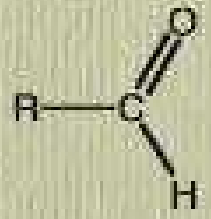
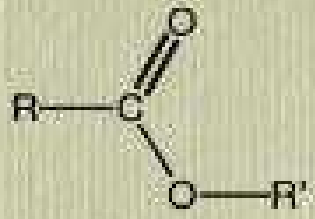
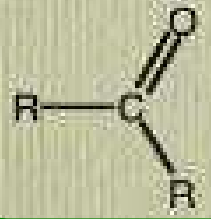
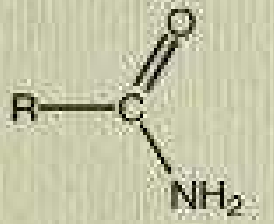
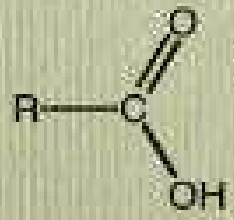
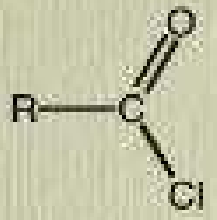
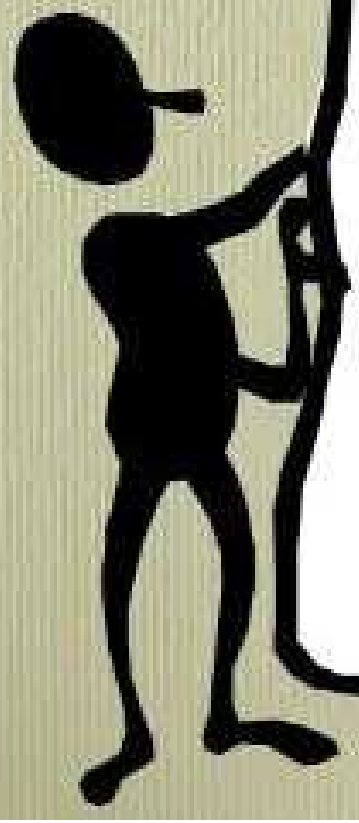
# Aldehydes and Ketones

# Carbonyl containing compounds

| Formula | Family | Formula | Family |
|---|---|---|---|
|  | Aldehyde |  | Ester |
|  | Ketone |  | Amide |
|  | Carboxylic acid |  | Acid Chloride |

# Properties



**Moderately polar**

Due to C=O group.

**Boiling points**

Lower than alcohols and

Higher than alkanes.

**Solubility**

Low MW species are soluble in water

Decreases as the R chain gets longer.

## 18.2 Nomenclature

The common names of **aldehydes** are derived from the names of the corresponding carboxylic acids by replacing *-ic acid* by *-aldehyde*. (For the common names of carboxylic acids, see Sec. 19.2.) Branched-chain aldehydes are named as derivatives of straight-chain aldehydes. To indicate the point of attachment, the Greek letters, $\alpha$-, $\beta$-, $\gamma$-, $\delta$-, etc., are used; the $\alpha$-carbon is the one bearing the —CHO group.

$$\overset{\delta}{\text{C}}\text{—}\overset{\gamma}{\text{C}}\text{—}\overset{\beta}{\text{C}}\text{—}\overset{\alpha}{\text{C}}\text{—CHO}$$

*Used in common names*

The IUPAC names of aldehydes follow the usual pattern. The longest chain carrying the —CHO group is considered the parent structure and is named by replacing the *-e* of the corresponding alkane by *-al*. The position of a substituent is indicated by a number, the carbonyl carbon always being considered as C–1. We

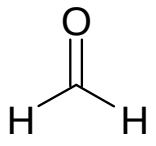
$$\overset{5}{\text{C}}\text{—}\overset{4}{\text{C}}\text{—}\overset{3}{\text{C}}\text{—}\overset{2}{\text{C}}\text{—}\overset{1}{\text{C}}\text{HO}$$

*Used in IUPAC names*

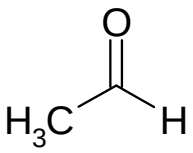
notice that C–2 of the IUPAC name corresponds to *alpha* of the common name.

# Nomenclature of Aldehydes and Ketones

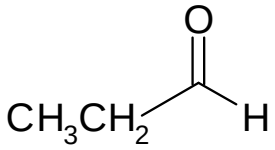
## Common aldehydes



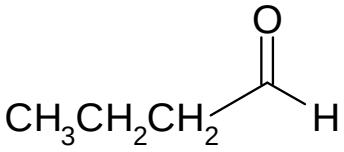

**Methanl**
(formaldehyde)



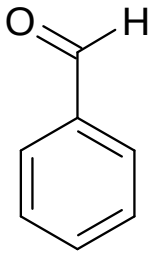

**ethanl**
(acetaldehyde)



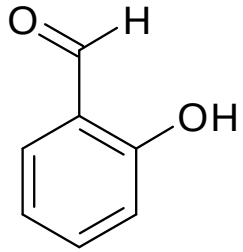

**propanal**
(propionaldehyde)



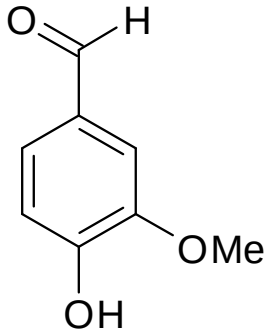

**butanal**
(n-butyraldehyde)



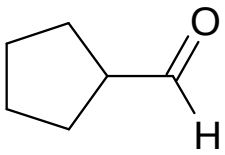

**benzaldehyde**




**salicylaldehyde**
**(2-hydroxybenzenecarbaldehyde)**

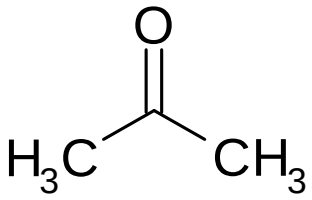



**Vanillin**

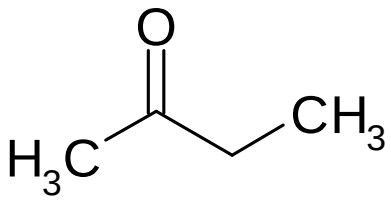



**cyclopentanecarbaldehyde**

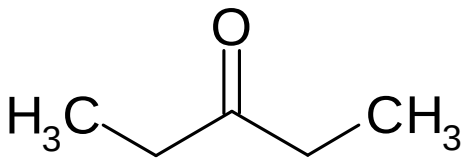
# Common Ketones



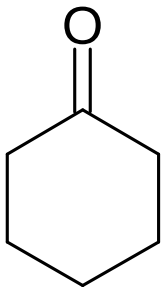

**propanone (acetone)**



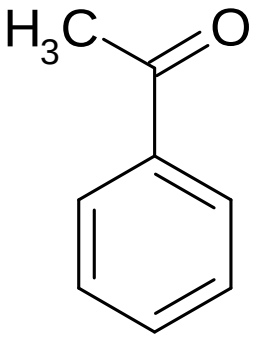

**2-butanone (ethyl methyl ketone)**



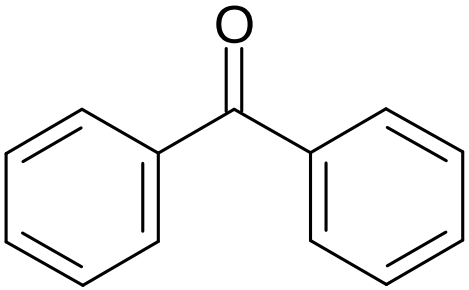

**3-pentanone (diethyl ketone)**




**cyclohexanone**




**acetophenone (methyl phenyl ketone)**



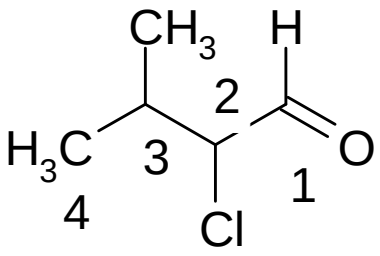

**benzophenone (diphenyl ketone)**

# Nomenclature of aldehydes and ketones

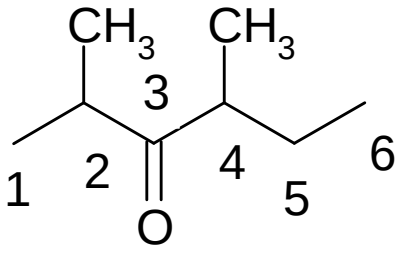
(al) aldehyde, (one) ketone

alkanes < alkenes < OH < ketone < aldehyde < acid < ester

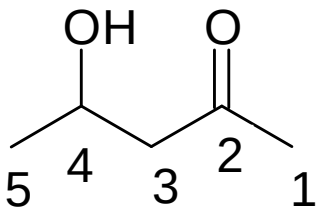
**Examples**



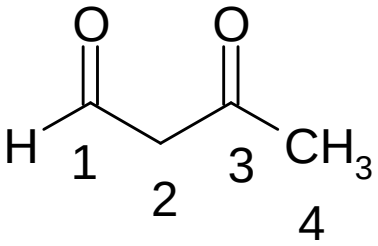

2-cholro-3-methylbutanal



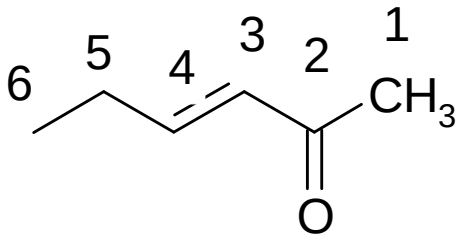

2,4-dimethyl-3-hexanone



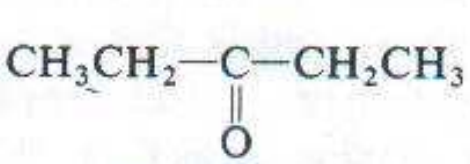

4-hydroxy-2-pentanone



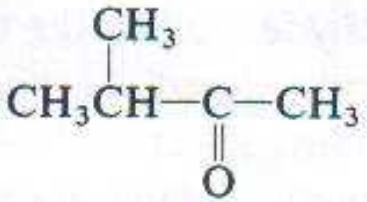

3-oxobutanl



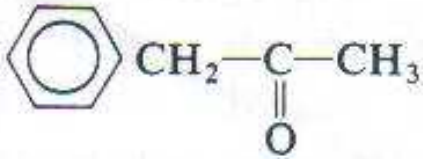

3-hexen-2-one



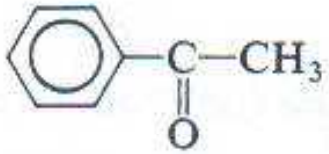
Diethyl ketone
3-Pentanone



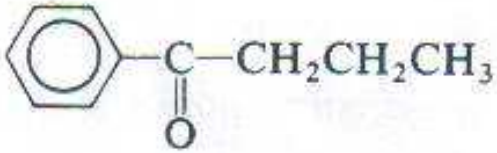
Isopropyl methyl ketone
3-Methyl-2-butanone



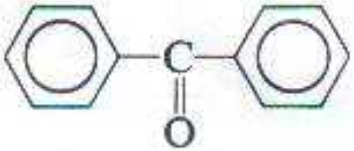
Benzyl methyl ketone
1-Phenyl-2-propanone



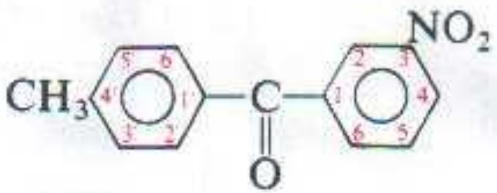
Acetophenone



*n*-Butyrophenone

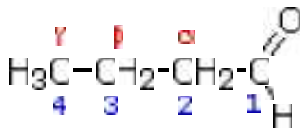


Benzophenone

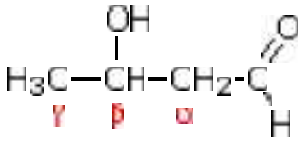


4′-Methyl-3-nitrobenzophenone

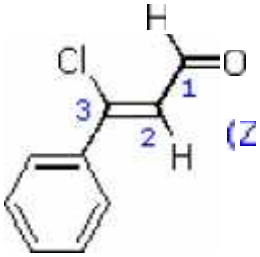
## Aldehydes



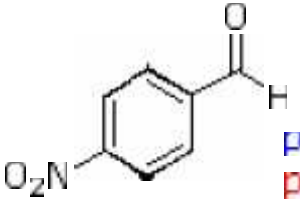
butanal
butyraldehyde



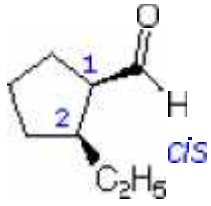
3-hydroxybutanal
β-hydroxybutyraldehyce
or aldol



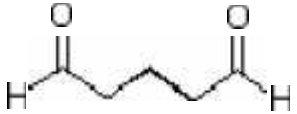
(Z)-3-chloro-3-phenyl-2-propenal



p-nitrobenzenecarbaldehyde
p-nitrobenzaldehyde

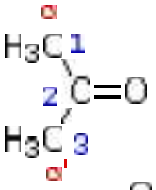


*cis*-2-ethylcyclopentanecarbaldehyde

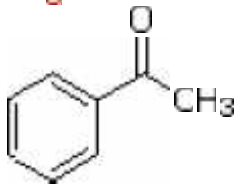


pentanedial
glutaraldehyde

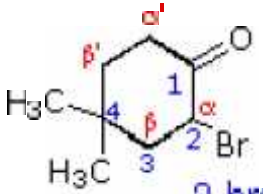
## Ketones



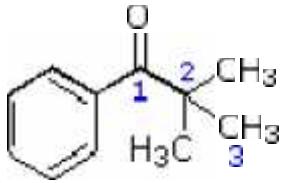
propanone
acetone



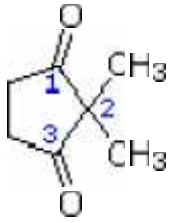
phenylethanone
acetophenone
methyl phenyl ketone



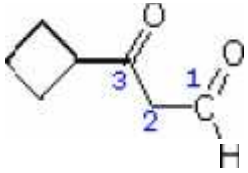
2-bromo-4,4-dimethylcyclohexanone



2,2-dimethyl-1-phenylpropanone
t-butyl phenyl ketone

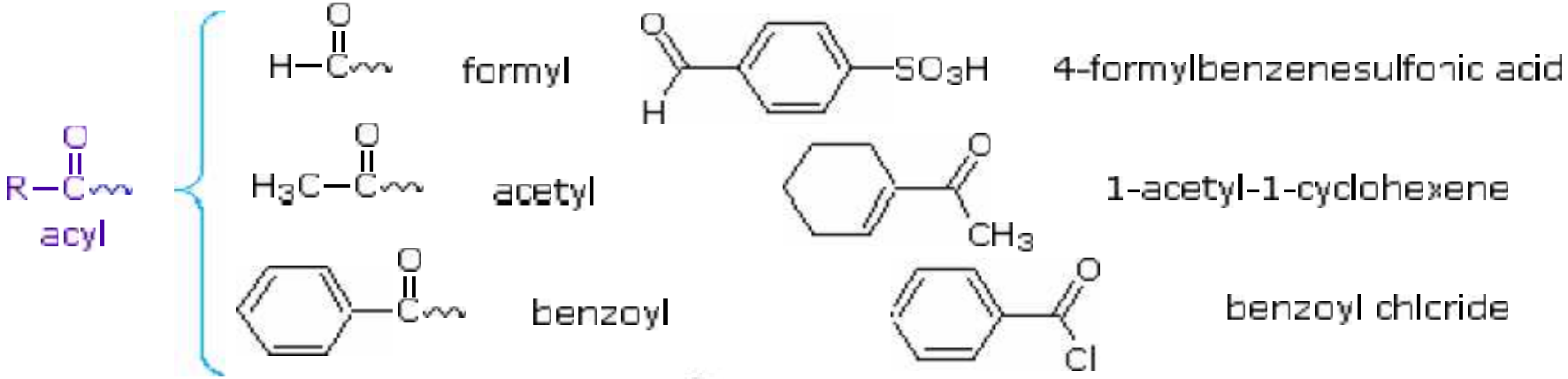


2,2-dimethyl-1,3-cyclopentanedione

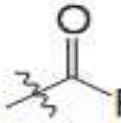


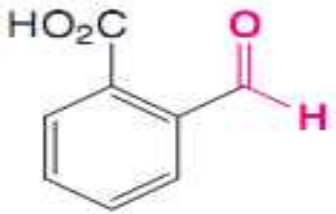
3-cyclobutyl-3-oxopropanal

# Acyl groups

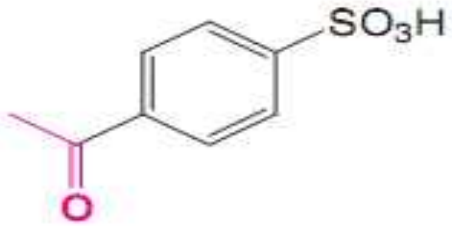



When it is necessary to name the  group as a prefix, it is the **methanoyl** or **formyl group.** The  group is called the **ethanoyl** or **acetyl group** (often abbreviated as Ac).

