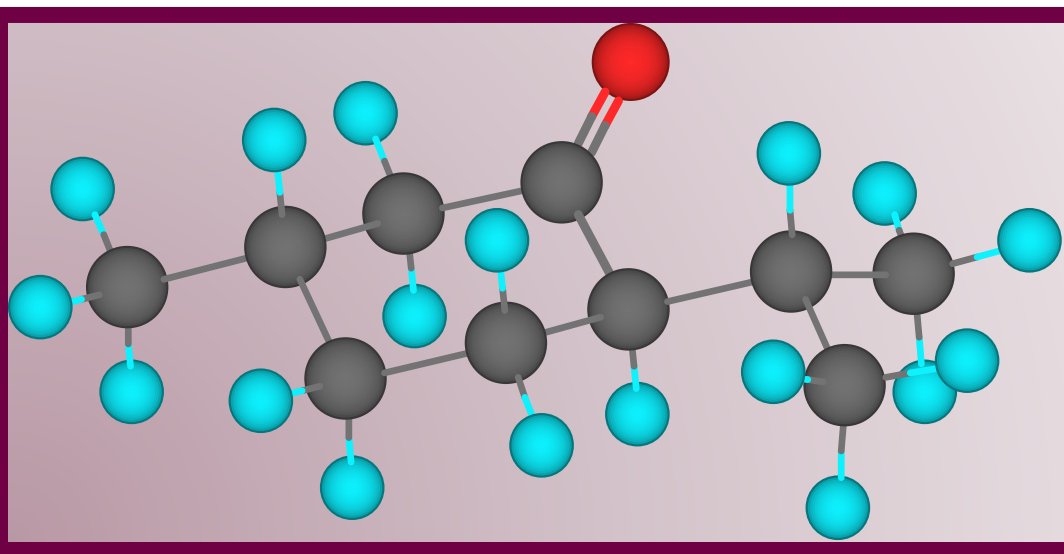


Aldehydes and Ketones

Dr Gohar Taqi Kazimi

Department of Chemistry

University of Sargodha



The Carbonyl Group

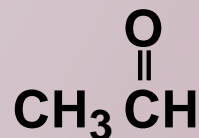
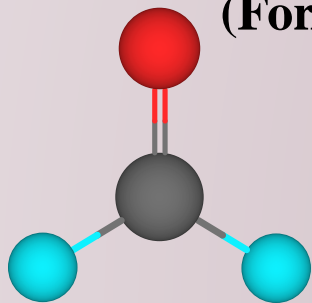
Aldehydes, ketones, carboxylic acids, acid halides, acid anhydrides, esters, amides, enolate anions **are** organic compounds having the carbonyl group, C=O

Structure

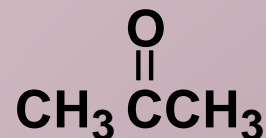
The functional group of an aldehyde C=O group bonded to a H atom while the functional group of a ketone is a carbonyl group bonded to two carbon atoms



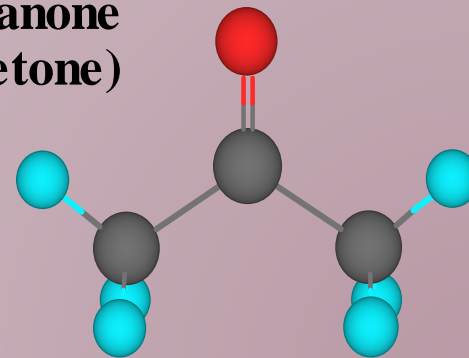
Methanal
(Formaldehyde)



Ethanal
(Acetaldehyde)



Propanone
(Acetone)

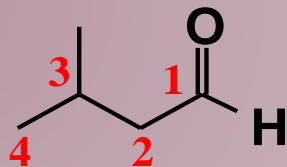


Nomenclature

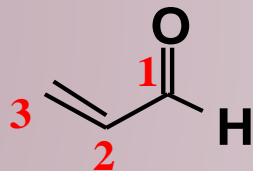
IUPAC names:

- Select the longest chain as the parent chain containing the carbonyl group.
- Start the numbering from aldehydic carbon
- For an aldehyde, change the suffix from **-e** to **-al**
- For an unsaturated aldehyde, show the carbon-carbon double bond by changing the infix from **-an-** to **-en-**; the location of the suffix determines the numbering pattern
- For a cyclic molecule in which **-CHO** is bonded to the ring, add the suffix **-carbaldehyde**

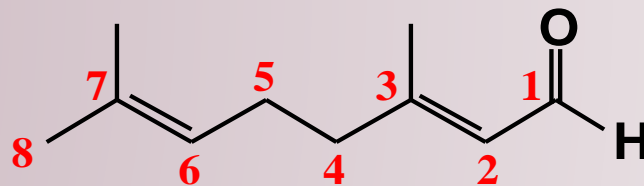
Nomenclature



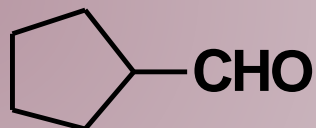
3-Methylbutanal



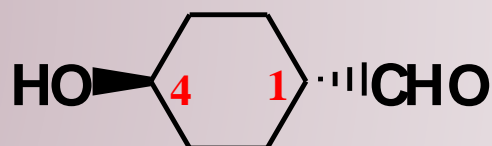
2-Propenal
(Acrolein)



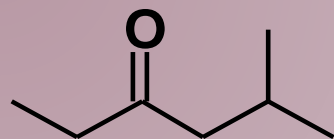
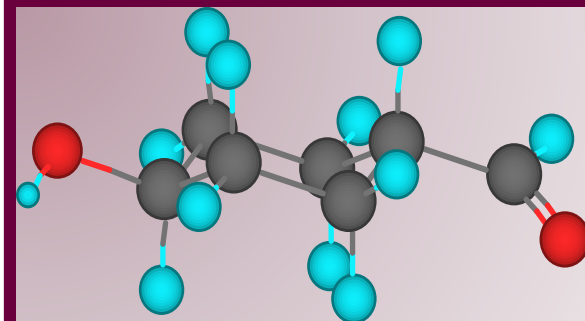
(2E)-3,7-Dimethyl-2,6-octadienal
(Geranial)



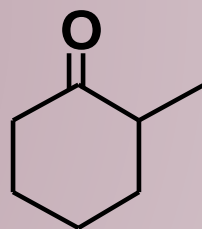
Cyclopentanecarbaldehyde



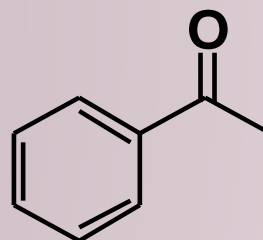
trans-4-Hydroxycyclohexanecarbaldehyde



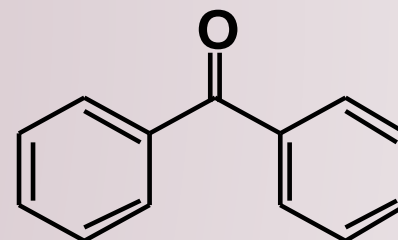
5-Methyl-3-hexanone



2-Methylcyclohexanone

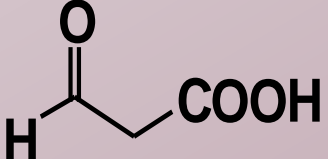
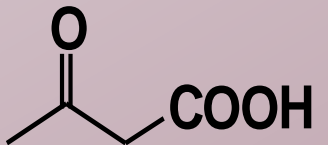
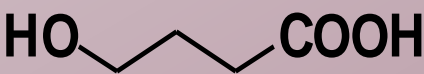
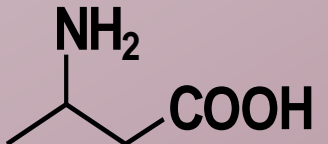



Acetophenone



Benzophenone

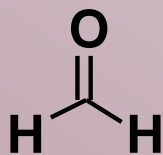
Nomenclature

Functional Group	Suffix	Prefix	Example of When the Functional Group Has a Lower Priority	
Carboxyl	-oic acid	—		
Aldehyde	-al	oxo-	3-Oxopropanoic acid	
Ketone	-one	oxo-	3-Oxobutanoic acid	
Alcohol	-ol	hydroxy-	4-Hydroxybutanoic acid	
Amino	-amine	amino-	3-Aminobutanoic acid	
Sulfhydryl	-thiol	mercapto-	2-Mercaptoethanol	

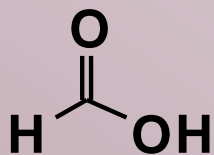
Nomenclature

Common names

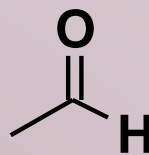
- For an aldehyde, the common name is derived from the common name of the corresponding carboxylic acid
- For a ketone, name the two alkyl or aryl groups bonded to the carbonyl carbon and add the word ketone



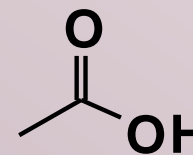
Formaldehyde



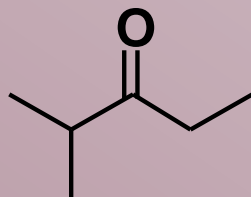
Formic acid



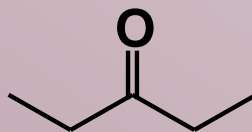
Acetaldehyde



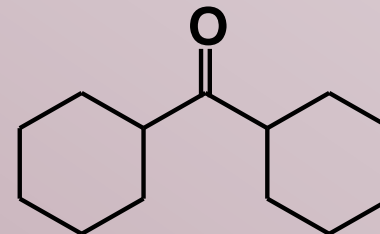
Acetic acid



Ethyl isopropyl ketone



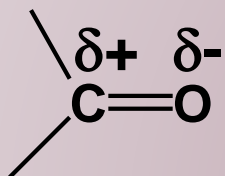
Diethyl ketone



Dicyclohexyl ketone

Physical Properties

C=O group is polar because oxygen is more EN than carbon (3.5 vs 2.5)



