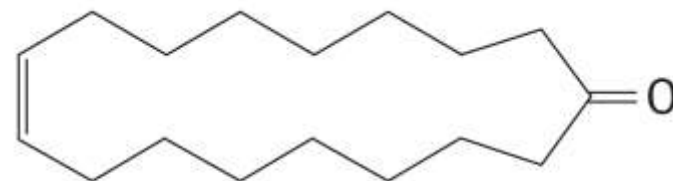
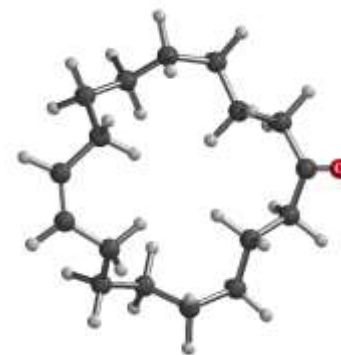


# Chapter 9: Aldehydes and Ketones

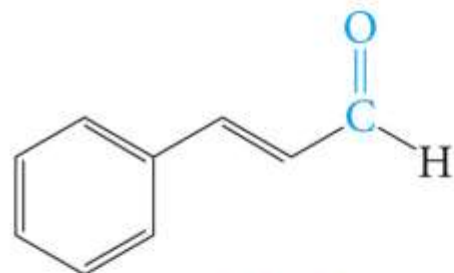


civetone



The Civet Cat is the original source of civetone, a sweet and pungent ketone used as a fixative in perfumery

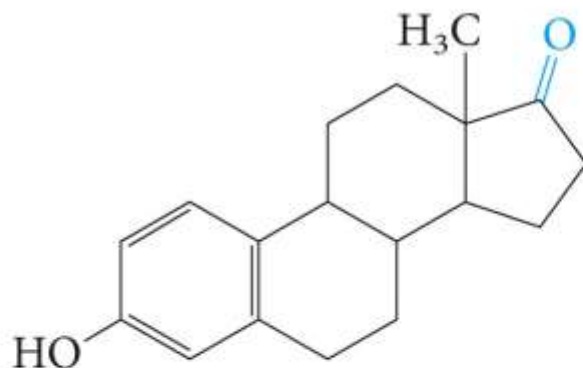
Aldehydes and ketones are found in many fragrant odors of many fruits, fine perfumes, hormones etc. some examples are listed below.