When  groups are named as substituents, they are called **alkanoyl** or **acyl groups.**




**2-Methanoylbenzoic acid**
**(*o*-formylbenzoic acid)**




**4-Ethanoylbenzenesulfonic acid**
**(*p*-acetylbenzenesulfonic acid)**

# Common aldehydes and ketones

## Formaldehyde

$$CH_3OH \xrightarrow[600 - 700\ ^oC]{Ag} CH_2 = O + H_2$$

Formaldehyde is a gas (b. p. -21 $^o$C) Formalin (37% aqueous solution of formaldehyde)

## Acetaldehyde (Wacker synthesis)

$$2\ CH_2 = CH_2 + O_2 \xrightarrow[100 - 130\ ^oC]{Pd - Cu} 2\ CH_3CH = O$$

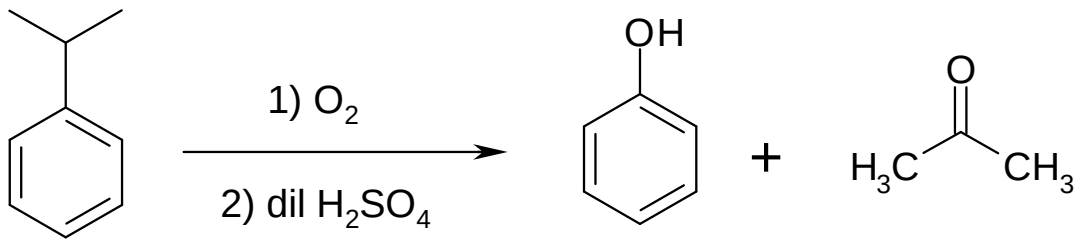
(bp 20 $^o$C)

## Acetone (Wacker synthesis)

$$2\ CH_3CH_2 = CH_2 + O_2 \xrightarrow[100 - 130\ ^oC]{Pd - Cu} 2\ CH_3\,C(=O)\,CH_3$$

(bp 56 $^o$C)

## From isopropylbenzene

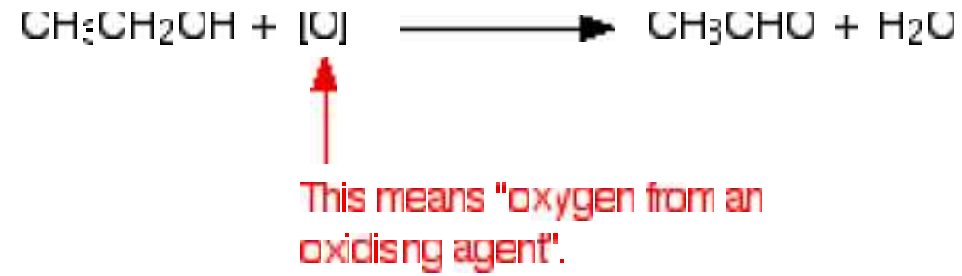


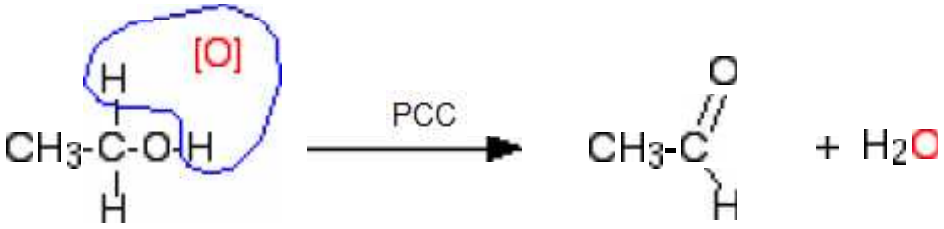
# Synthesis of aldehydes and Ketones

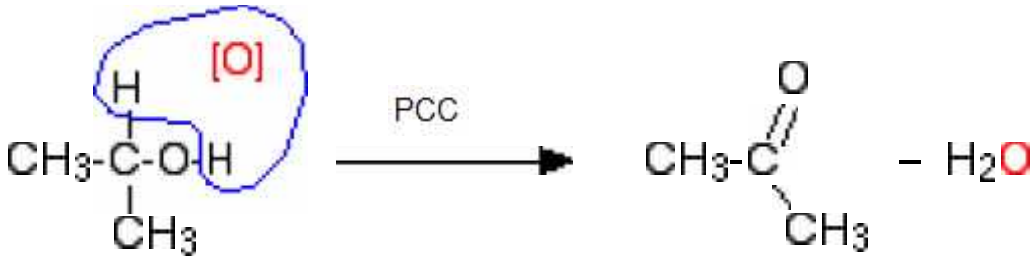
## 1) Oxidation of Alcohols

primary gives aldehydes using pyridinium chlorochromate (PCC).

secondary gives ketones



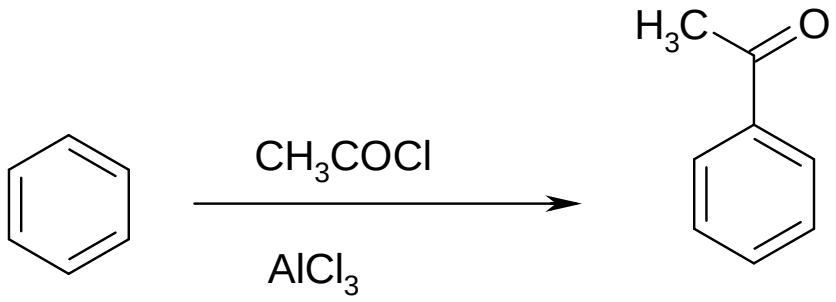



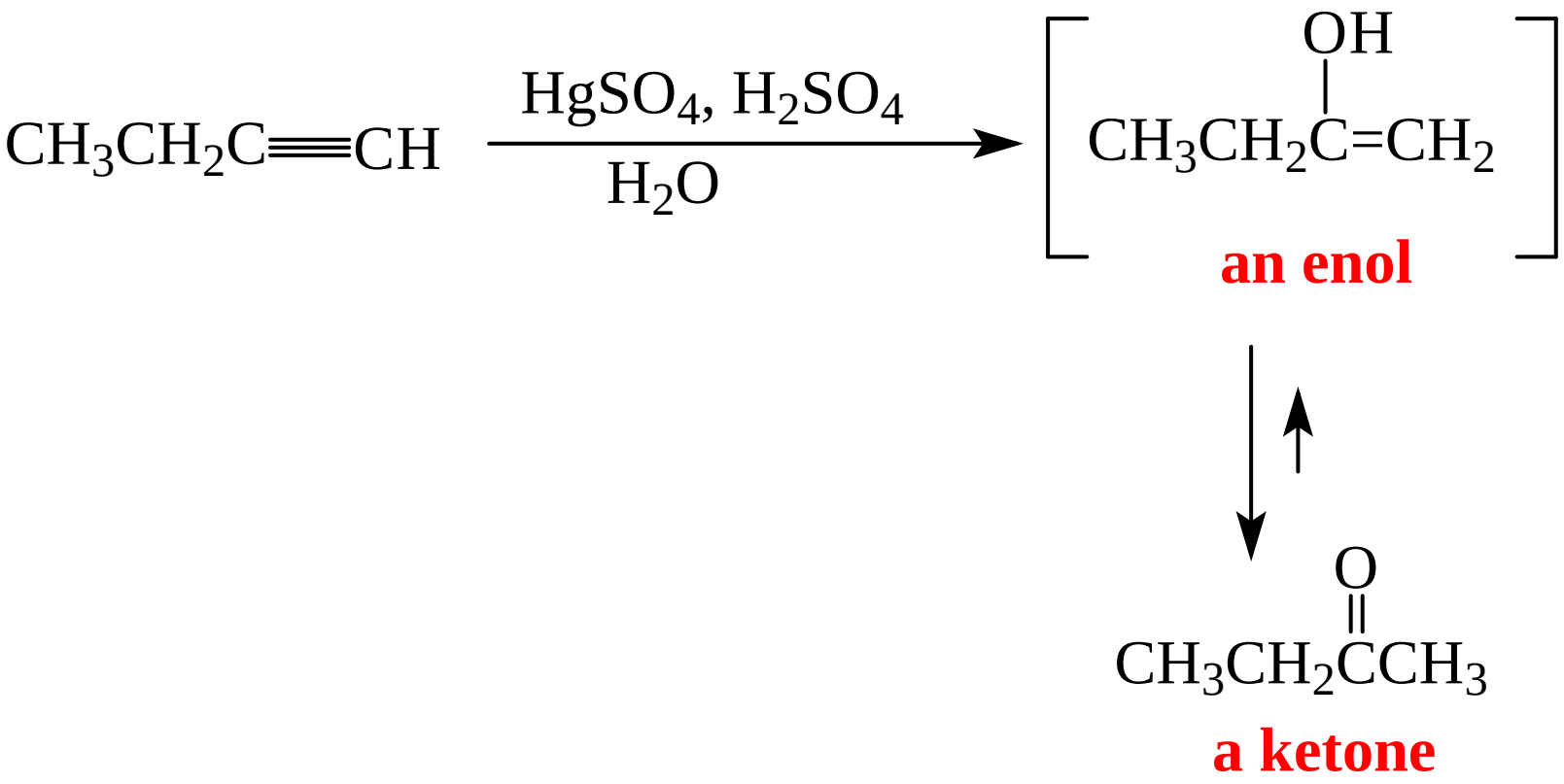

propan-2-ol

propanone

2) **Friedel-Crafts**

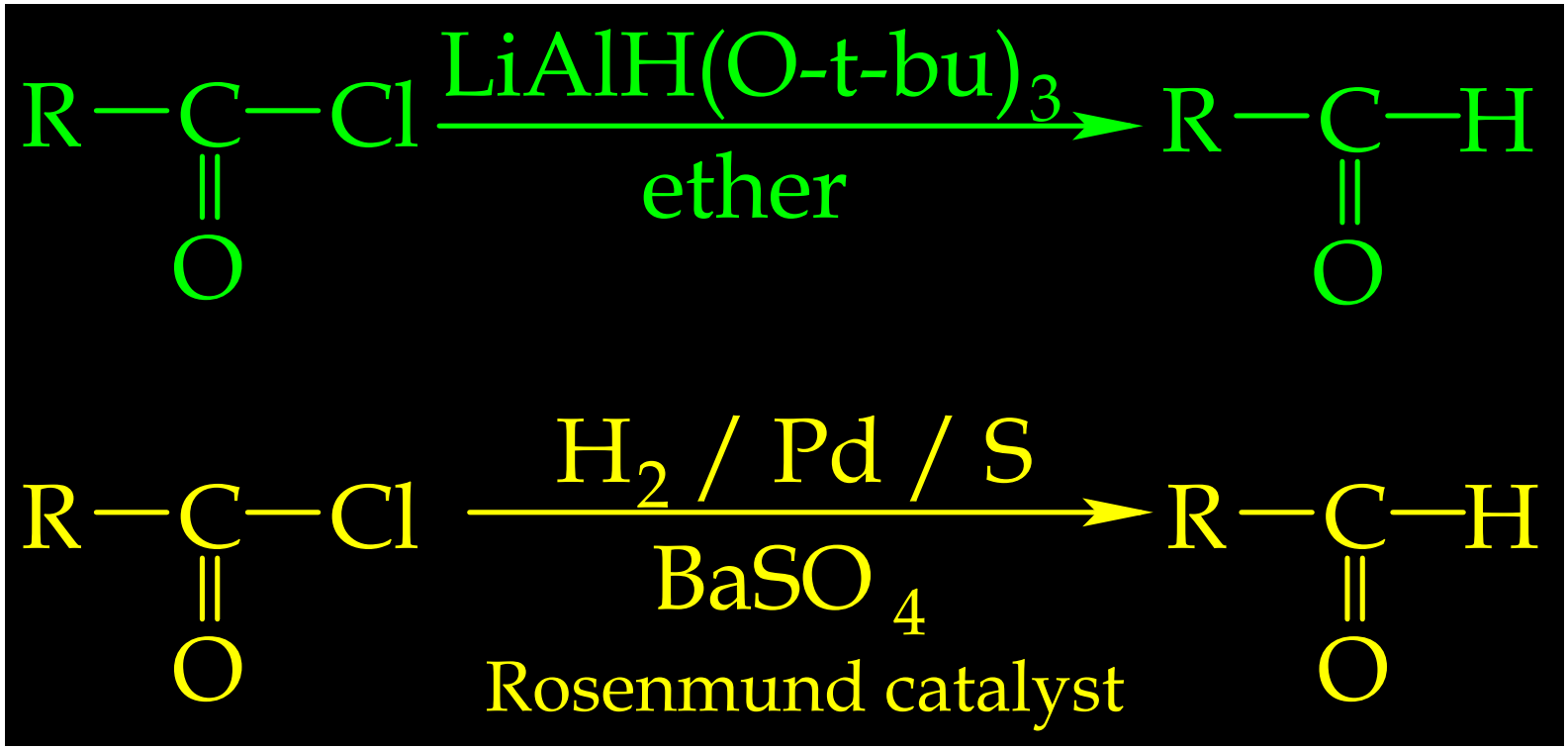


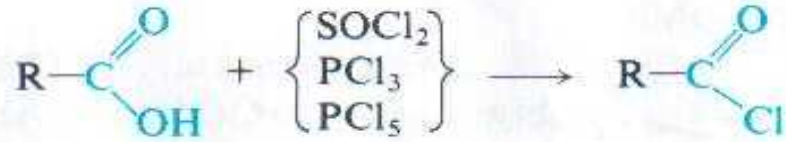

3) **From Alkynes : Oxymercuration Hydration Markovnikov**



# 4- Aldehydes from Acid Chlorides

- Lithium tri-t-butoxyaluminum hydride reduction
- Rosenmund reduction






Carboxylic acid — Acid chloride

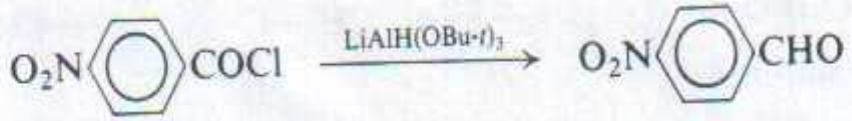
**3. Reduction of acid chlorides.** Discussed in Sec. 18.4.

$$\text{R—COCl or Ar—COCl} \xrightarrow{\text{LiAlH(OBu-}t\text{)}_3} \text{R—CHO or Ar—CHO}$$