Polarity of a carbonyl group

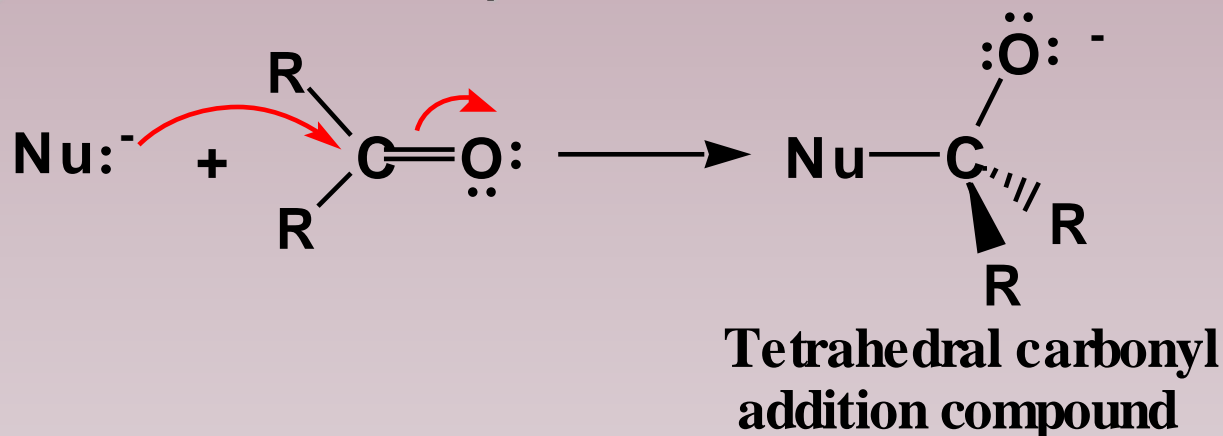


More important contributing structure

- Aldehydes and ketones are polar compounds and interact in the pure state by dipole-dipole interactions
- They have higher boiling points and are more soluble in water than nonpolar compounds of comparable molecular weight.

Reactions

Nucleophilic addition are the most common reaction offered by carbonyl group to form a tetrahedral carbonyl addition compound.



Addition of carbon nucleophiles is one of the most important types of nucleophilic additions to a C=O group. As a result a new carbon-carbon bond is formed in the process

Grignard Reagents

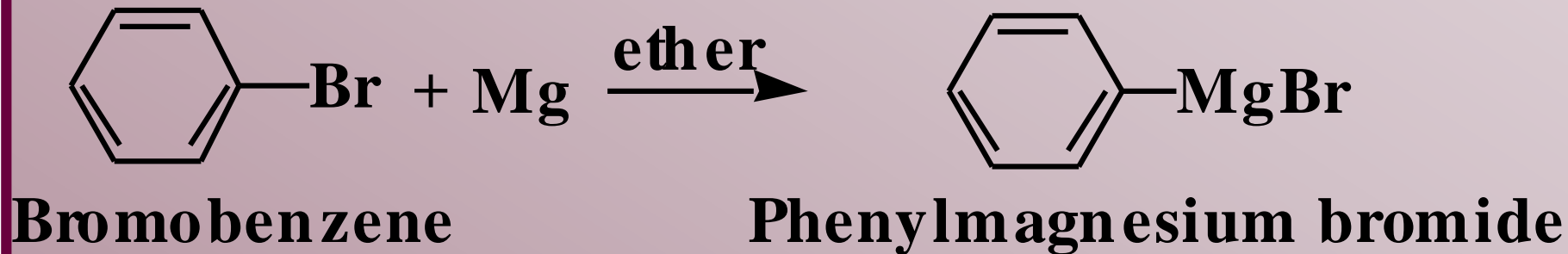
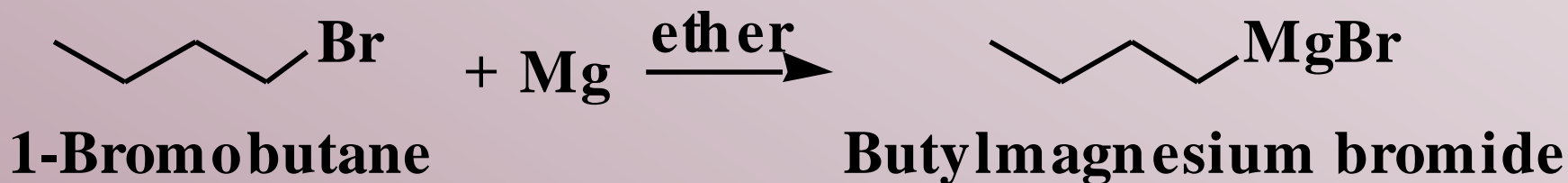
Grignard reagents

Alkyl magnesium halides having the general formula RMgX , where R is an alkyl or aryl group and X is a halogen called GR

Due to difference in EN between carbon and magnesium (2.5 - 1.3), the C-Mg bond is polar covalent, with $\text{C}\delta^-$ and $\text{Mg}\delta^+$ so a Grignard reagent behaves as a carbanion in its reactions.

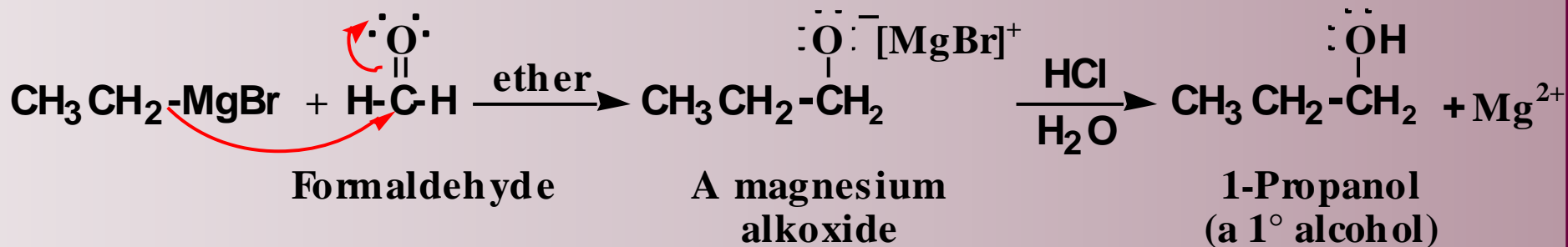
Synthesis of Grignard Reagents

GR are prepared by adding an alkyl or aryl halide to a suspension of Mg metal in diethyl ether