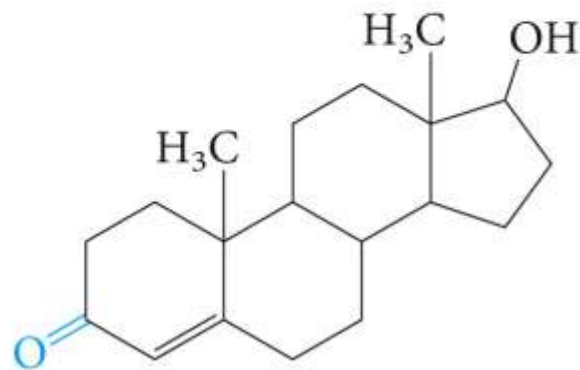
cinnamaldehyde



formaldehyde

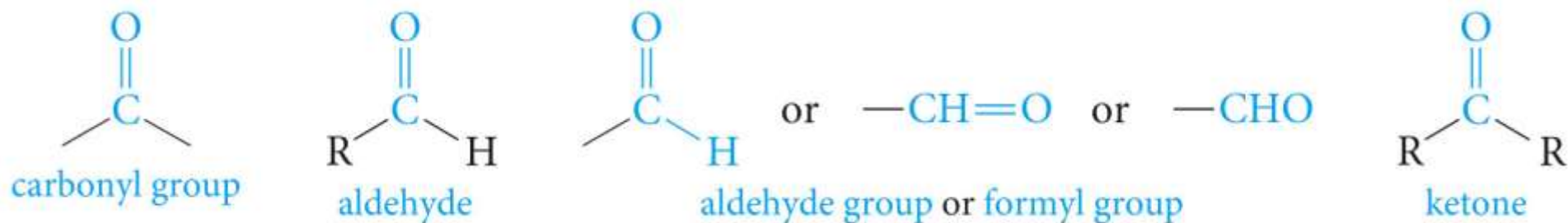


estrone



testosterone

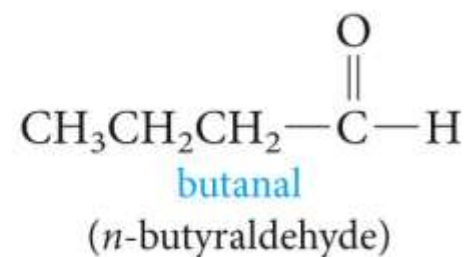
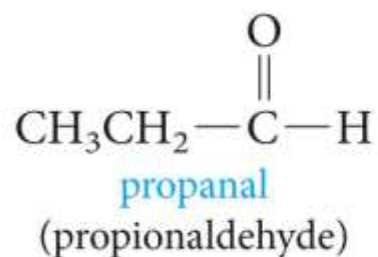
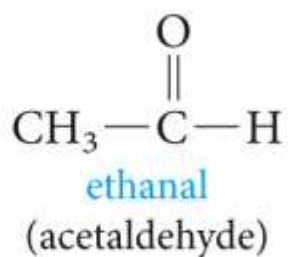
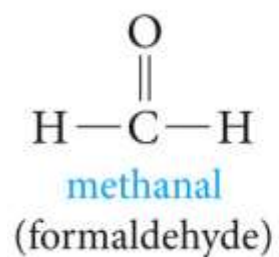
Aldehydes and ketones are characterized by the presence of the **carbonyl group**, which is perhaps the most important functional group in organic chemistry. Aldehydes have at least one hydrogen atom attached to the carbonyl carbon atom. The remaining group may be another hydrogen atom or any aliphatic or aromatic group. The  $-\text{CH}=\text{O}$  group characteristic of aldehydes is often called a **formyl group**. In ketones, the carbonyl carbon atom is connected to two other carbon atoms



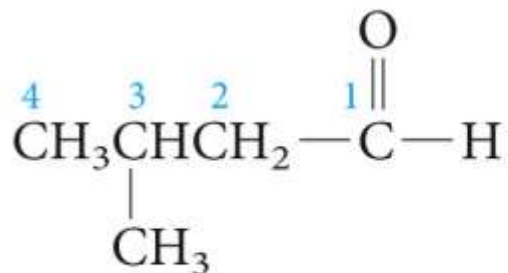
The carbonyl group is in many compounds including carboxylic acids and their derivatives.

## Nomenclature;

In the IUPAC system, the characteristic ending for aldehydes is *-al* (from the first syllable of *aldehyde*)



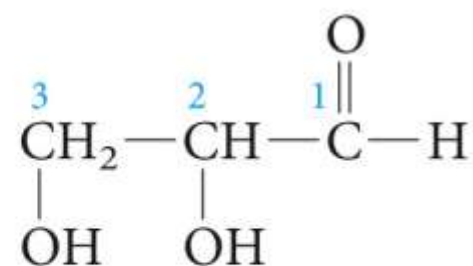
In the presence of a double bond or an alcohol group, the aldehyde group takes priority



3-methylbutanal

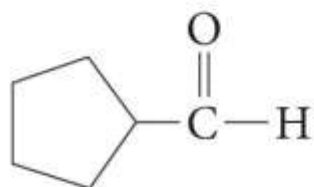


3-butenal

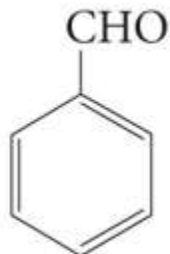


2,3-dihydroxypropanal  
(glyceraldehyde)

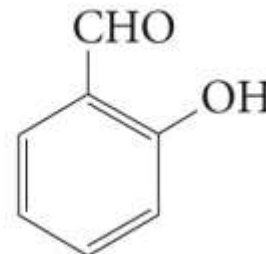
For cyclic aldehydes the suffix *-carbaldehyde* is used. Most of the aromatic aldehydes have common names.