Acid chloride — Aldehyde

CONTINUED

*Example:*

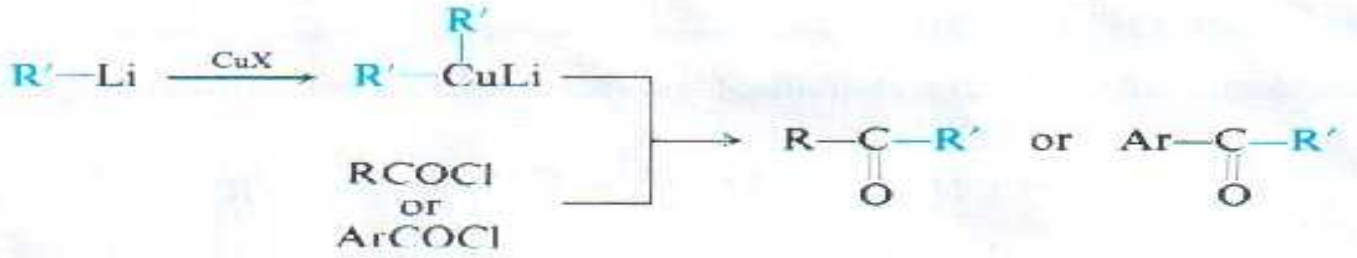


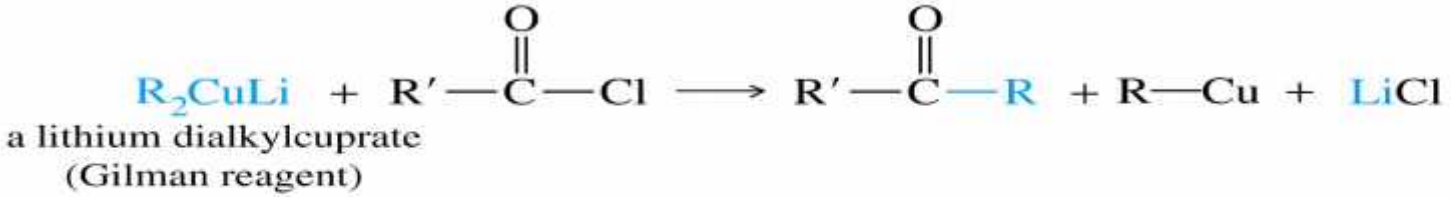

*p*-Nitrobenzoyl chloride — *p*-Nitrobenzaldehyde

# 5- Ketones from Acid Chlorides

**Gilman Reagent with Acid Chlorides** $R_2CuLi$ a lithium dialkylcuprate

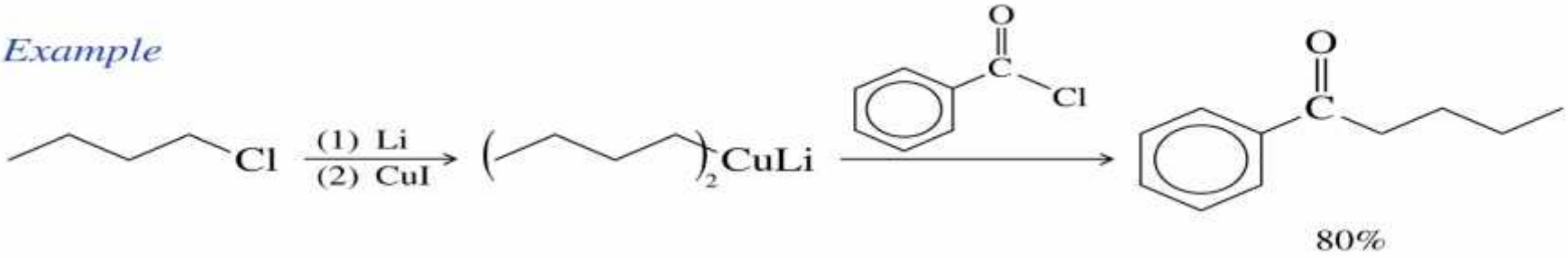
**3. Reaction of acid chlorides with organocopper compounds.** Discussed in Sec. 18.6.



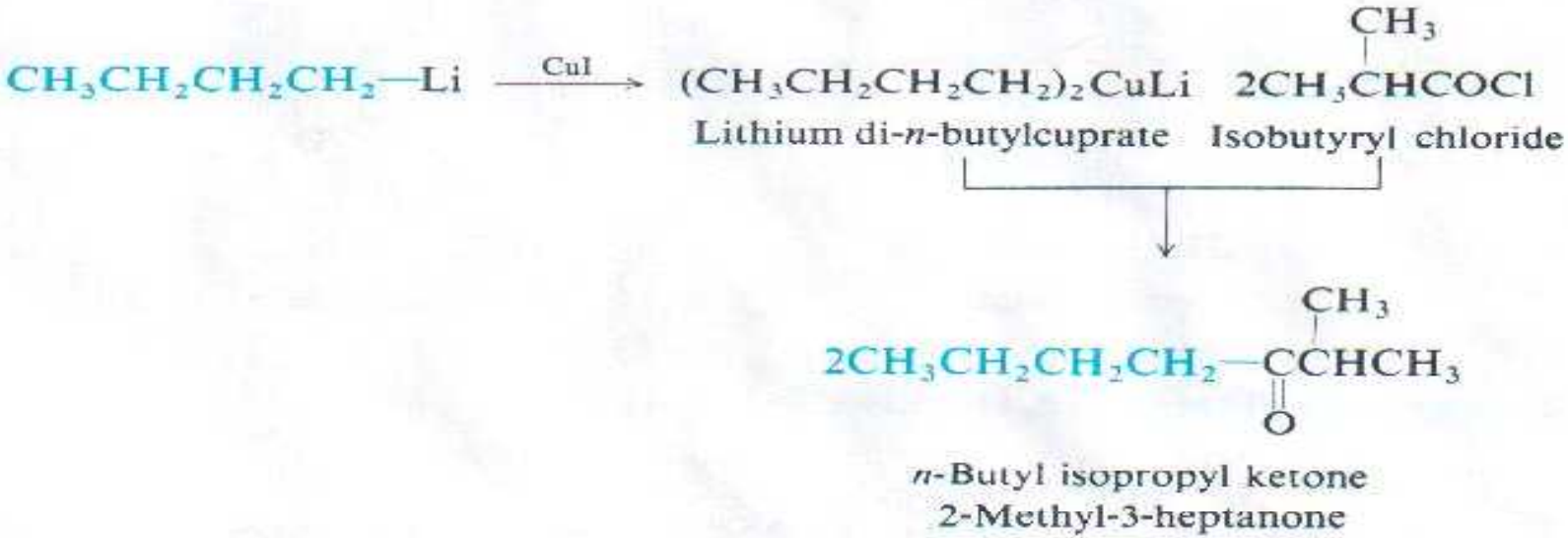



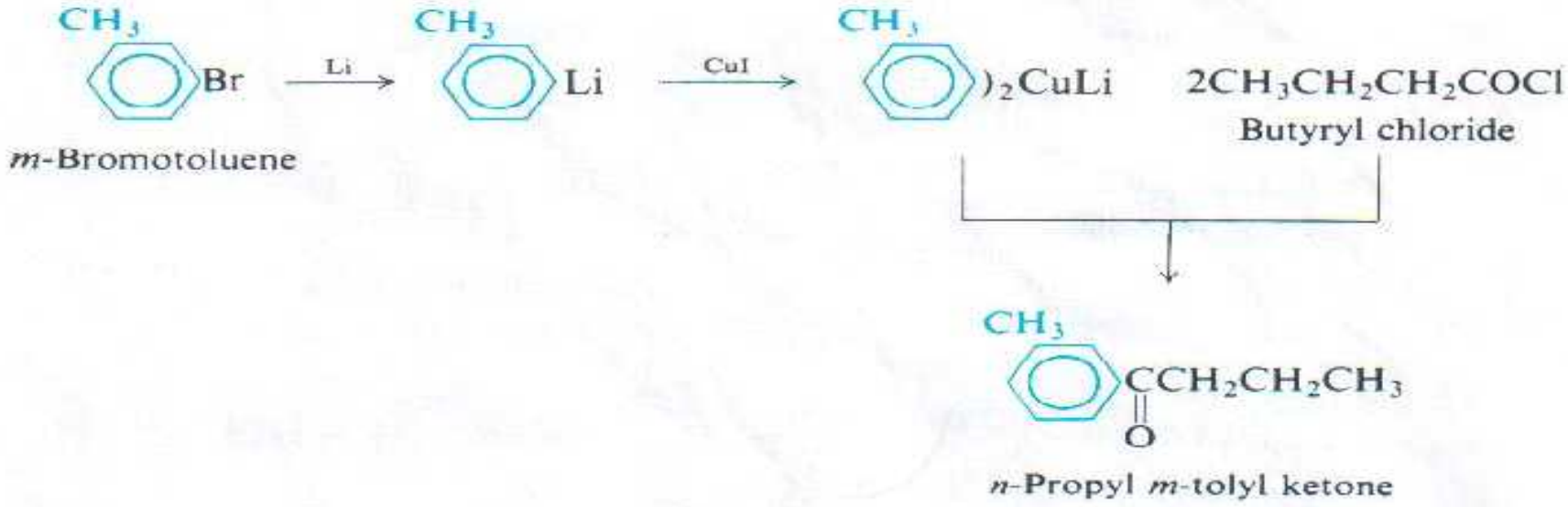


*Example*



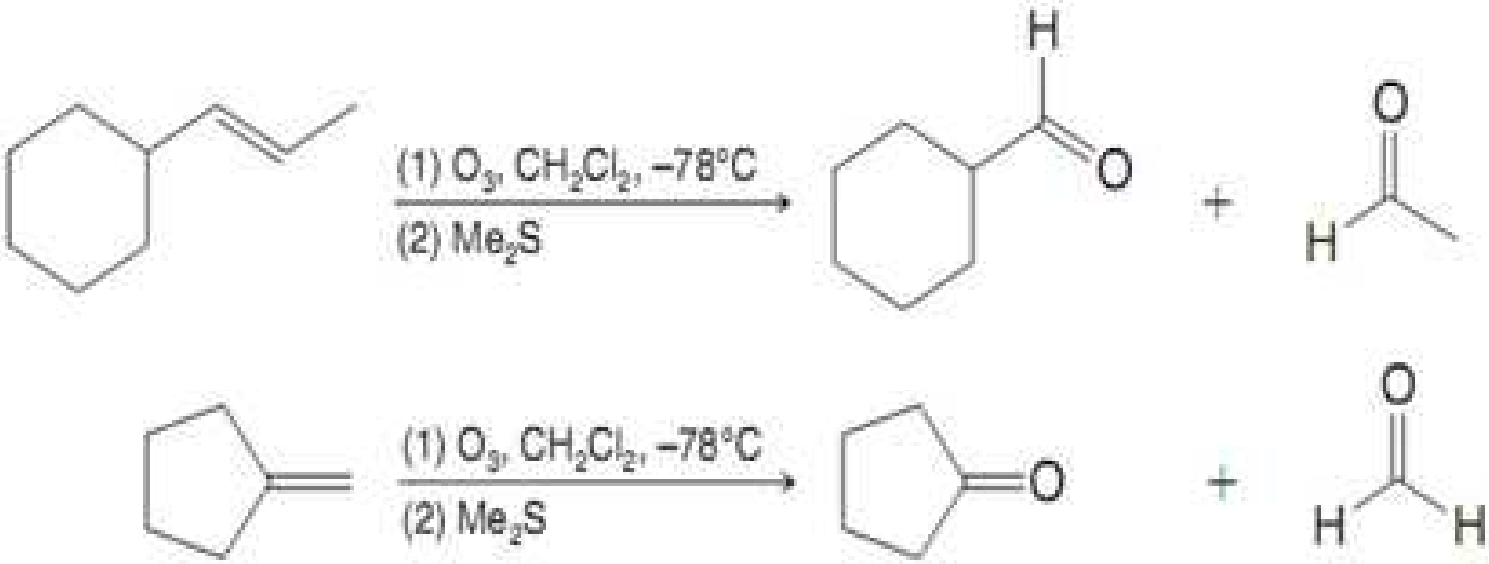
***Examples:***

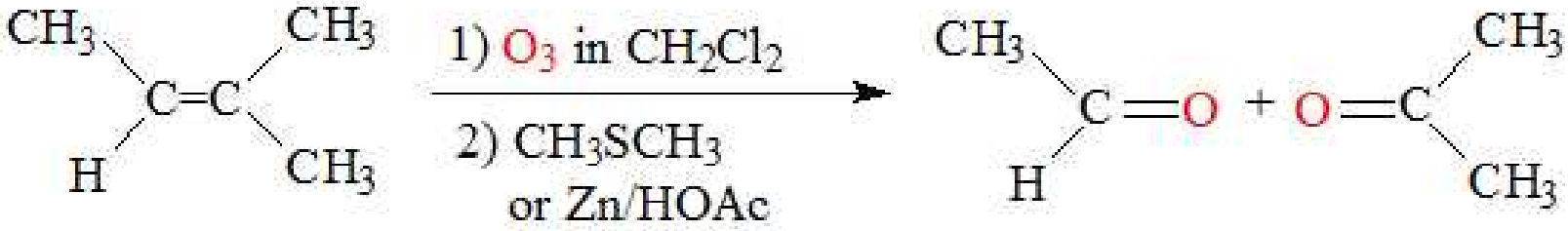

CH3CH2CH2CH2—Li
CuI
(CH3CH2CH2CH2)2CuLi
Lithium di-n-butylcuprate
2CH3CHCOCl
CH3
Isobutyryl chloride
2CH3CH2CH2CH2—CCHCH3
CH3
O
n-Butyl isopropyl ketone
2-Methyl-3-heptanone


CH3
Br
Li
CuI
)2CuLi
2CH3CH2CH2COCl
Butyryl chloride
m-Bromotoluene
CCH2CH2CH3
O
n-Propyl m-tolyl ketone

# 6- Ozonolysis Alkene Cleavage

- Alkenes can be cleaved by ozonolysis of their double bond (Section 8.17B). The products are aldehydes and ketones.



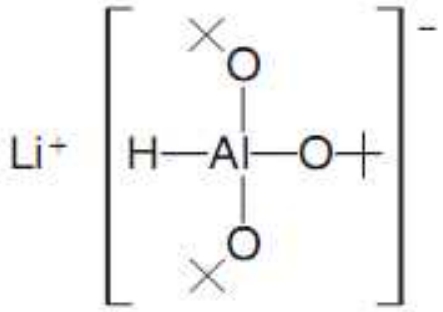



# 7-Reduction of Acids and their derivatives by Lithium Aluminum hydride (LAH)

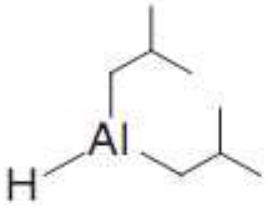

**Carboxylic acid** **Aldehyde** **1° Alcohol**

- Acyl chlorides (RCOCl), esters ($RCO_2R'$), and nitriles (RCN) are all easily prepared from carboxylic acids (Chapter 17), and they all are more easily reduced.