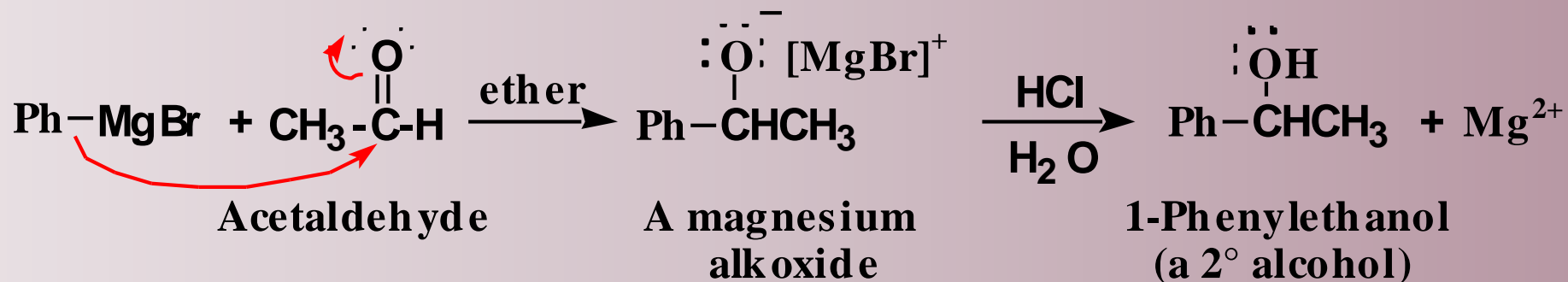


Grignard Reagents

Reaction with formaldehyde gives a 1° alcohol

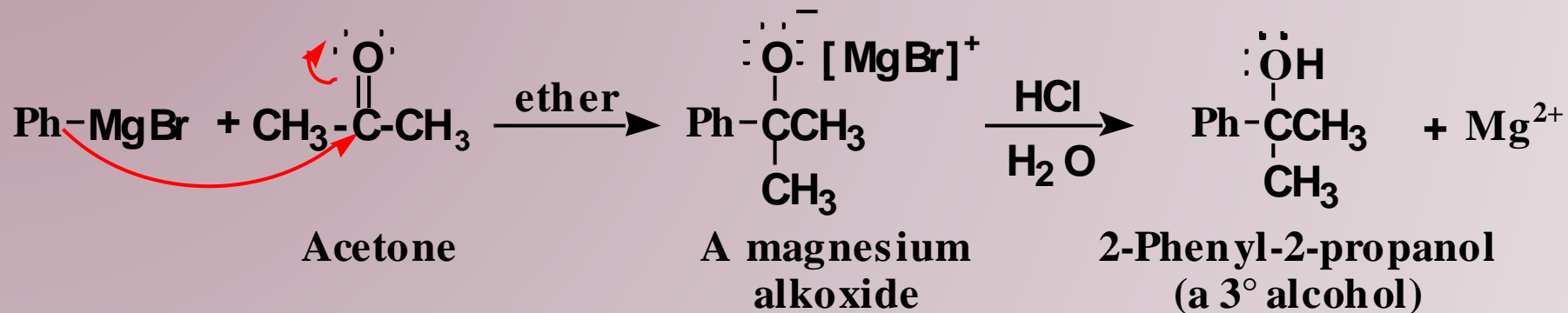


Reaction with any other aldehyde gives a 2° alcohol

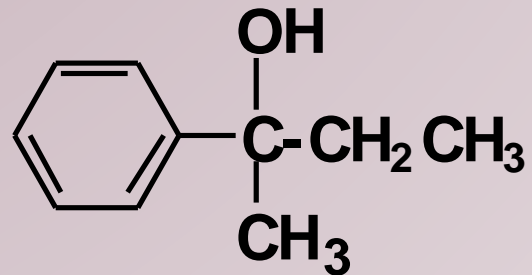


Grignard Reagents

- Reaction with a ketone gives a 3° alcohol

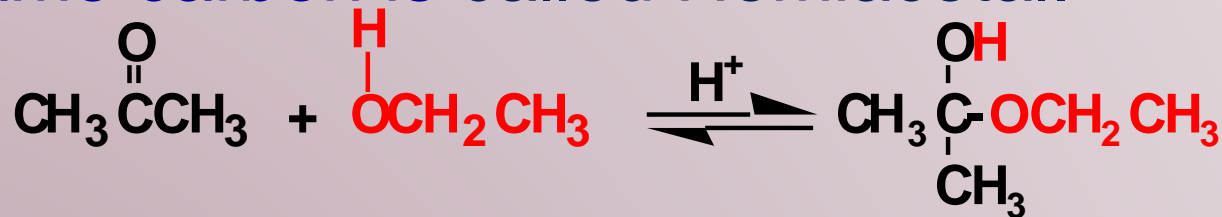


- Draw a scheme for the synthesis of the following 3° alcohol by various routes.



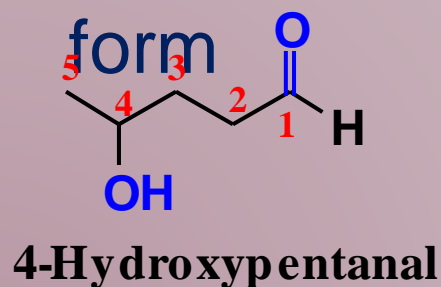
Addition of Alcohols

A compound having both -OH and -OR group bonded to the same carbon is called Hemiacetal.

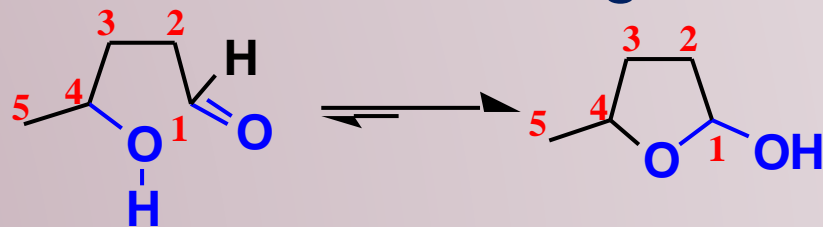


A hemiacetal

These are minor components of an equilibrium mixture except where a 5- or 6-membered ring can



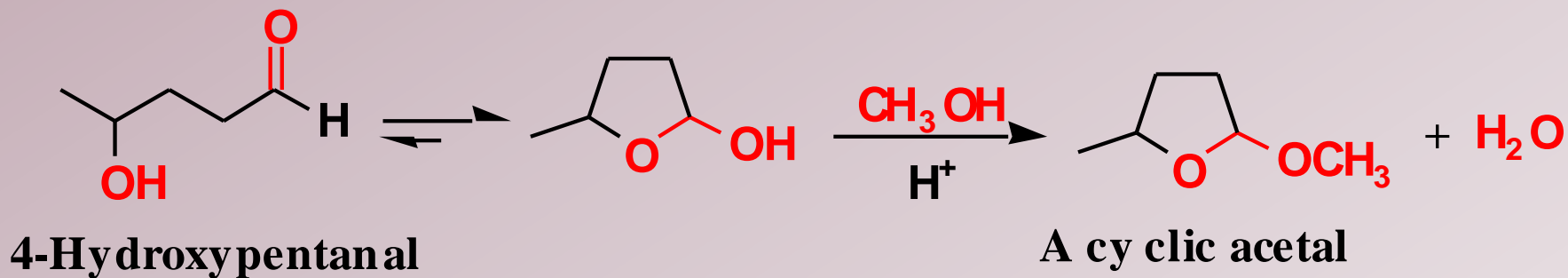
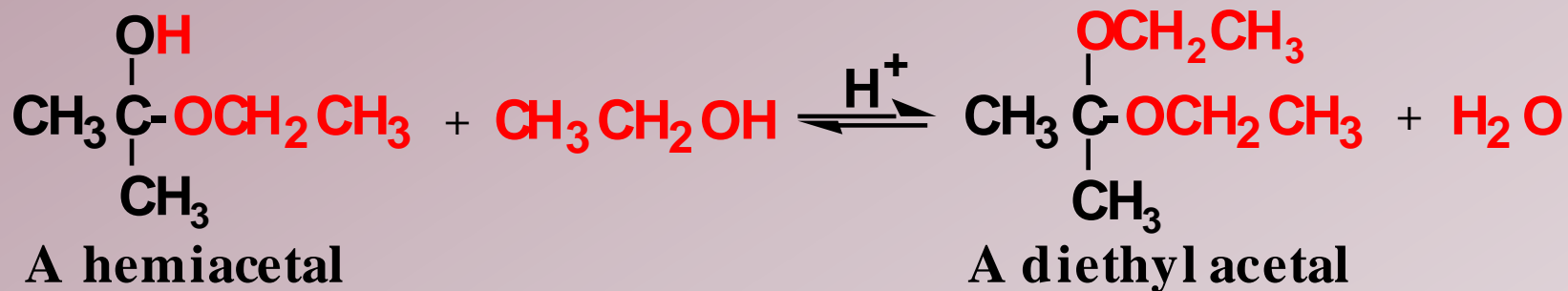
redraw to show
the OH close to
the CHO group



A cyclic hemiacetal
(major form present
at equilibrium)

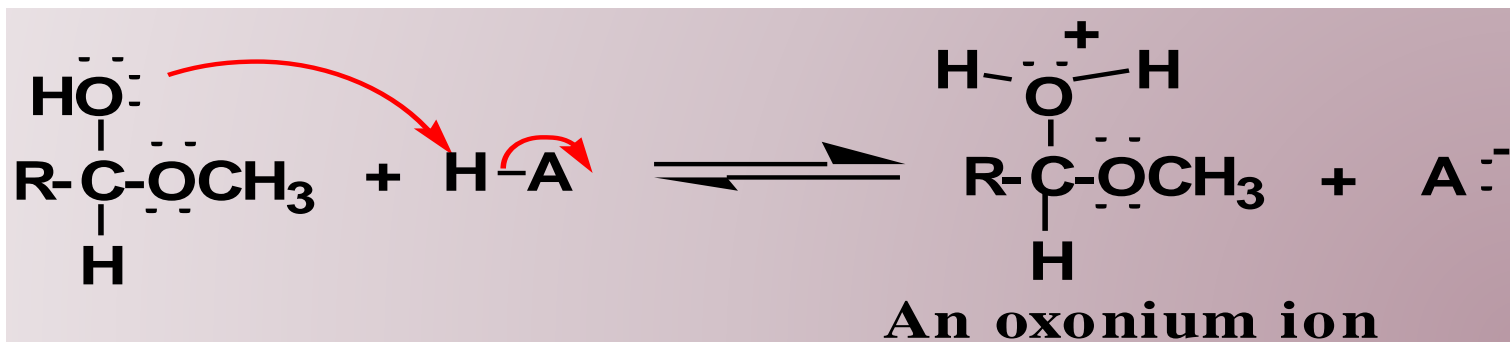
Addition of Alcohols

A molecule having two -OR groups bonded to the same carbon is called an acetal and are formed by the addition of a molecules of alcohol to hemiacetal