cyclopentanecarbaldehyde  
(formylcyclopentane)

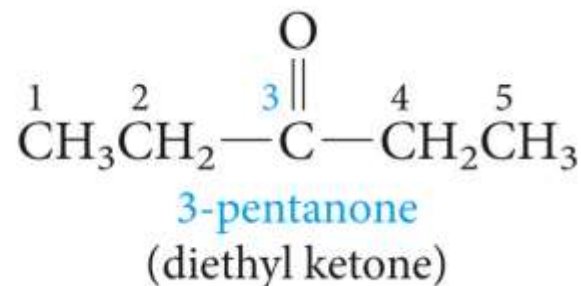
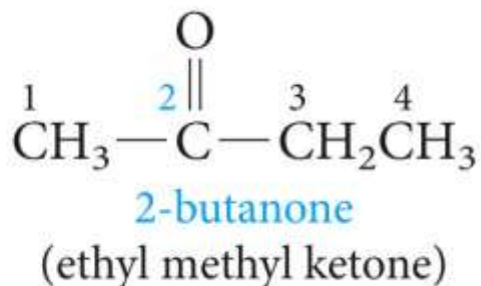
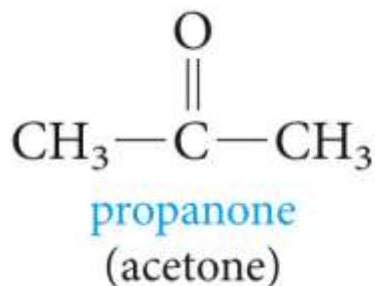


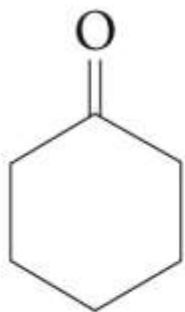
benzaldehyde  
(benzenecarbaldehyde)



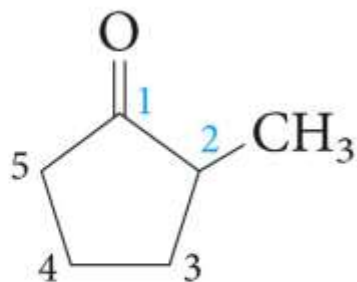
salicylaldehyde  
(2-hydroxybenzenecarbaldehyde)

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

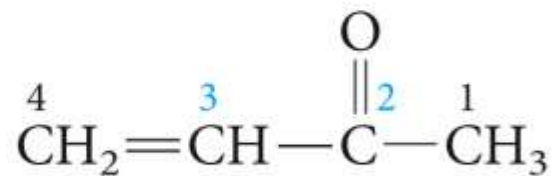




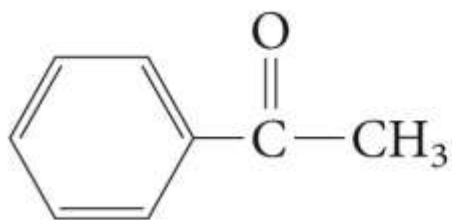
cyclohexanone



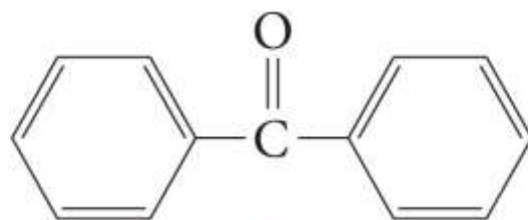
2-methylcyclopentanone



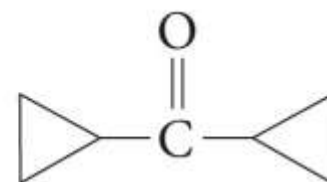
3-buten-2-one  
(methyl vinyl ketone)



acetophenone  
(methyl phenyl ketone)



benzophenone  
(diphenyl ketone)