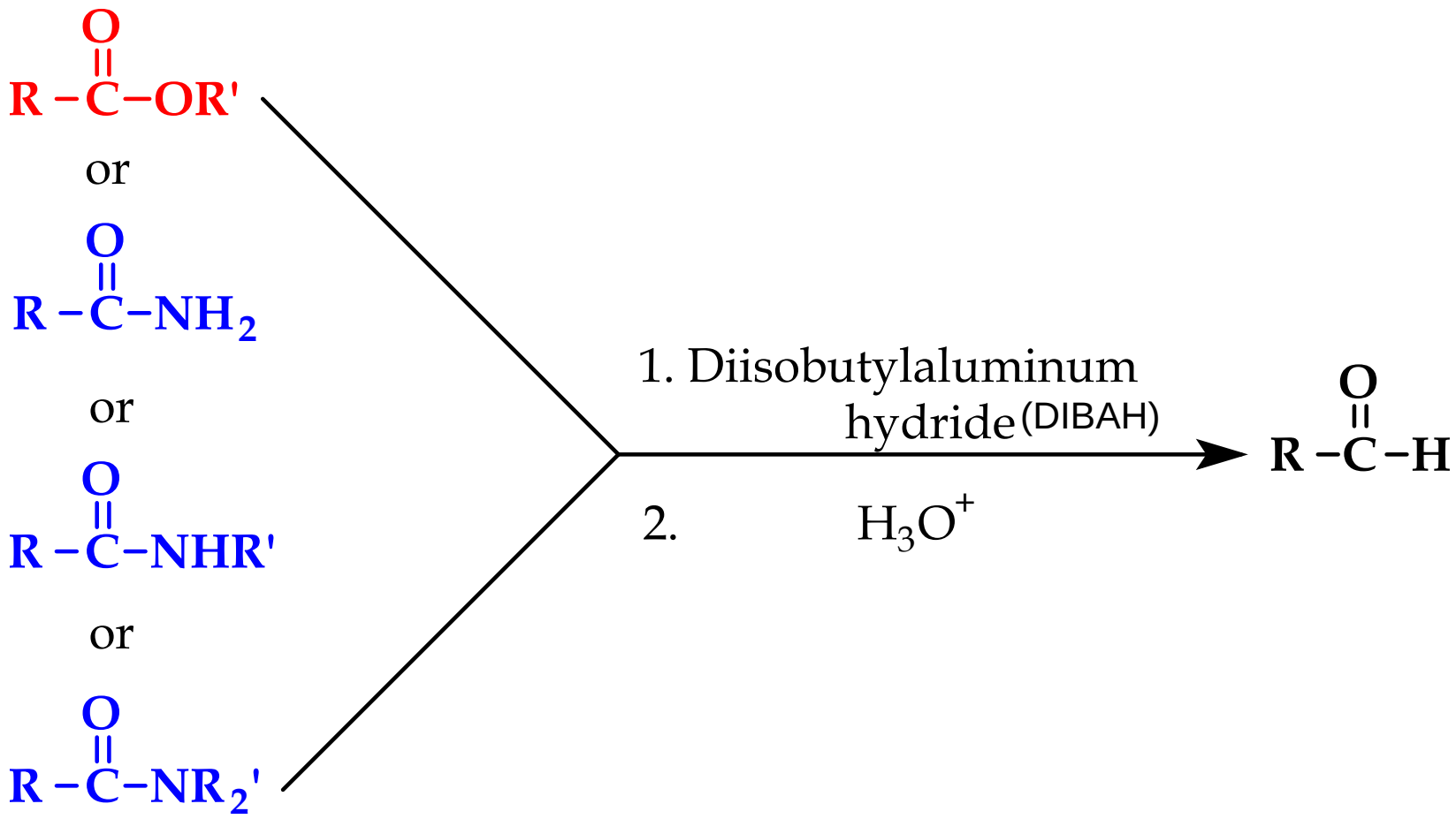
- Two derivatives of aluminum hydride that are less reactive than LAH, in part because they are much more sterically hindered, are **lithium tri-*tert*-butoxyaluminum hydride** and **diisobutylaluminum hydride (DIBAL-H)**:



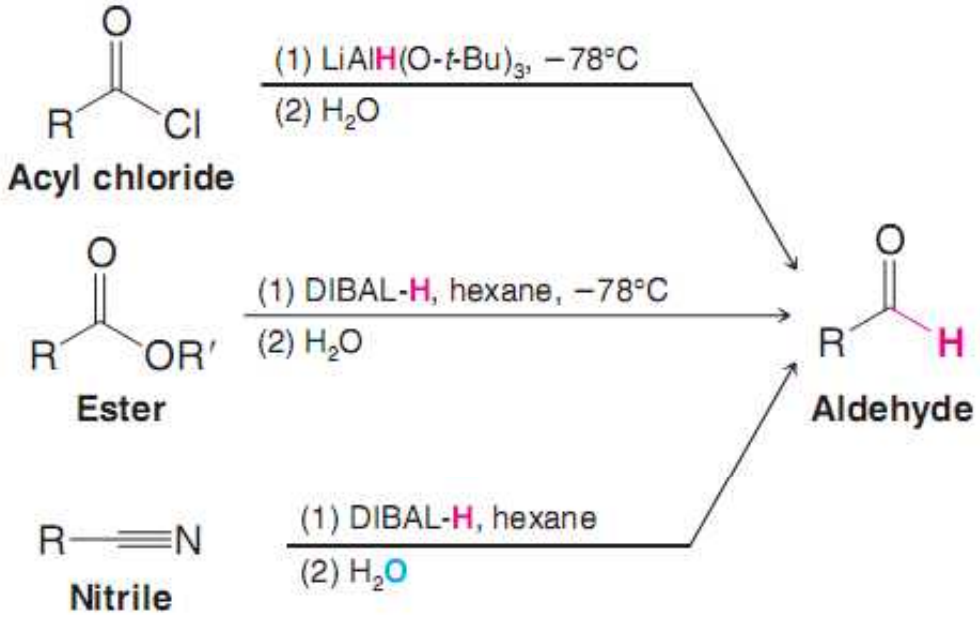

**Lithium tri-*tert*-butoxyaluminum hydride**

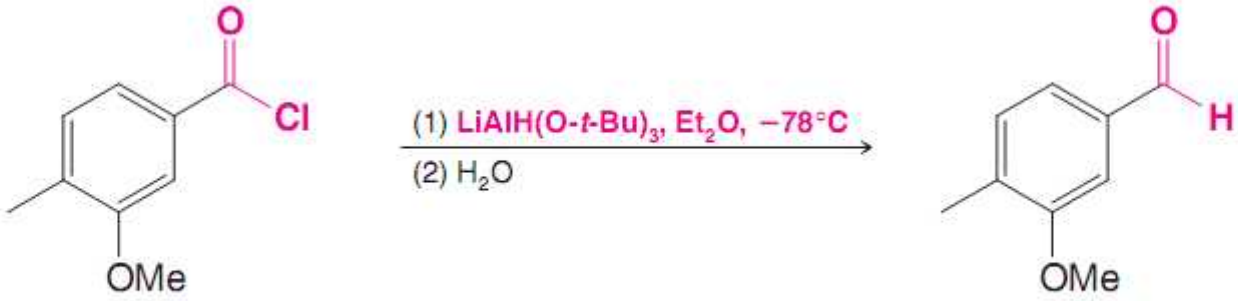



**Diisobutylaluminum hydride (abbreviated *i*-$Bu_2AlH$ or DIBAL-H)**


R–C–OR'
or
R–C–NH2
or
R–C–NHR'
or
R–C–NR2'
1. Diisobutylaluminum hydride (DIBAH)
2. H3O+
R–C–H

- The following scheme summarizes how lithium tri-*tert*-butoxyaluminum hydride and DIBAL-H can be used to synthesize aldehydes from acid derivatives:



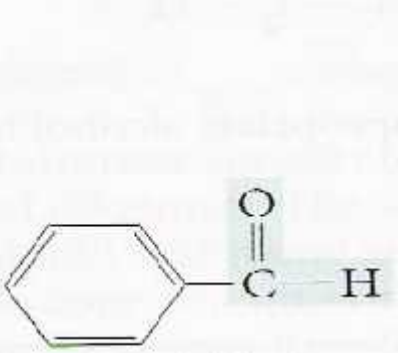

**3-Methoxy-4-methylbenzoyl chloride** **3-Methoxy-4-methylbenzaldehyde**

## 16.5B Ketones from Nitriles

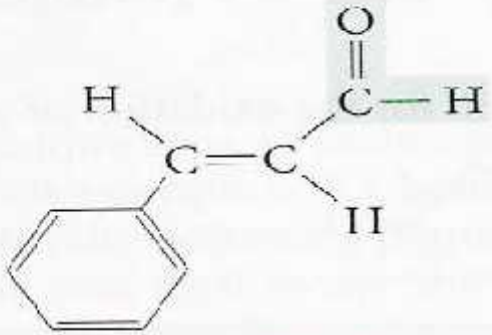
Treating a nitrile (R—C≡N) with either a Grignard reagent or an organolithium reagent followed by hydrolysis yields a ketone.

***General Reactions***

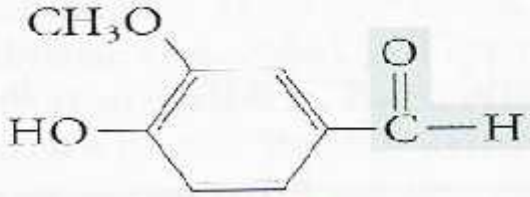
# Naturally occuring aldehydes and Ketones



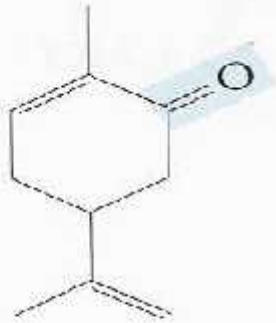
benzaldehyde
(oil of almonds)
bp 178.1°C



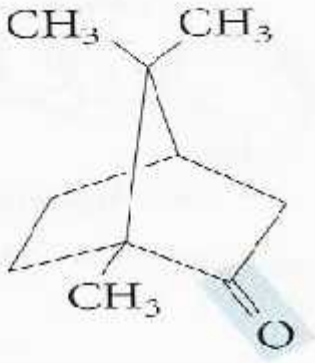
cinnamaldehyde
(cinnamon)
bp 253°C



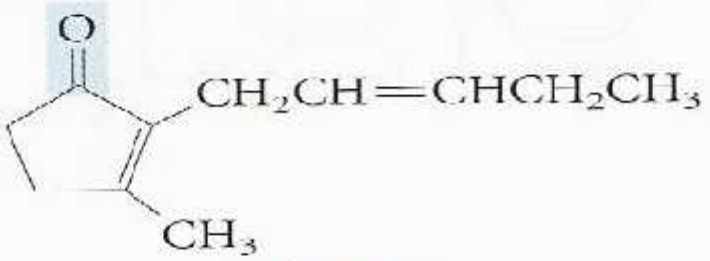
vanillin
(vanilla bean)
mp 80°C, bp 285°C



carvone
(spearmint oil)
bp 231°C

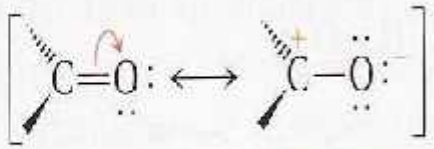


camphor
mp 179°C

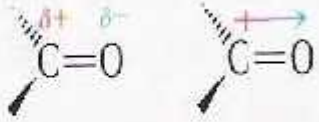


jasmone
(from oil of jasmine)

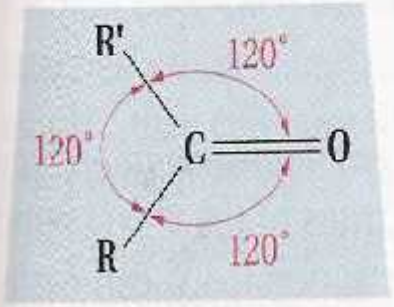
# The carbonyl group



resonance contributors to the carbonyl group



polarization of the carbonyl group



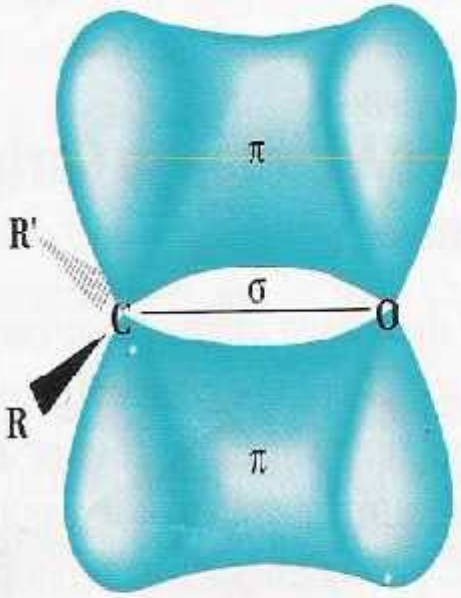
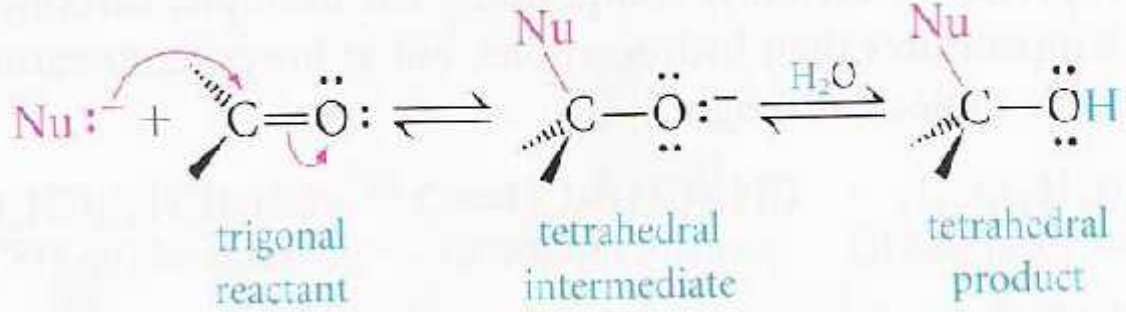




**Figure 9.2**
Bonding in the carbonyl group (see the text for a description of this bonding).

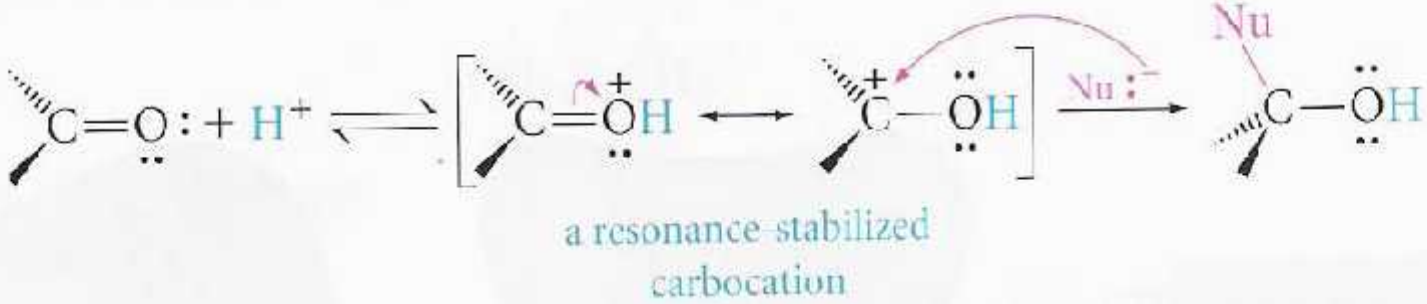
# Reactions of the carbonyl group




(9.8)

The carbonyl carbon, which is trigonal and $sp^2$-hybridized in the starting aldehyde or ketone, becomes tetrahedral and $sp^3$-hybridized in the reaction product.

Because of the unshared electron pairs on the oxygen atom (Figure 9.2c), carbonyl compounds are weak Lewis bases and can be protonated. *Acids can catalyze the addition of weak nucleophiles to carbonyl compounds* by protonating the carbonyl oxygen atom.

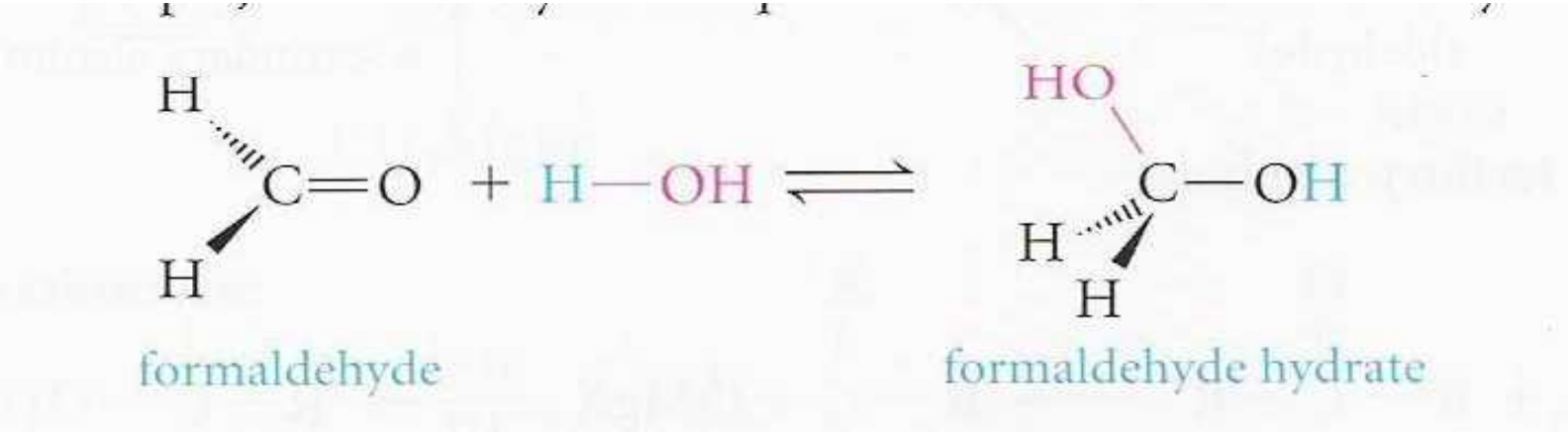


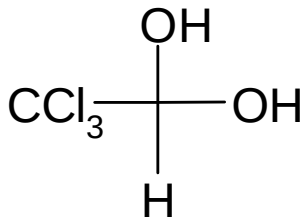

(9.9)

This converts the carbonyl carbon to a carbocation and enhances its susceptibility to attack by nucleophiles.