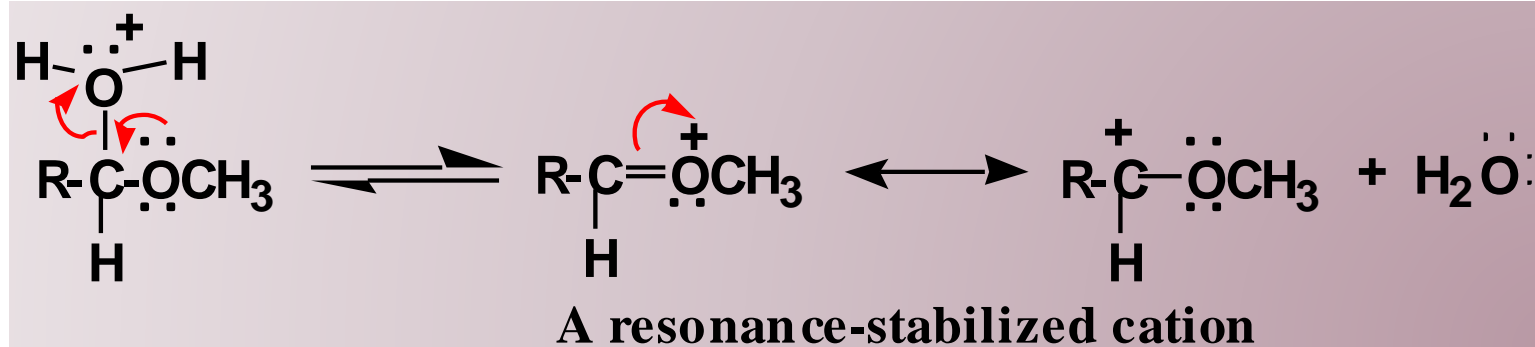


Acetal Formation

1. Proton transfer from HA to the hemiacetal oxygen

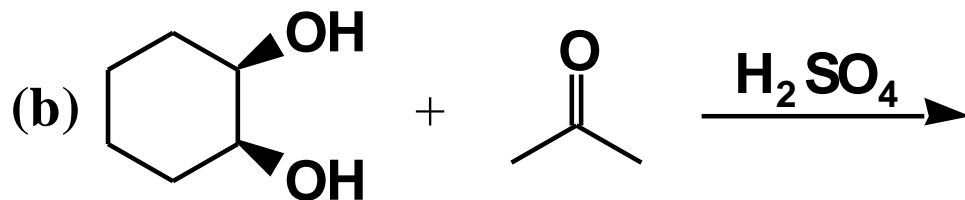
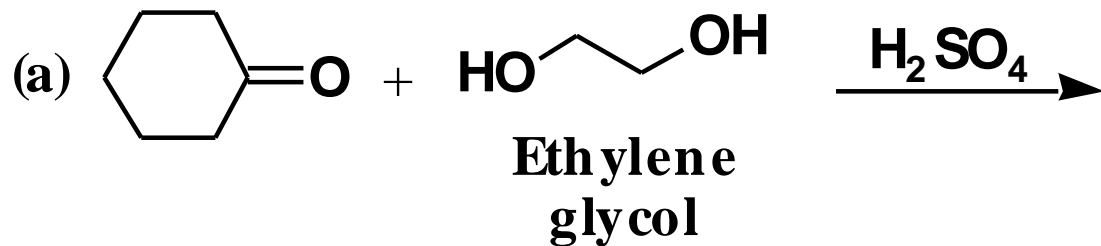


2. Loss of H₂O gives a cation



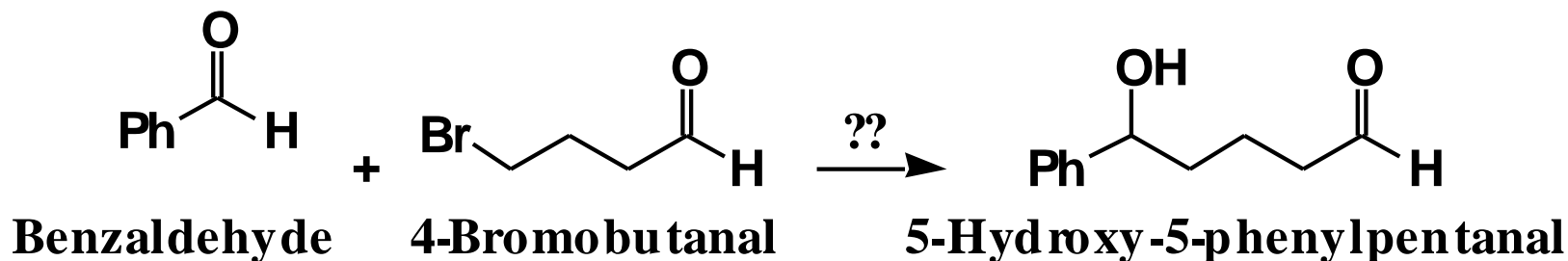
Acetals

Draw a structural formula for the acetal formed in each reaction

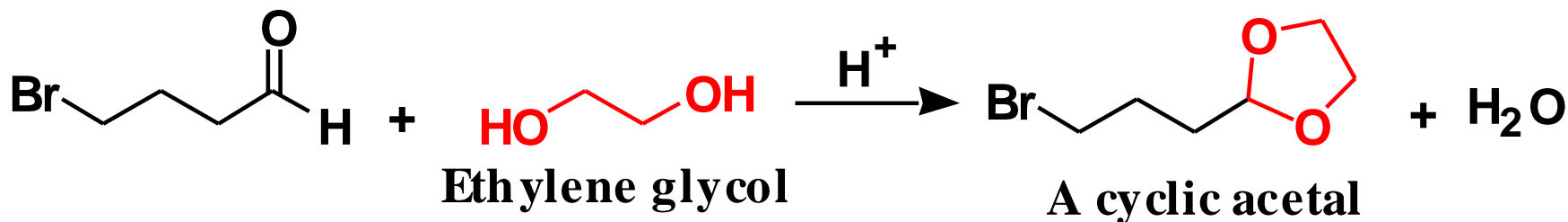


Acetals as Protecting Groups

- one way to synthesize the ketoalcohol on the right is by a Grignard reaction

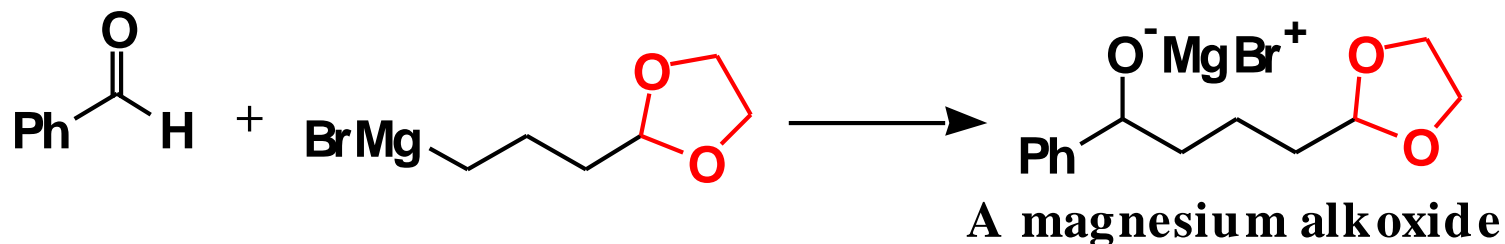
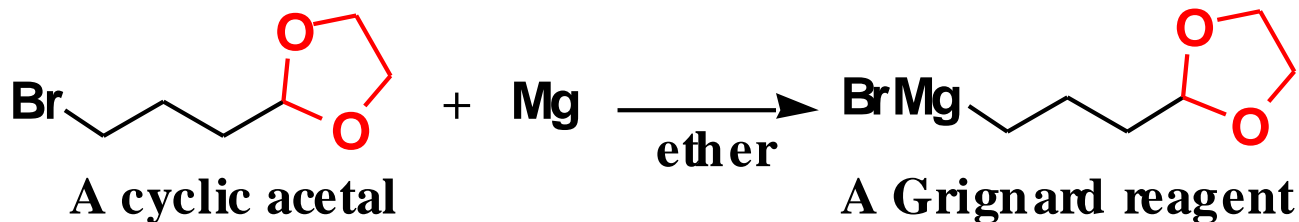


- but first the aldehyde of the bromoaldehyde must be protected; one possibility is as a cyclic acetal

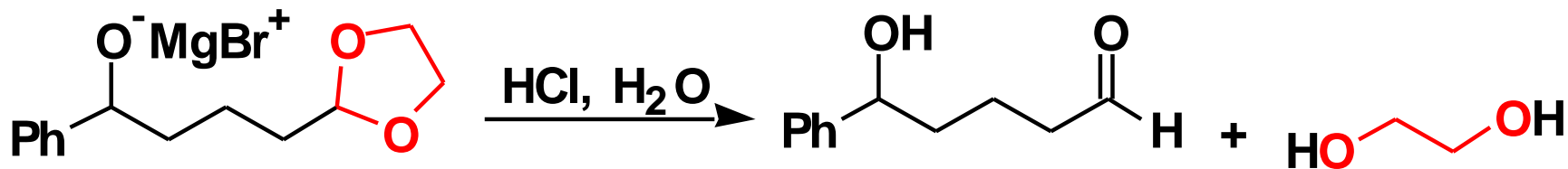


An Acetal as a Protecting Group

- now the Grignard reagent can be prepared and the new carbon-carbon bond formed



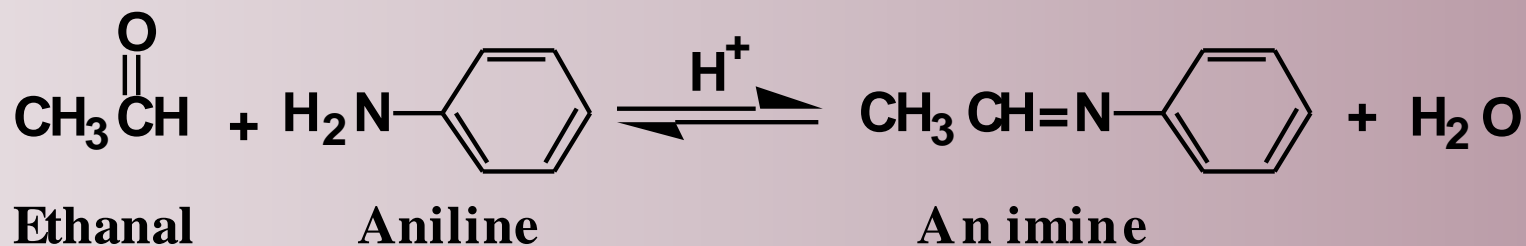
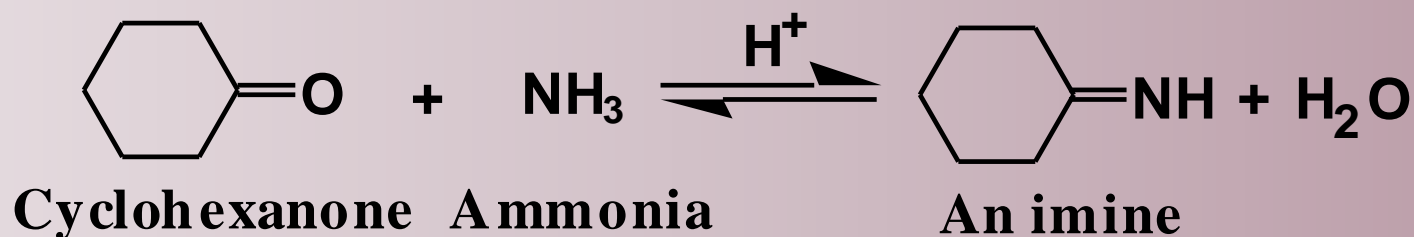
- hydrolysis gives the hydroxyaldehyde