# A. Hydration and Hemiacetal Formation

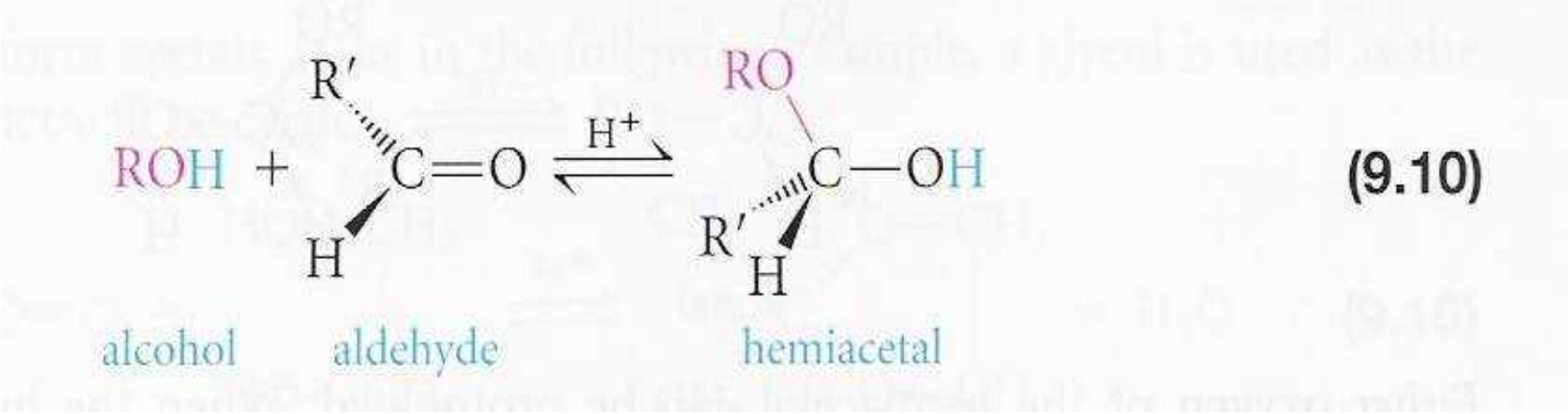
- Water adds rapidly to the carbonyl function of aldehydes and ketones. In most cases the resulting **hydrate** (a geminal-diol) is unstable relative to the reactants and cannot be isolated.
- Exceptions to this rule exist,
- one being formaldehyde (a gas in its pure monomeric state).
- Thus, a solution of formaldehyde in water (formalin) is almost exclusively the hydrate, or polymers of the hydrate.
- Another is chloral hydrate



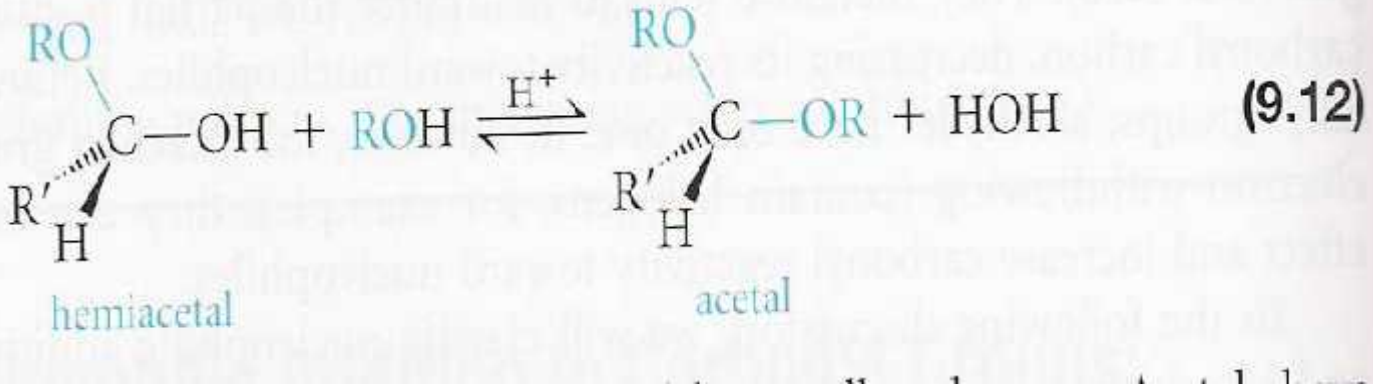




**Chloral hydrate**

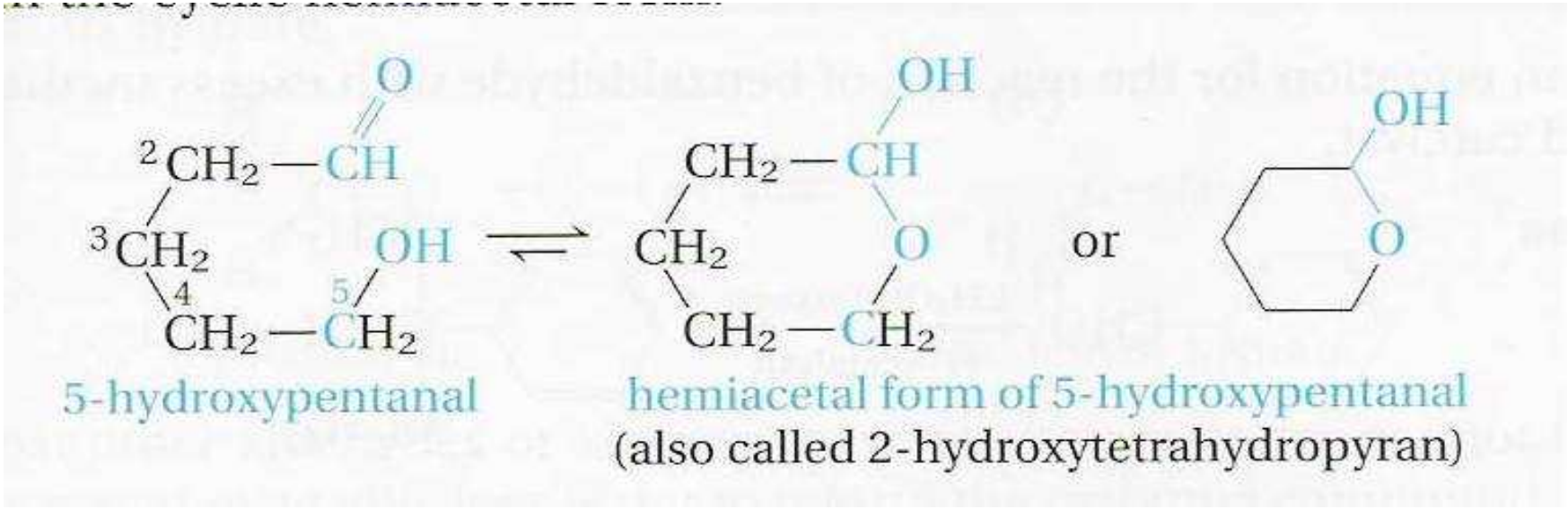
# Addition of Alcohols

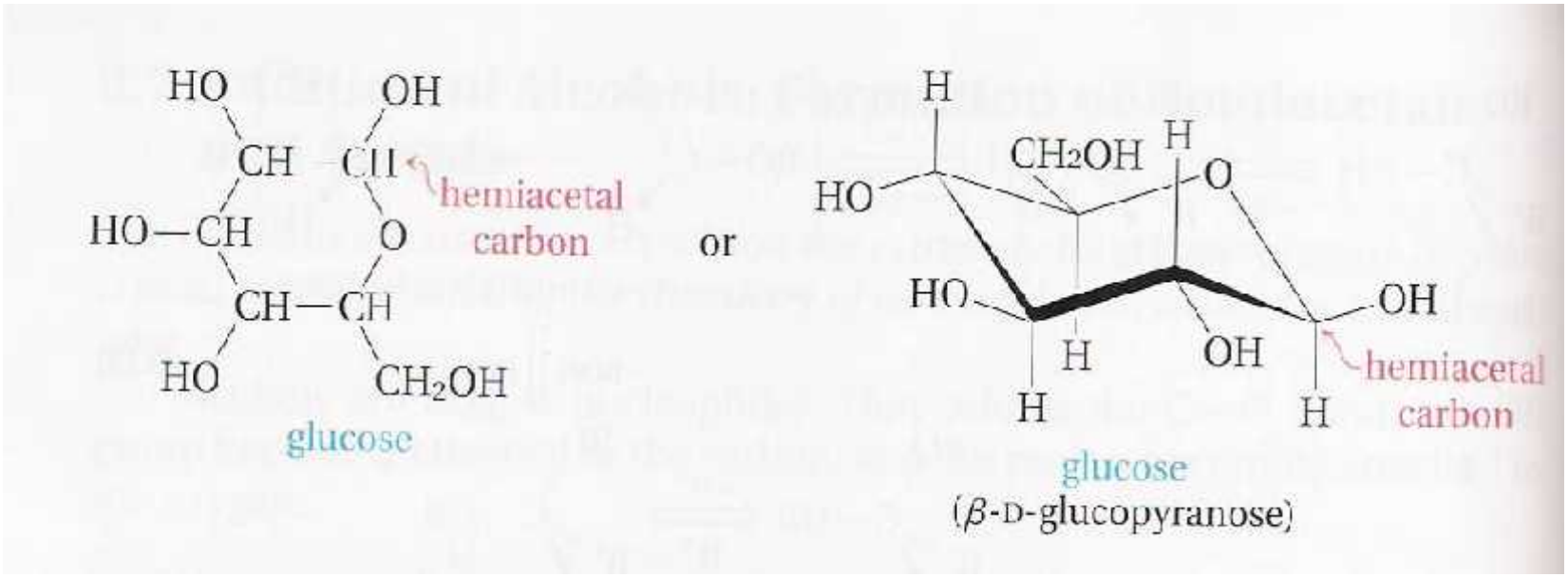


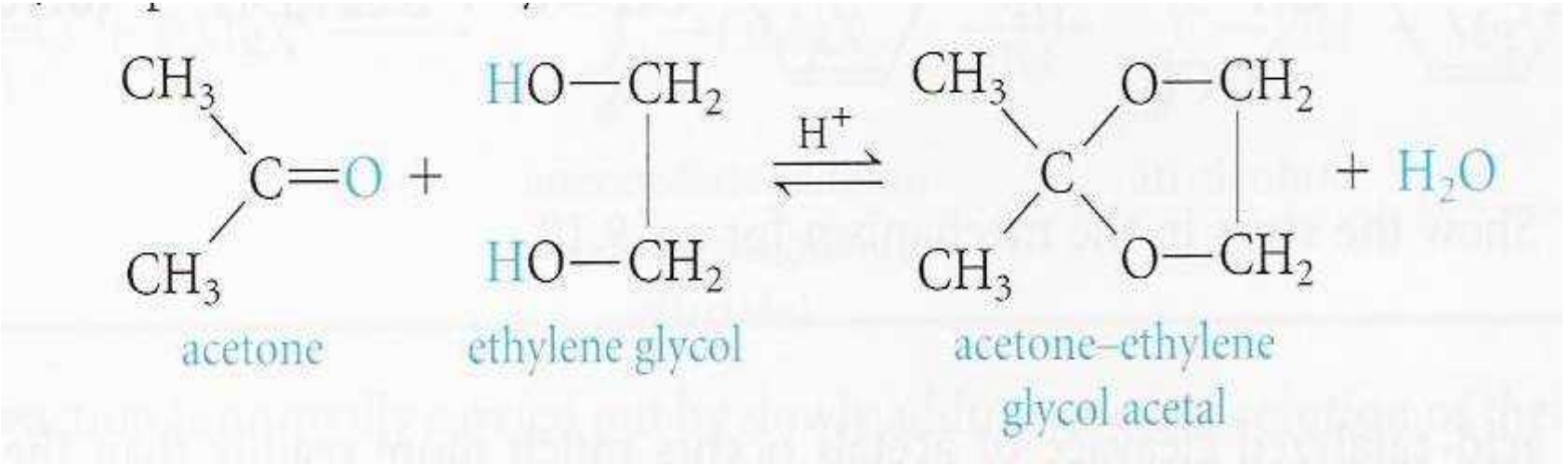

In the presence of *excess alcohol*, hemiacetals react further to form acetals.



# Examples


O
2CH2—CH
3CH2
OH
4
5
CH2—CH2
5-hydroxypentanal
OH
CH2—CH
CH2
O
CH2—CH2
hemiacetal form of 5-hydroxypentanal
(also called 2-hydroxytetrahydropyran)
or
OH
O


HO
OH
CH
CH
hemiacetal
carbon
HO—CH
O
CH—CH
HO
CH2OH
glucose
or
H
CH2OH
H
HO
O
HO
OH
H
OH
H
H
hemiacetal
carbon
glucose
(β-D-glucopyranose)

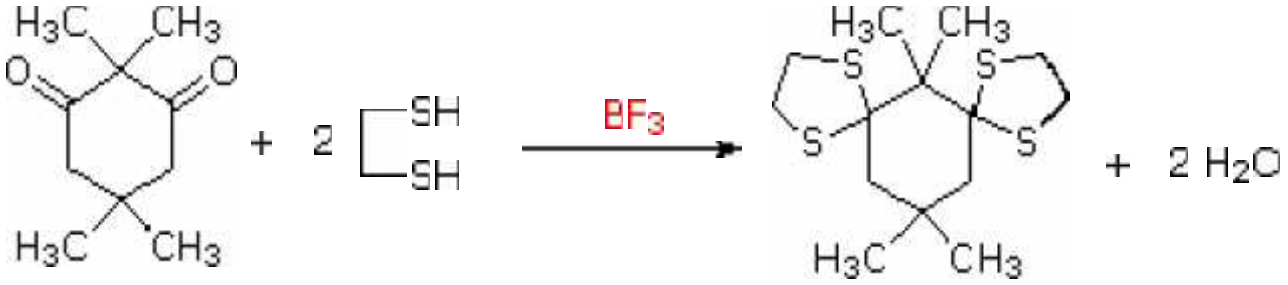

CH3
C=O
CH3
+
HO—CH2
HO—CH2
H+
CH3
O—CH2
C
O—CH2
CH3
+ H2O
acetone
ethylene glycol
acetone–ethylene
glycol acetal

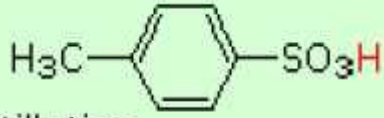
1. 


2. 


3. 


4. 

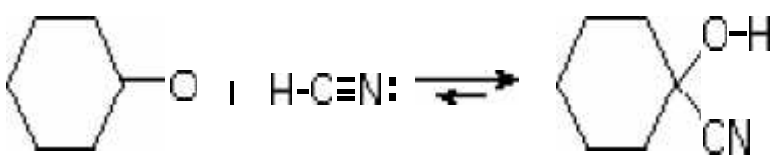

5. 


The acid often used to catalyze acetal formation is p-toluenesulfonic acid 

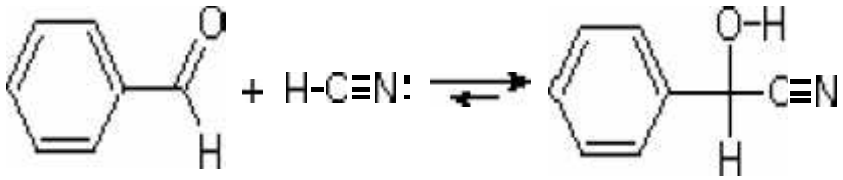
Toluene is usually the solvent, and water is removed azeotropically by distillation

# Addition of hydrogen cyanide to aldehydes and ketones





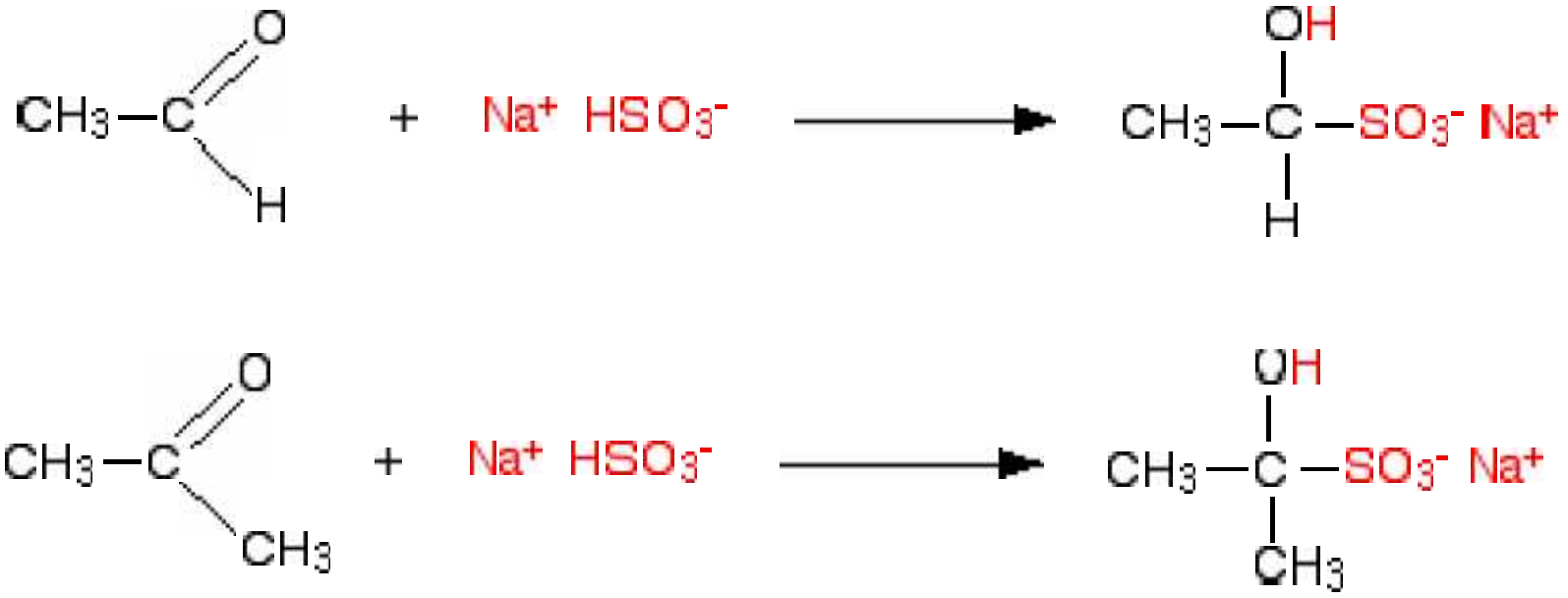

cyclohexanone
cyanohydrin



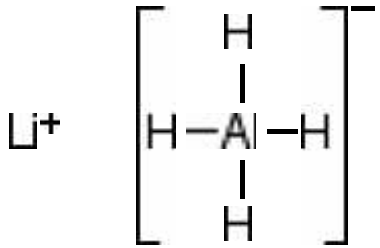

mandelonitrile

# Addition of sodium hydrogensulphite to aldehydes and ketones

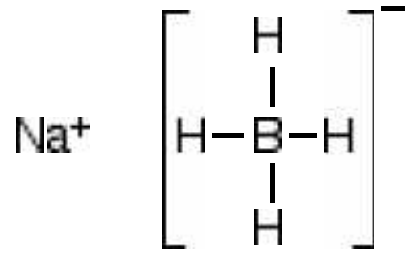
- **Uses of the reaction** The reaction is usually used during the purification of aldehydes (and any ketones that it works for). The addition compound can be split easily to regenerate the aldehyde or ketone by treating it with either dilute acid or dilute alkali.



# Reducing Agents




ithium tetrahydridoaluminate

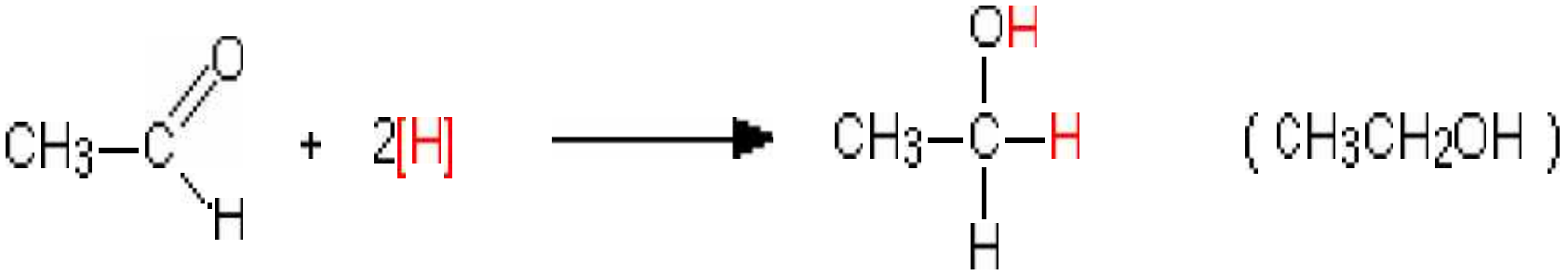



sodium tetrahydridoborate

***The reduction of an aldehyde***

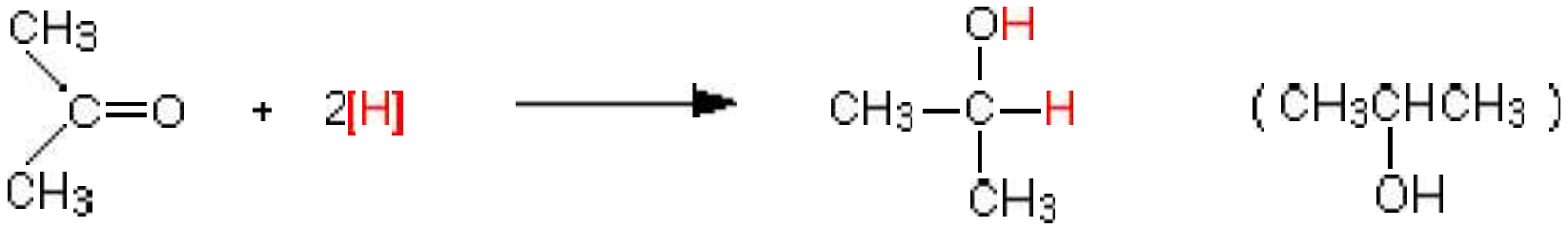
You get exactly the same organic product whether you use lithium tetrahydridoaluminate or sodium tetrahydridoborate.

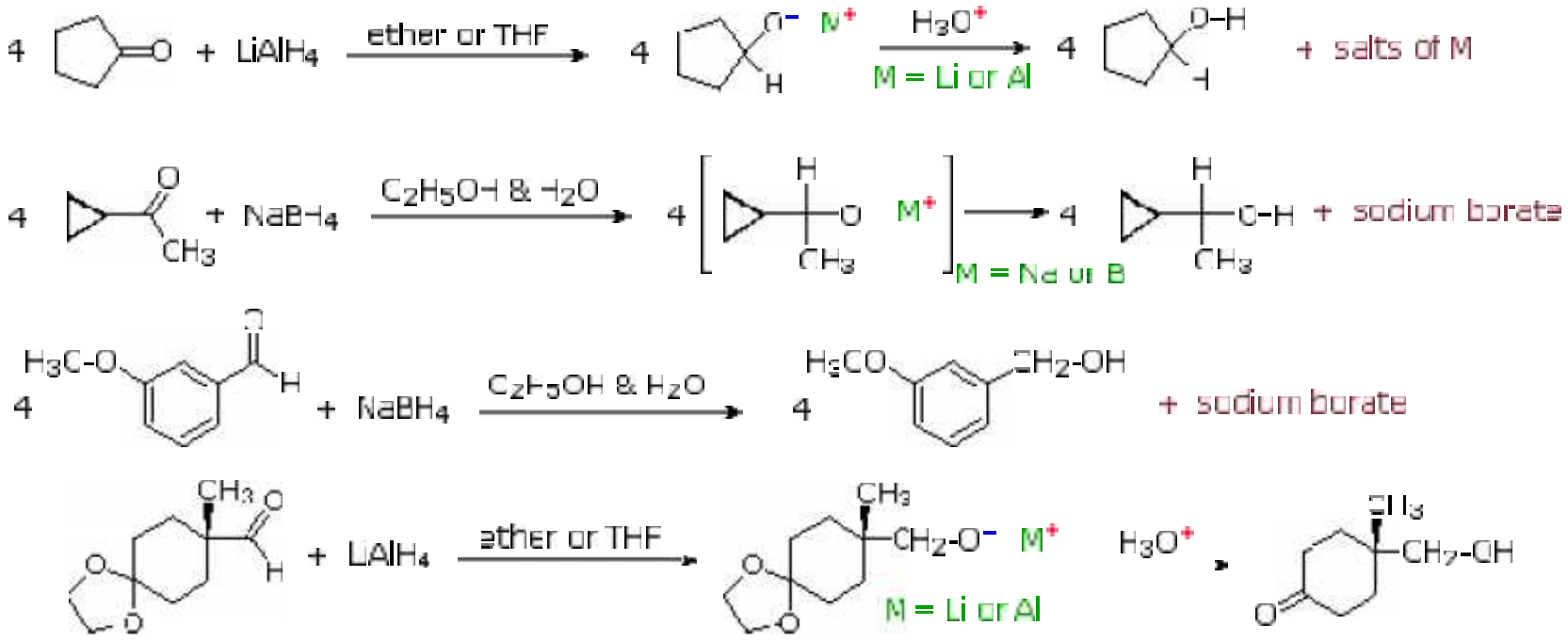
For example, with ethanal you get ethanol:



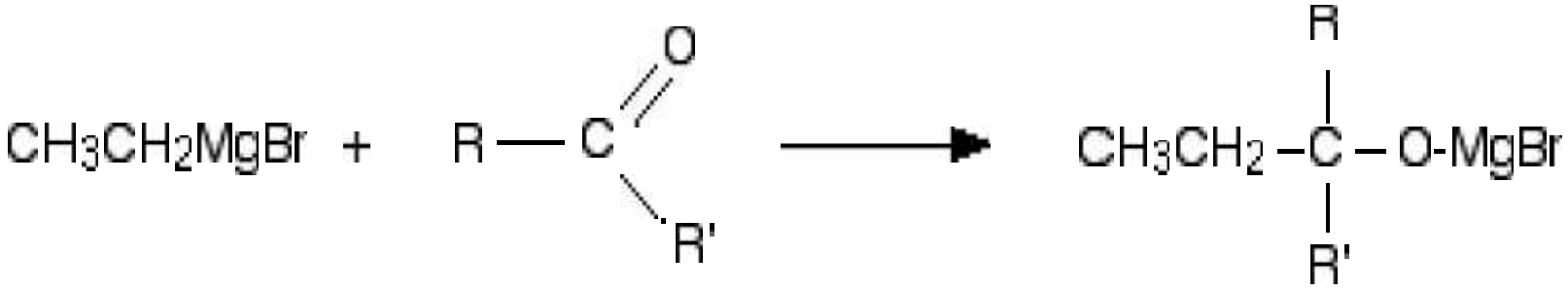
## *The reduction of a ketone*

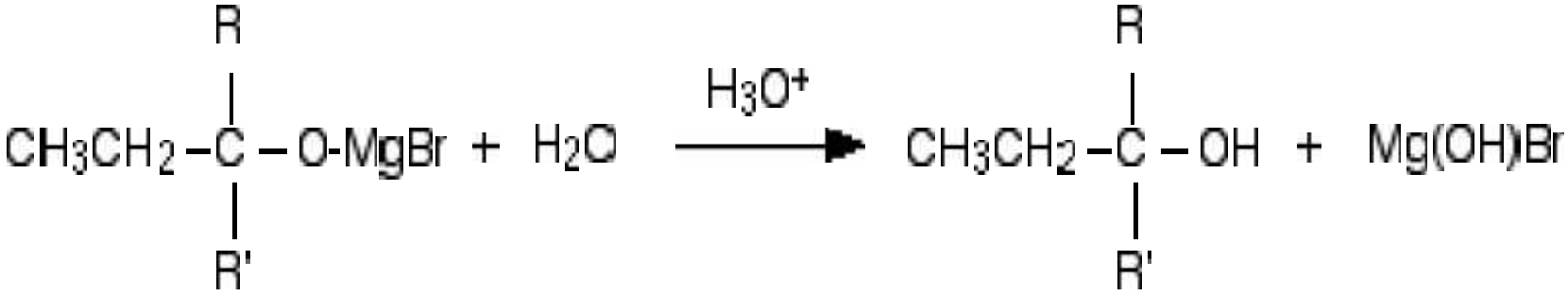
- Again the product is the same whichever of the two reducing agents you use.
- For example, with propanone you get propan-2-ol:
- Reduction of a ketone leads to a ***secondary alcohol***.



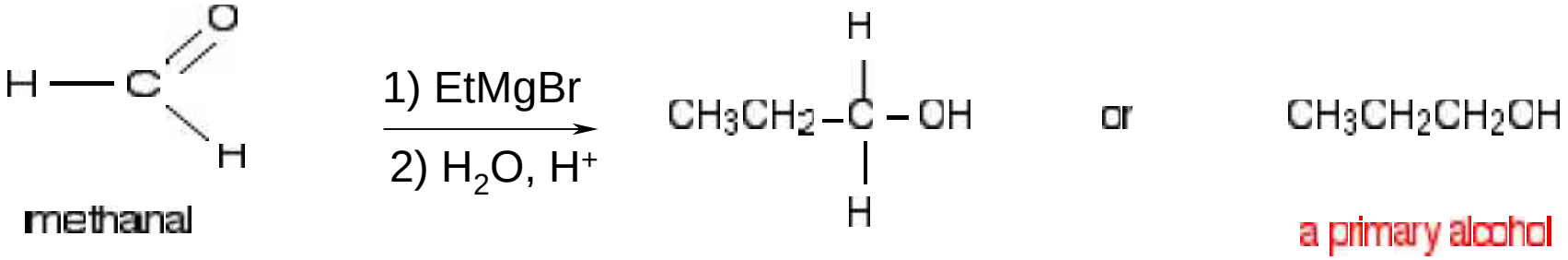

4
+ LiAlH4
ether or THF
4
M+
H3O+
M = Li or Al
4
+ salts of M
4
+ NaBH4
C2H5OH & H2O
4
M+
4
+ sodium borate
M = Na or B
H3C-O
4
+ NaBH4
C2H5OH & H2O
4
+ sodium borate
+ LiAlH4
ether or THF
M+
M = Li or Al
H3O+

# REACTION OF ALDEHYDES AND KETONES WITH GRIGNARD REAGENTS



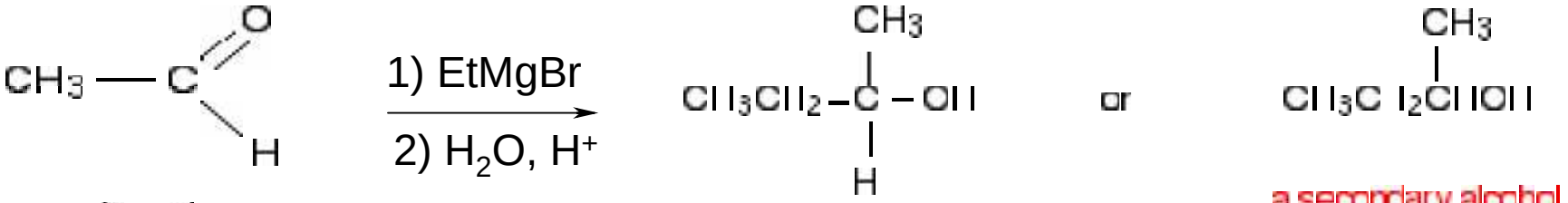



## The reaction between Grignard reagents and methanal



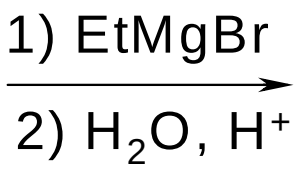

methanal

## The reaction between Grignard reagents and other aldehydes



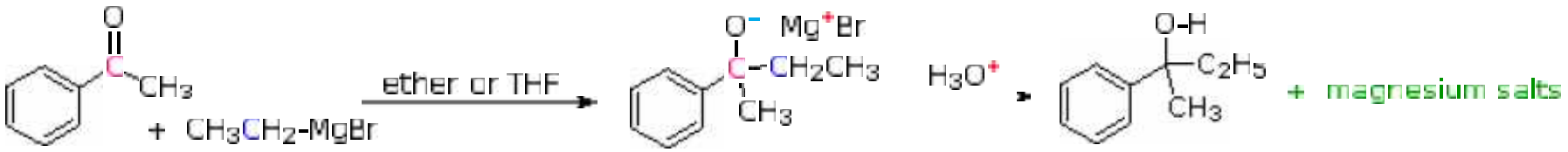

ethanal

## The reaction between Grignard reagents and ketones



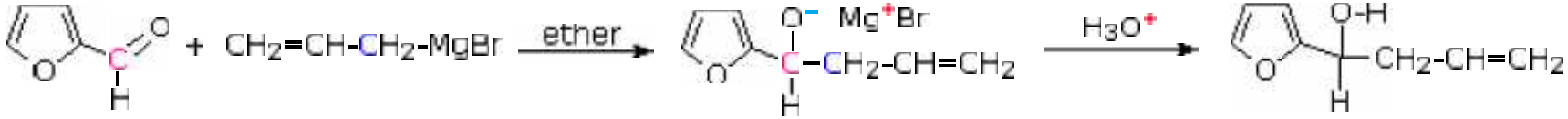
## Examples of Organometallic Addition Reactions