Imines

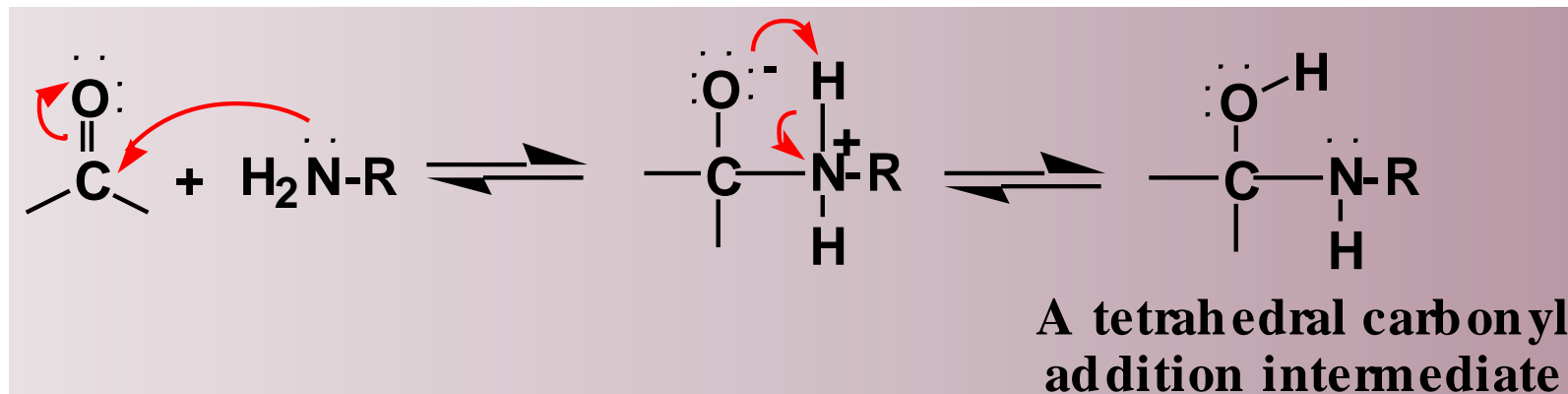
Imine: a compound containing a C=N bond; also called a Schiff base

- formed by the reaction of an aldehyde or ketone with ammonia or a 1° amine

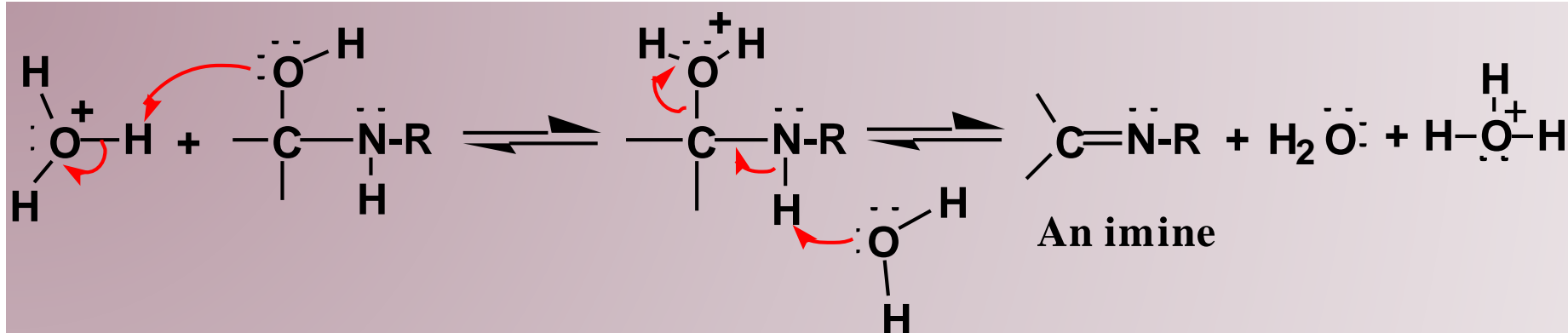


Imines

1. addition of the amine to the carbonyl carbon followed by proton transfer

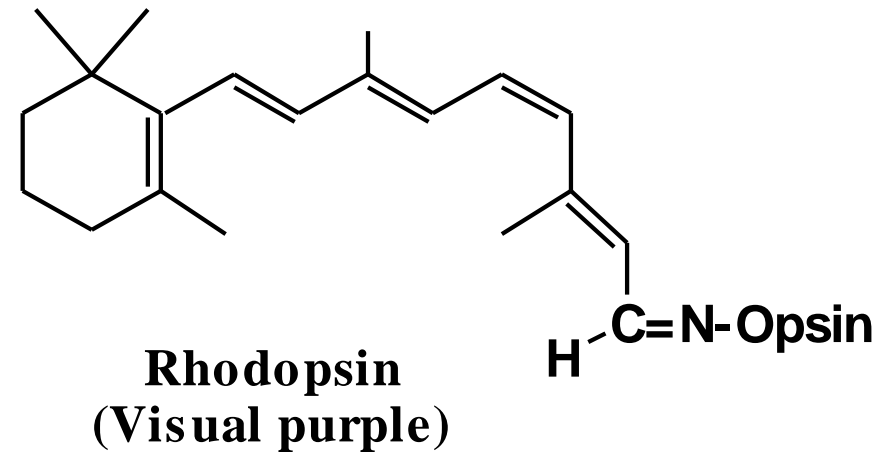
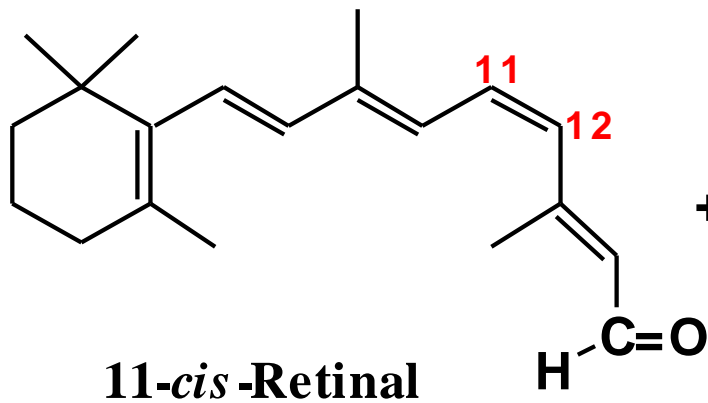


2. two proton-transfer reactions and loss of H₂O



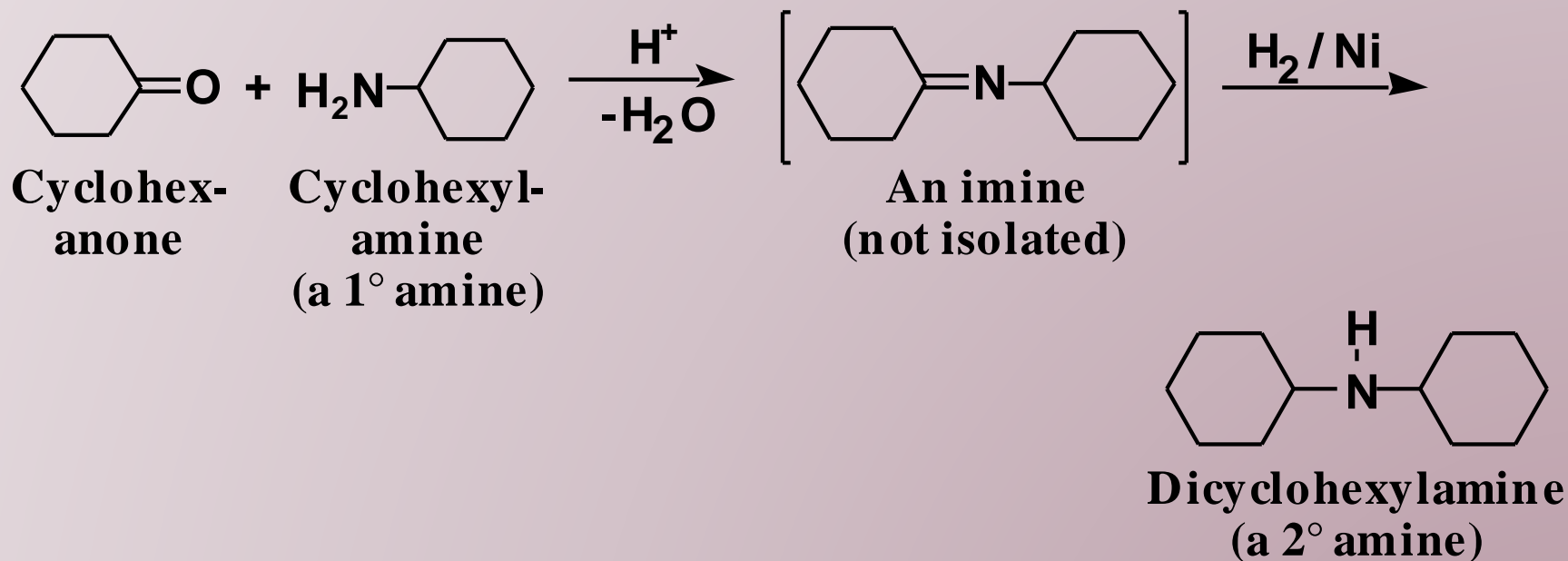
Rhodopsin

- reaction of vitamin A aldehyde (retinal) with an amino group on the protein opsin gives rhodopsin