**1.**

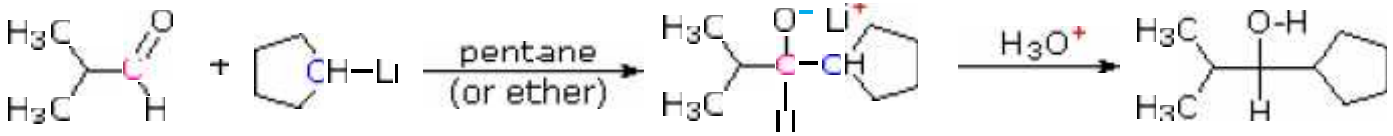



**2.**

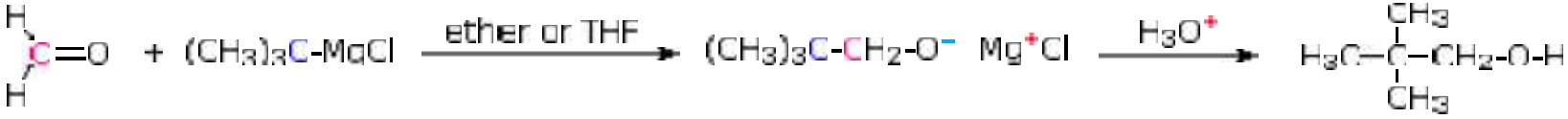

**3.**



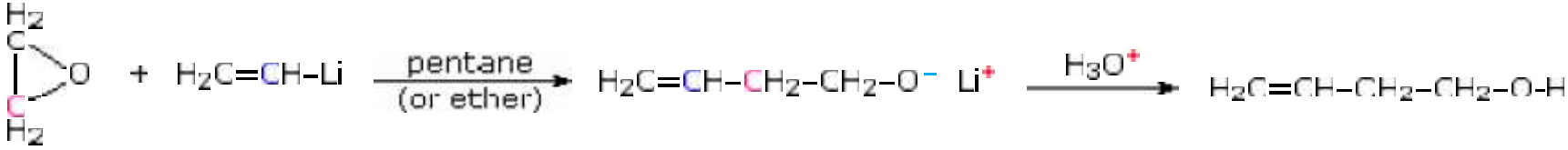

**4.**



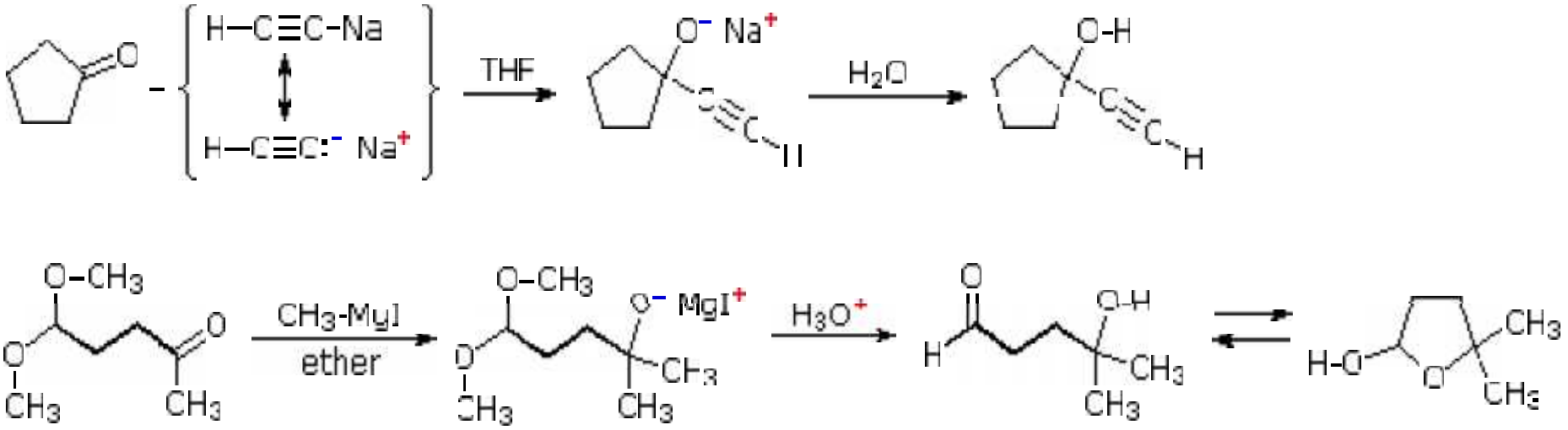

**5.**



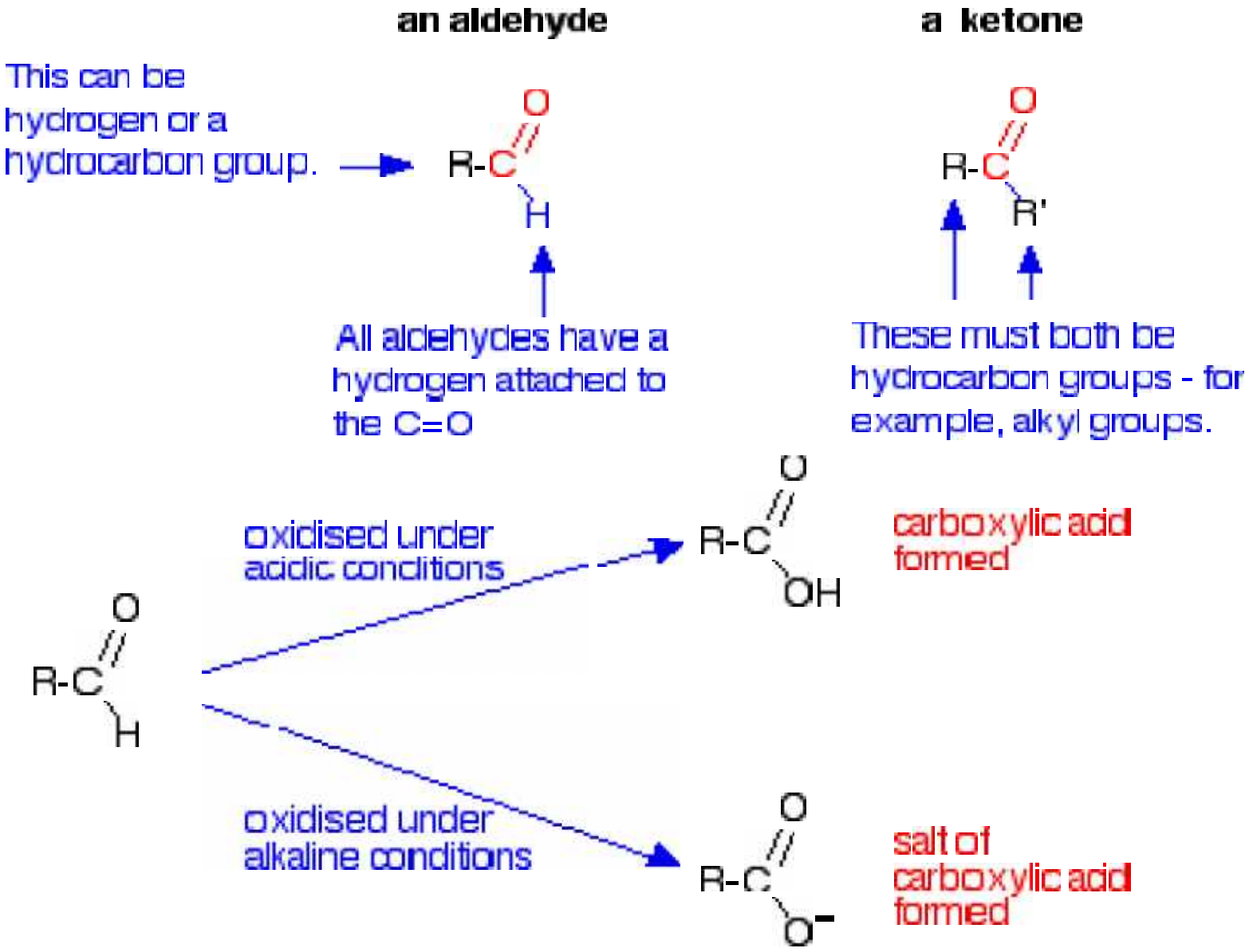

**6.**



# Reaction with Acetylides

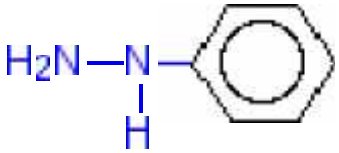


# OXIDATION OF ALDEHYDES AND KETONES

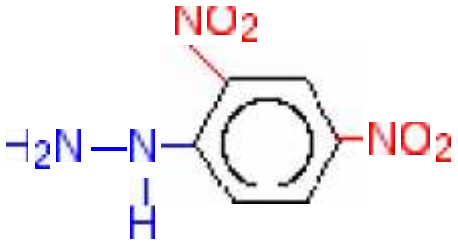


# ADDITION-ELIMINATION REACTIONS OF ALDEHYDES AND KETONES

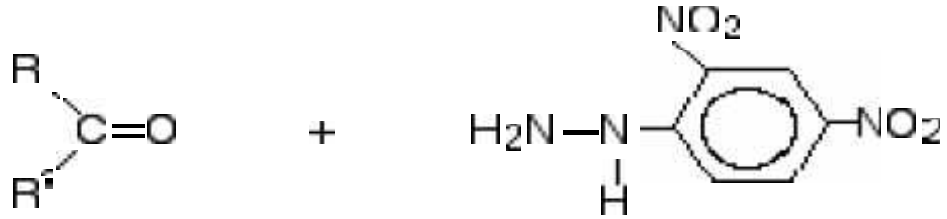
**hydrazine**

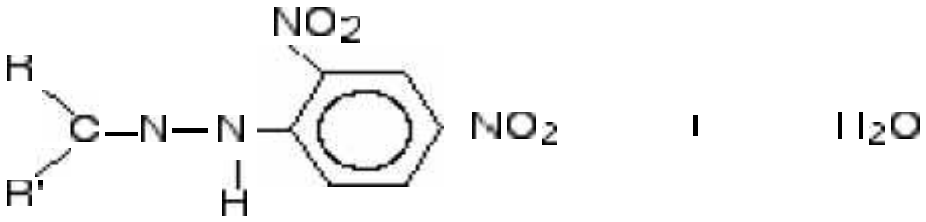


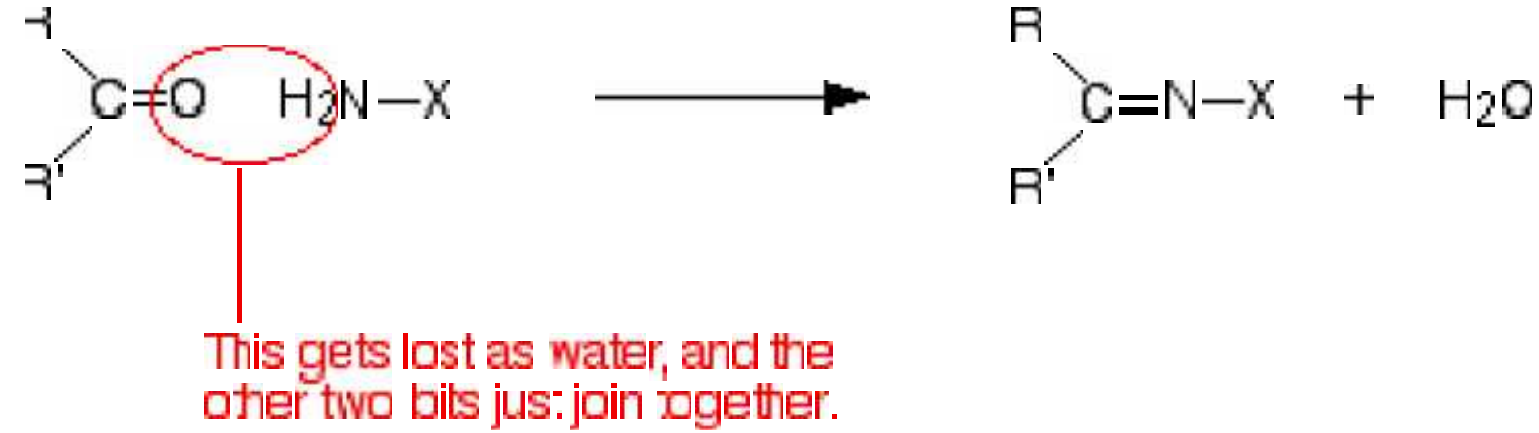
**phenyl**hydrazine

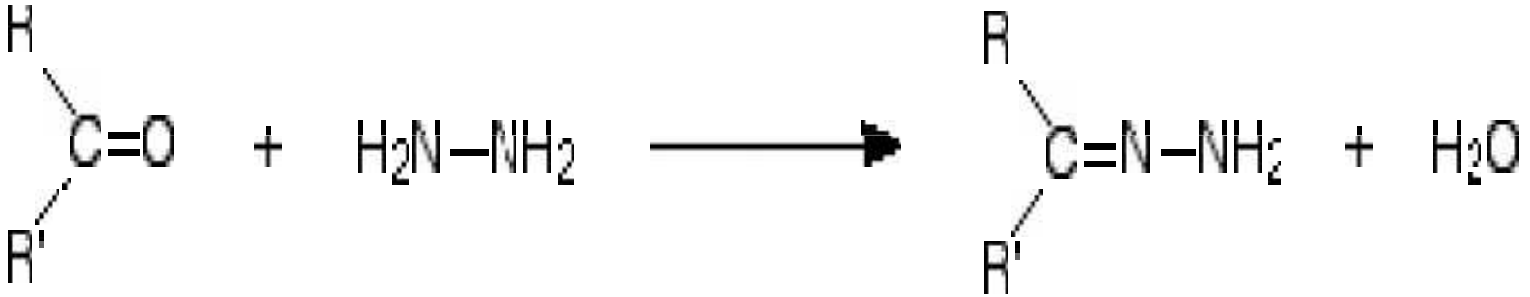


**2,4-dinitro**phenylhydrazine






C=O
H2N—X
R
R'
C=N—X
+
H2O
This gets lost as water, and the
other two bits just join together.