Importance of Reductive Amination

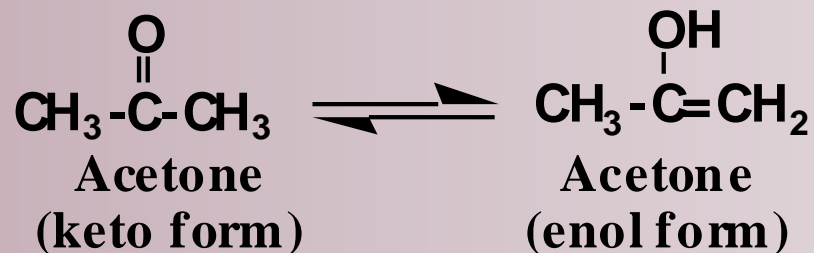
Reductive amination is the formation of an imine followed by its reduction to an amine



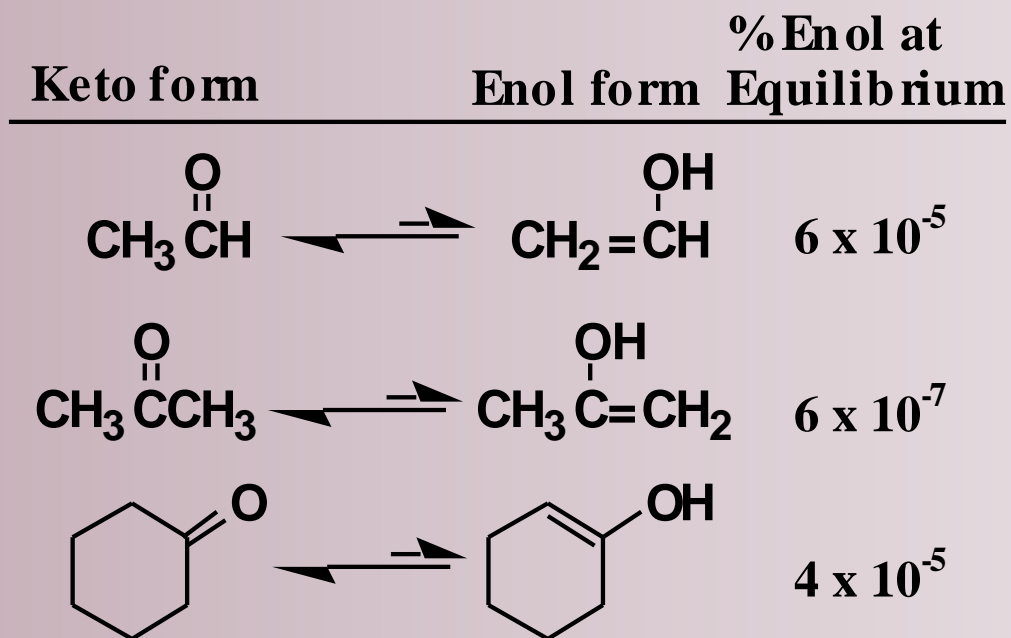
- This is a valuable method for the conversion of ammonia to a 1° amine, and a 1° amine to a 2° amine

Keto-Enol Tautomerism

A molecule containing an -OH group on a carbon-carbon double bond of an alkene is called enol.

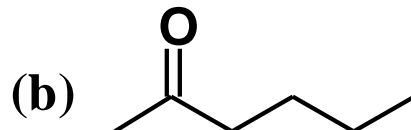
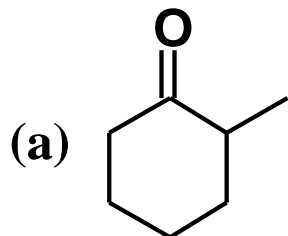


the keto form
predominates
for most
simple
aldehydes and
ketones

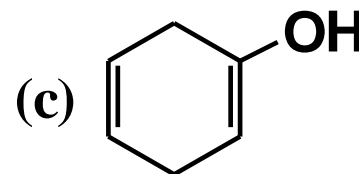
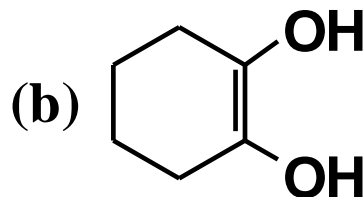
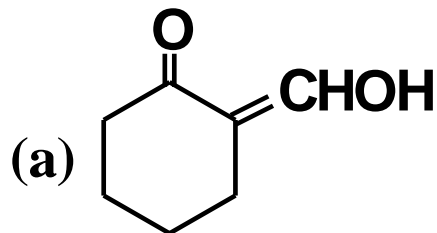


Keto-Enol Tautomerism

- **Problem: draw two enol forms for each ketone**



- **Problem: draw the keto form of each enol**

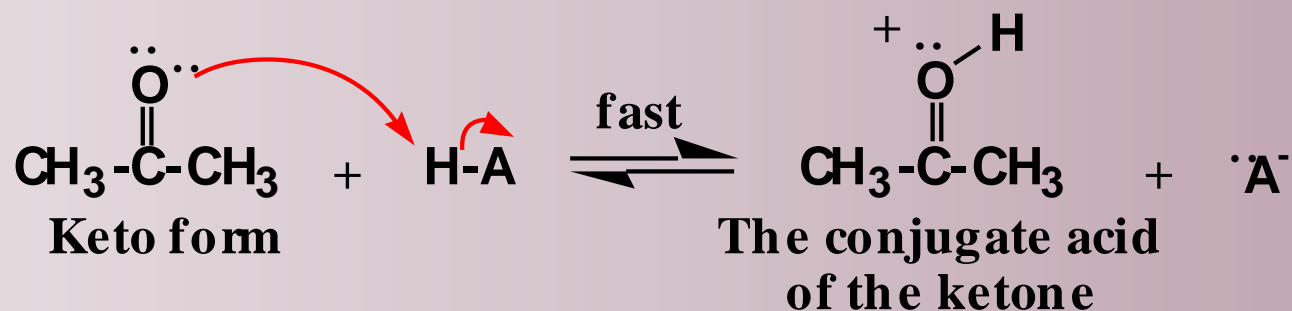


Keto-Enol Tautomerism

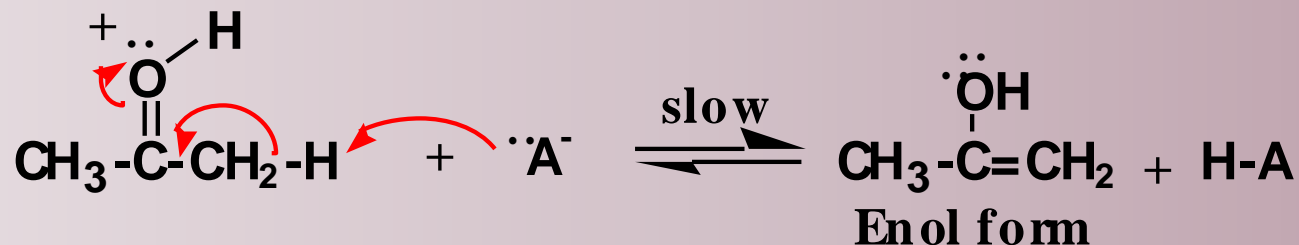
Interconversion of keto and enol forms is catalyzed by both acid and base

- following is a mechanism for acid catalysis

1. proton transfer to the carbonyl oxygen

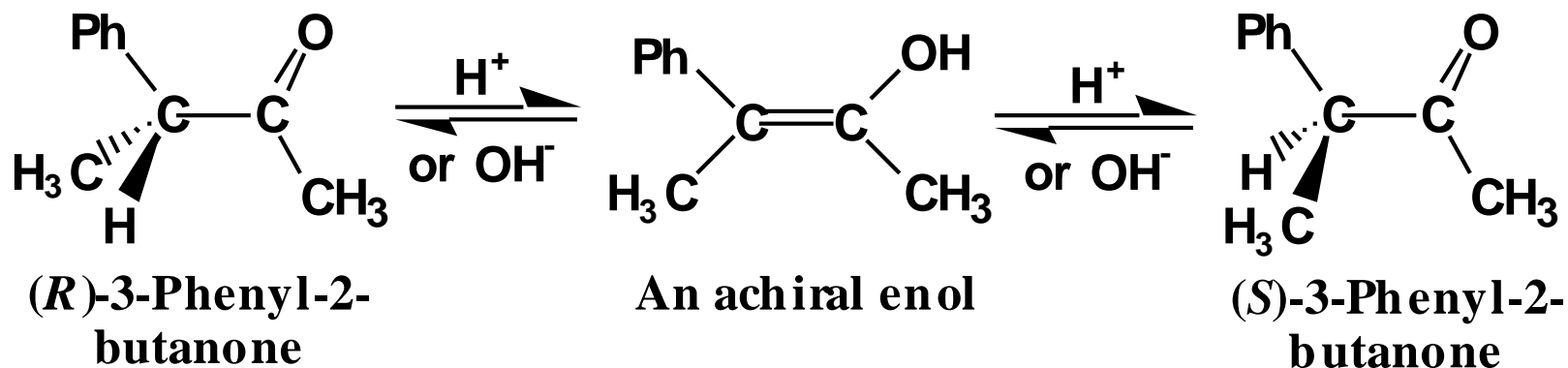


2. proton transfer from the α -carbon to A^-



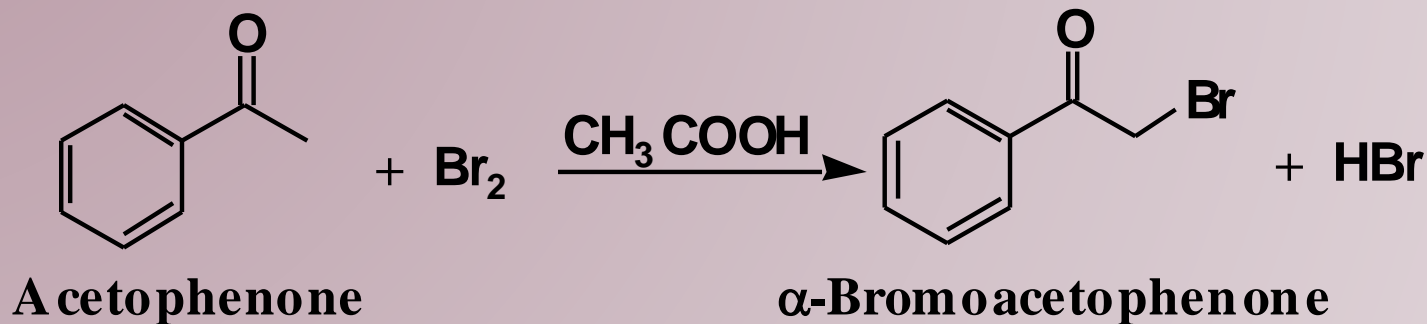
Racemization an at α -Carbon

when an enantiomerically pure aldehyde or ketone with at least one α -hydrogen is treated with a trace of acid or base, it gradually becomes a racemic mixture; it loses all optical activity



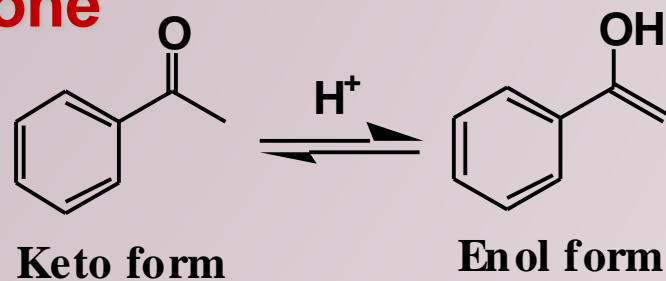
α -Halogenation

Aldehydes and ketones with an α -hydrogen react with Br_2 and Cl_2 to give
an the key intermediate in α -halogenation is an enol

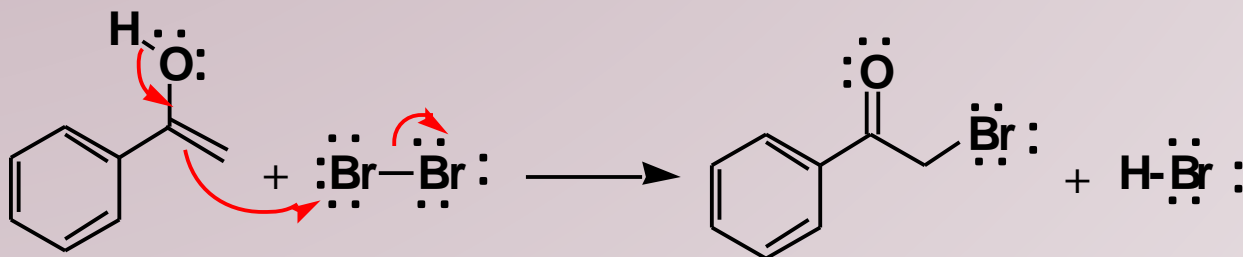


α -haloaldehyde or an α -haloketone

1. formation of the enol

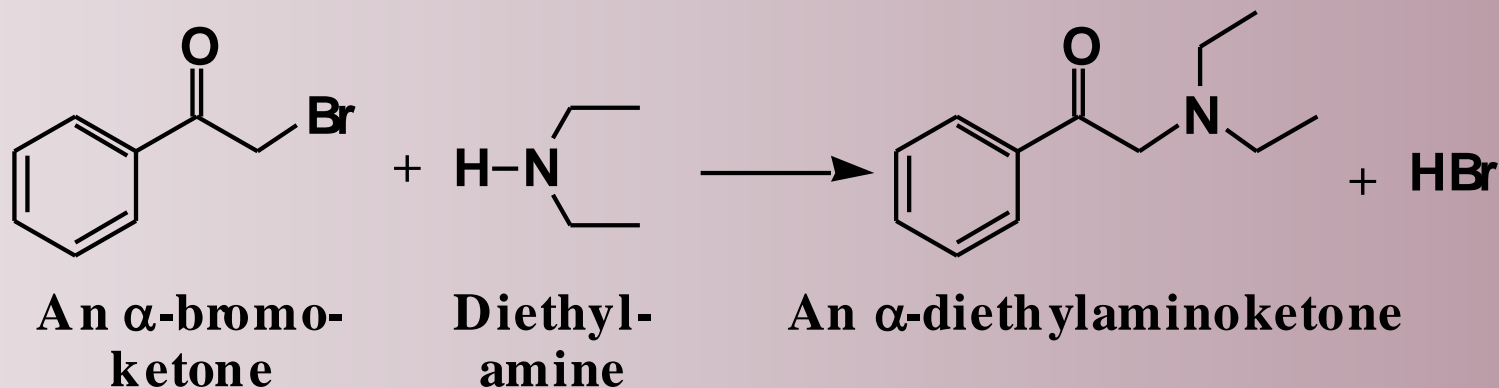


2. nucleophilic attack of the enol on the halogen



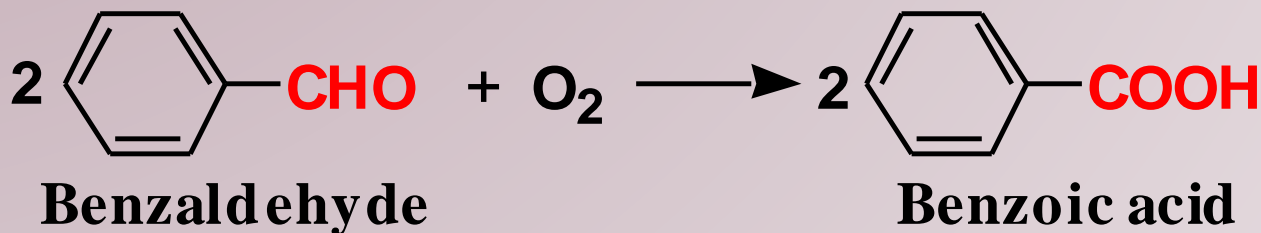
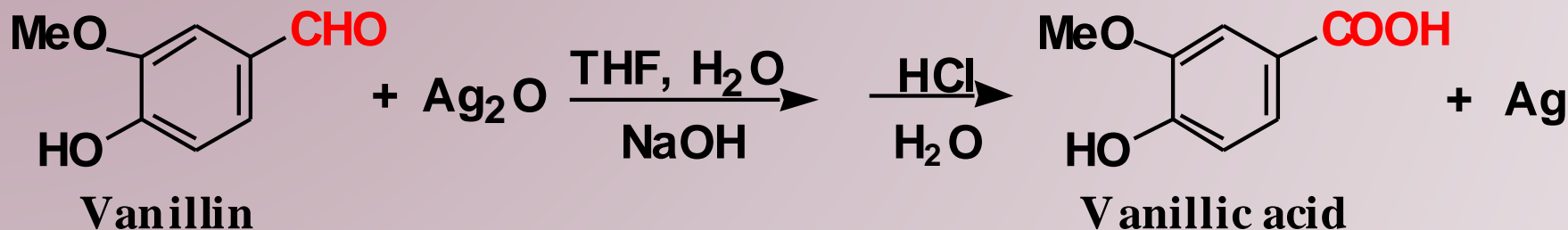
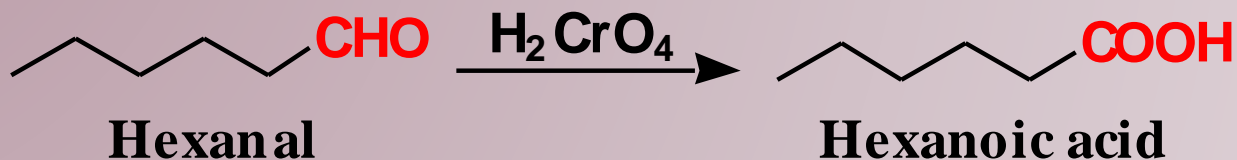
Importance of α -halogenation

A value of α -halogenation is that the carbon adjacent to the aldehyde or ketone now bears a good leaving group and is susceptible to nucleophilic attack



Oxidation

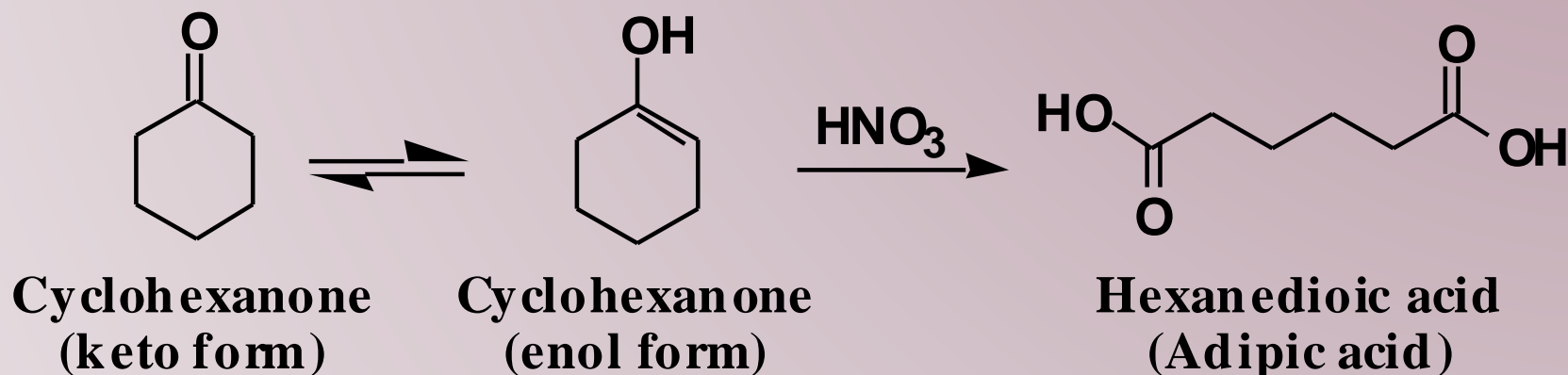
Aldehydes are one of the most easily oxidized of all functional groups