H
C=O
R'
+
H2N—NH2
R
C=N—NH2
+
H2O

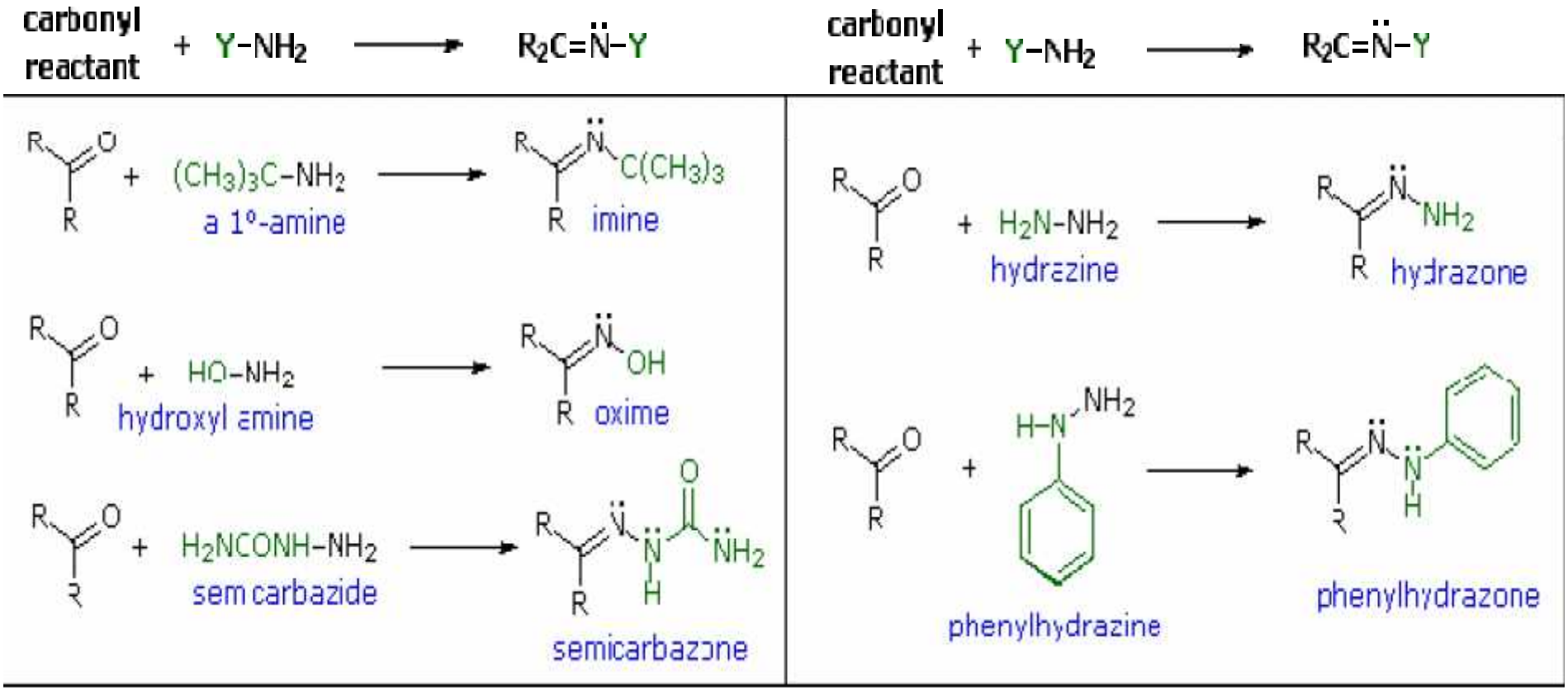
## with hydroxylamine

The product is an "oxime" - for example, ethanal oxime.

# Formation of Imines and Related Compounds

The reaction of aldehydes and ketones with ammonia or 1º-amines forms **imine derivatives**, also known as

**Schiff bases**, (compounds having a C=N function).



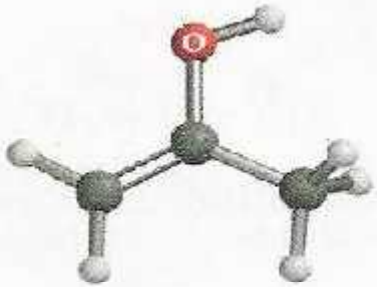
# Keto-Enol Tautomerism

- K**eto-enol tautomerism** refers to a chemical equilibrium between a **keto** form )a ketone or an aldehyde) and an **enol**. The enol and keto forms are said to be tautomers of each other. The interconversion of the two forms involves the movement of a proton and the shifting of bonding electrons; hence, the isomerism qualifies as tautomerism.
- A compound containing a carbonyl group (C=O) is normally in rapid equilibrium with an enol tautomer, which contains a pair of doubly bonded carbon atoms adjacent to a hydroxyl (−OH) group, C=C-OH. The keto form predominates at equilibrium for most ketones. Nonetheless, the enol form is important for some reactions. Furthermore, the deprotonated intermediate in the interconversion of the two forms, referred to as an enolate anion, is important in carbonyl chemistry, in large part because it is a strong nucleophile.

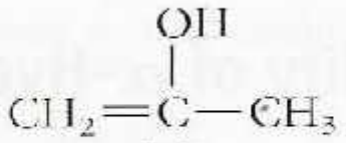
## EXAMPLE 9.7

Write formulas for the keto and enol forms of acetone.

**SOLUTION**



keto form



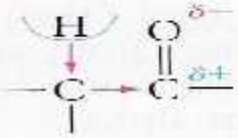
enol form

**PROBLEM 9.23** Draw the structural formula for the enol form of

a. cyclohexanone.
b. acetaldehyde ($CH_3CHO$).

# Acidity of α-Hydrogen

There are two reasons. First, the carbonyl carbon carries a partial positive charge. Bonding electrons are displaced toward the carbonyl carbon and away from the α-hydrogen (shown by the red arrows below), making it easy for a base to remove the α-hydrogen as a proton (that is, without its bonding electrons).



Second, the resulting anion is stabilized by resonance.

(9.44)

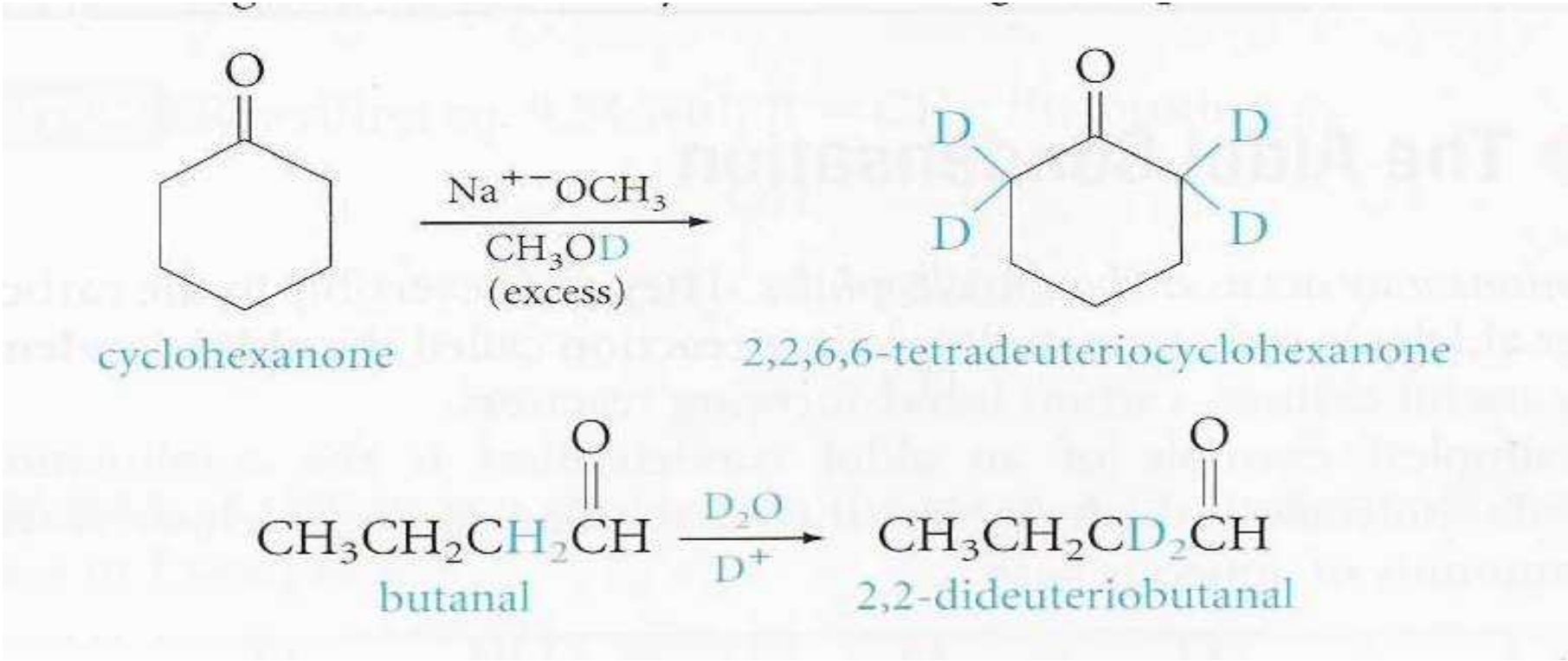
resonance structures of an enolate anion

The anion is called an **enolate anion**. Its negative charge is distributed between the α-carbon and the carbonyl oxygen atom.

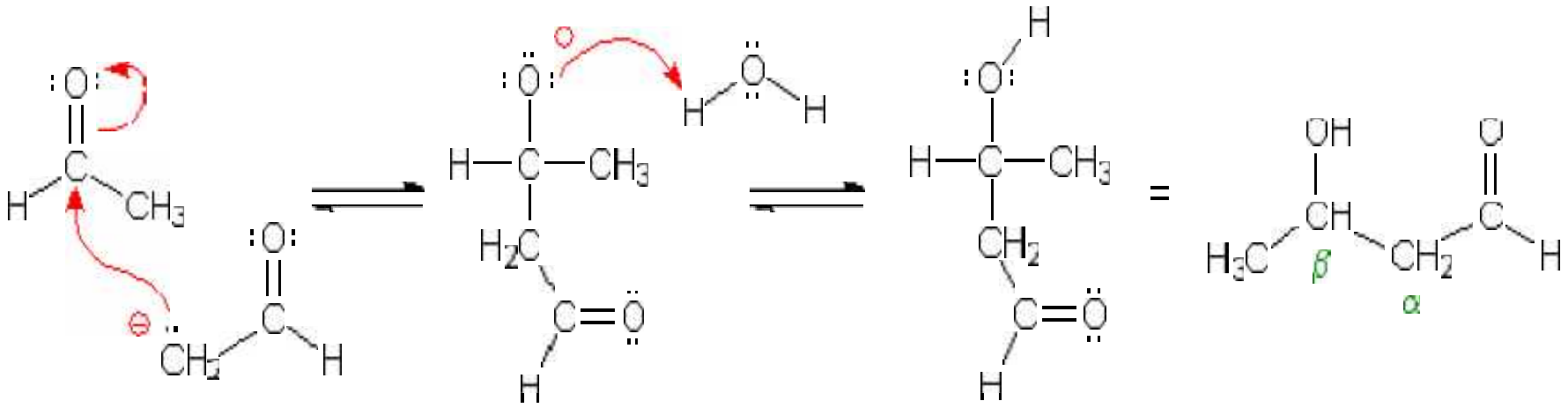
**TABLE 9.2 ACIDITY OF α-HYDROGENS**

| Compound | Name | p$K_a$ |
|---|---|---|
| $CH_3CH_2CH_3$ | propane | ~50 |
| $CH_3CCH_3$ (O) | acetone | 19 |
| $CH_3CH$ (O) | acetaldehyde | 17 |
| $CH_3CH_2OH$ | ethanol | 16 |

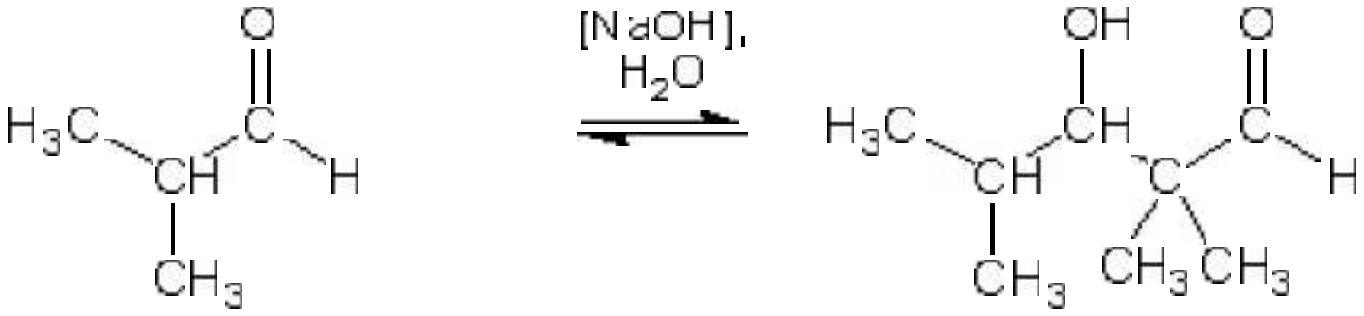
- **Examples of ó-Hydrogen exchange**



# The Aldol Condensation

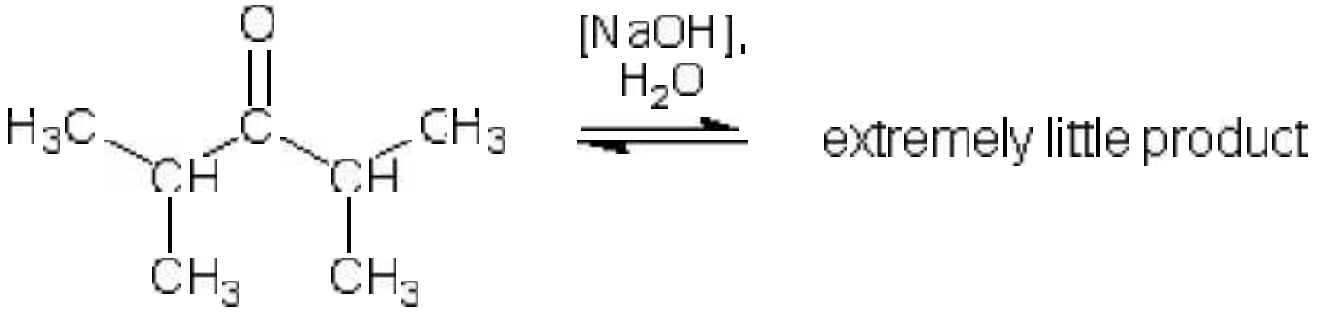


The name **aldol** is derived from "**ald**ehyde" and "alcoh**ol**". An aldol is a β-hydroxycarbonyl compound.

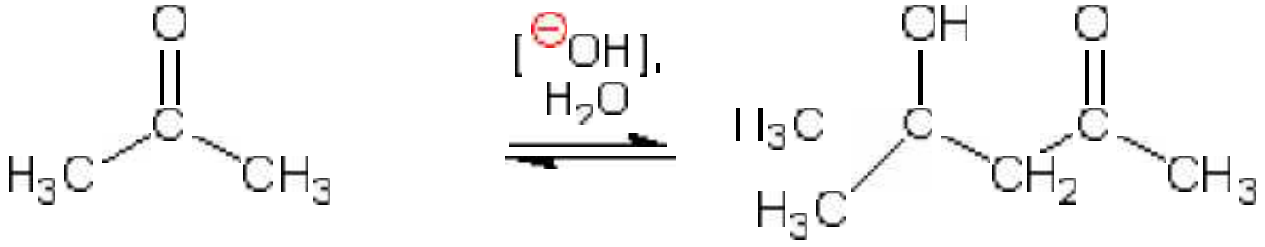



15 %

85 %




extremely little product

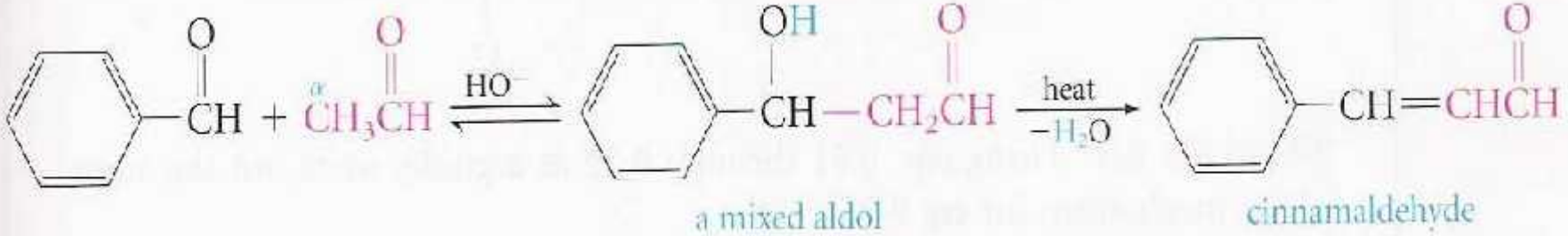



95 %

5 %

## 9.18 The Mixed Aldol Condensation

The aldol condensation is very versatile in that the enolate anion of *one* carbonyl compound can be made to add to the carbonyl carbon of *another*, provided that the reaction partners are carefully selected. Consider, for example, the reaction between acetaldehyde and benzaldehyde, when treated with base. Only acetaldehyde can form an enolate anion (benzaldehyde has no α-hydrogen). If the enolate ion of acetaldehyde adds to the benzaldehyde carbonyl group, a mixed aldol condensation occurs.




In this particular example, the resulting mixed aldol eliminates water on heating to give **cinnamaldehyde** (the flavor constituent of cinnamon).