Oxidation

Ketones are not normally oxidized by H_2CrO_4 ; in fact this reagent is used to oxidize 2° alcohols to ketones

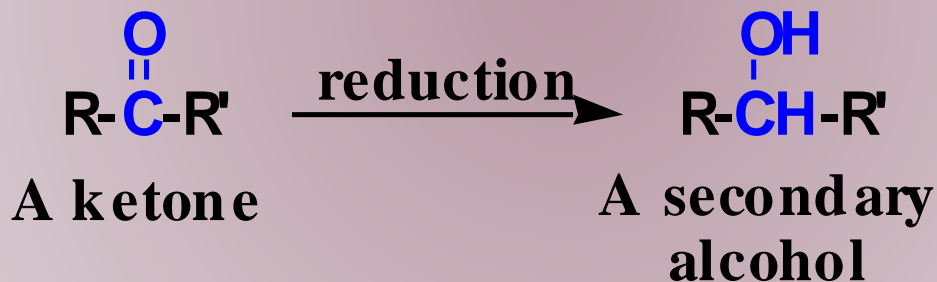
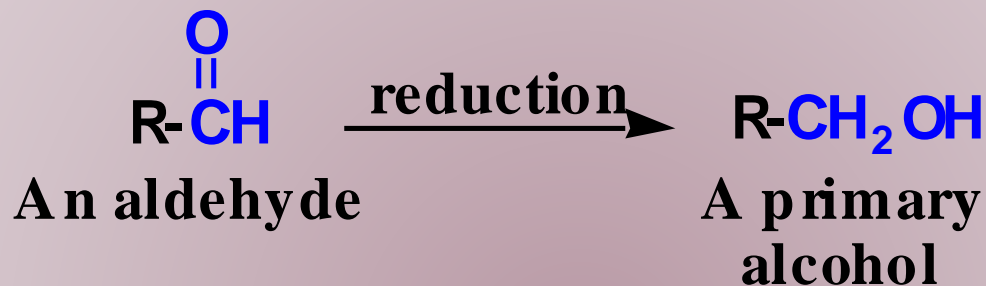
- they are oxidized by HNO_3 at higher temperatures
- oxidation is via the enol



- adipic acid is one of the starting materials for the synthesis of nylon 66

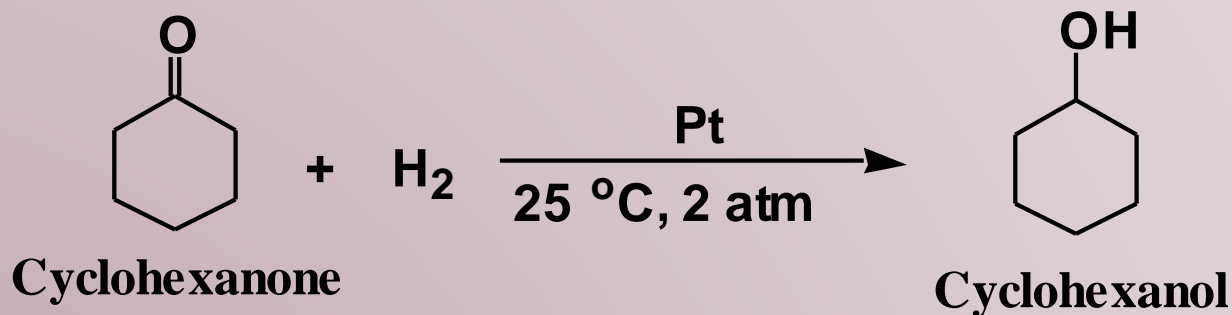
Reduction

- aldehydes can be reduced to 1° alcohols
- ketones can be reduced to 2° alcohols

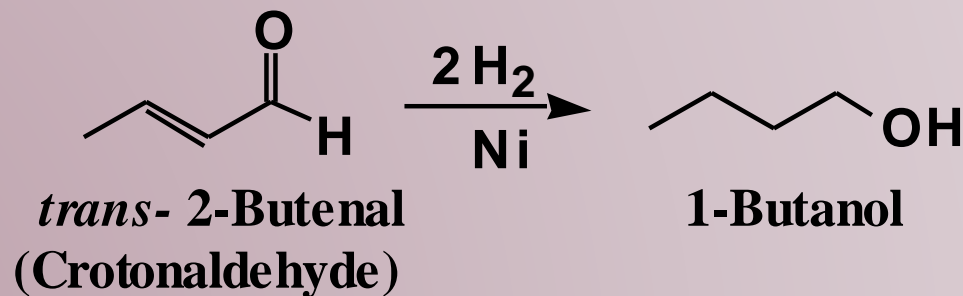


Catalytic Reduction

Catalytic reductions are generally carried out from 25° to 100°C and 1 to 5 atm H₂

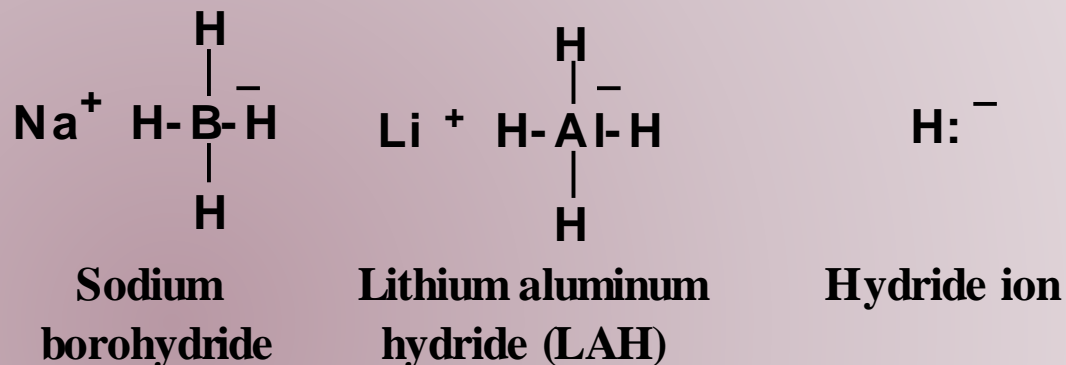


- a carbon-carbon double bond may also be reduced under these conditions



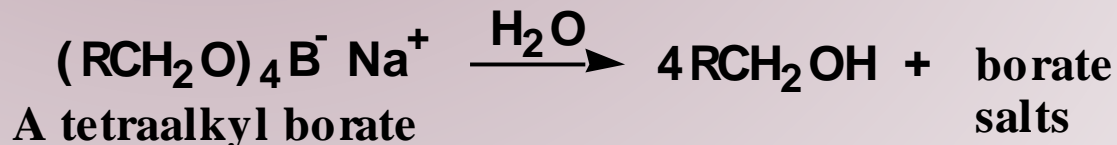
Metal Hydride Reductions

The most common laboratory reagents for the reduction of aldehydes and ketones are NaBH_4 and LiAlH_4 . Both reagents are sources of hydride ion, H^- , a very strong nucleophile



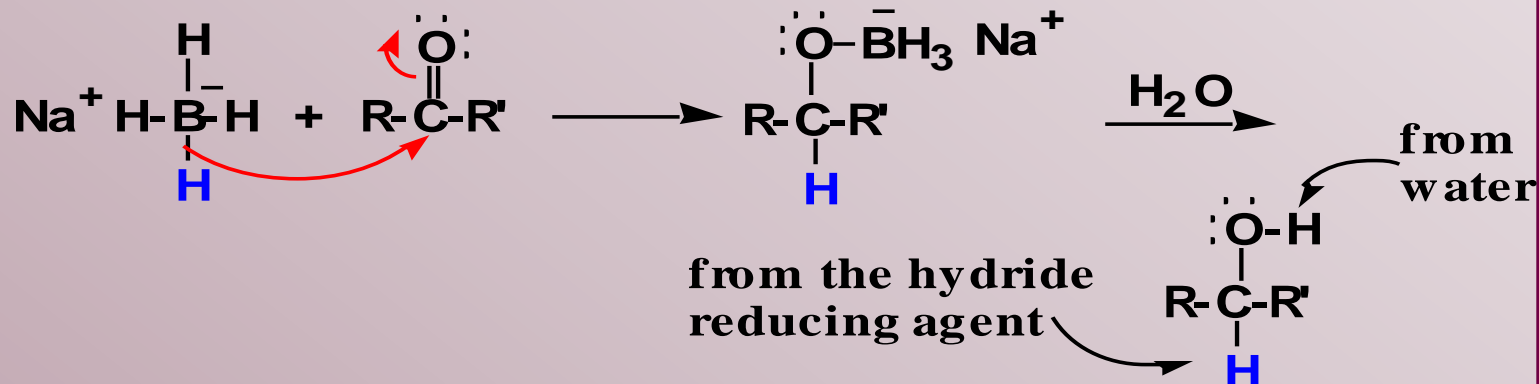
Reductions with NaBH_4 are most commonly carried out in aqueous methanol, in pure methanol, or in ethanol

- one mole of NaBH_4 reduces four moles of aldehyde or ketone



Metal Hydride Reductions

Transfer of a hydride ion to the C=O group to form a tetrahedral carbonyl addition compound



Selective reduction of C=O or C=C is often possible. Metal hydride reducing agents do not normally reduce carbon-carbon double bonds