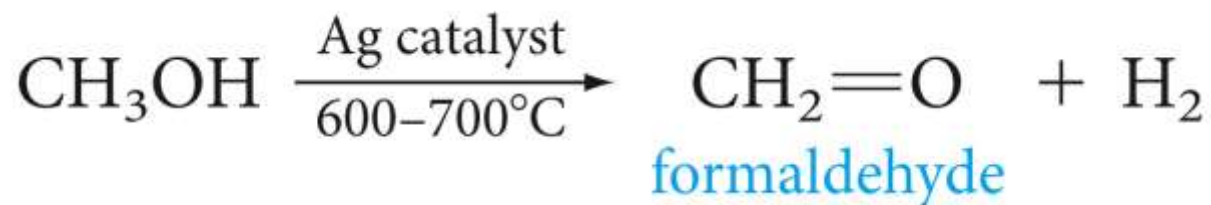


dicyclopropyl ketone

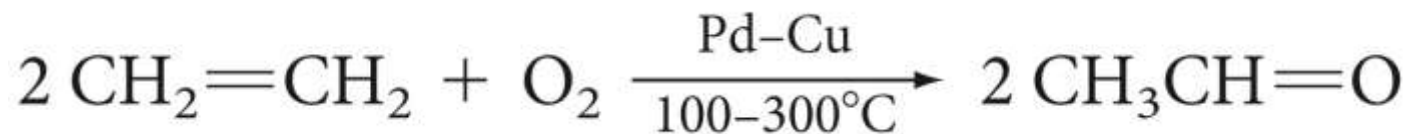


## Some Common Aldehydes and Ketones

**Formaldehyde**, which is the simplest aldehyde, is manufactured by the catalytic oxidation of methanol. The annual world production is more than 46 billion pounds.

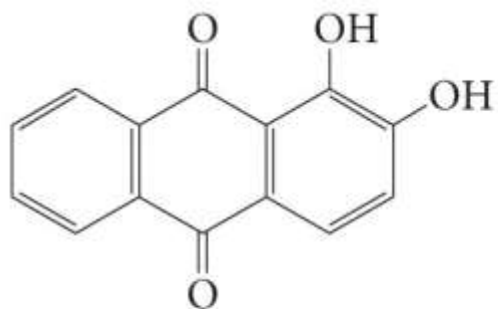


Acetaldehyde ( $\text{CH}_3\text{CH}=\text{O}$ ) is manufactured mainly by the oxidation of ethylene over palladium-copper catalyst. About 1 billion pounds are produced each year.

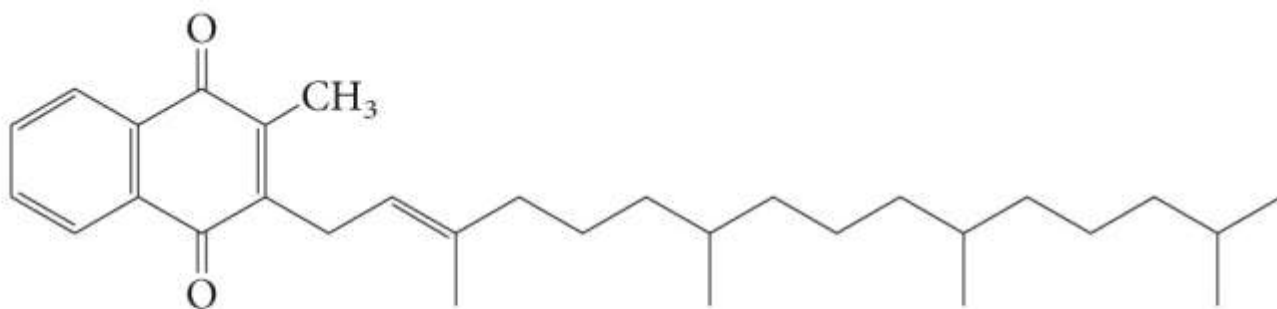


Acetone, the simplest ketone may be prepared using a similar method from the oxidation of propene.

Quinones; these compounds form a unique class of carbonyl compounds. They are cyclic conjugated diketones, the simplest being 1,4-benzoquinone. All quinones are colored and many occur naturally as pigments that can be used as dyes. Alizarin is the orange-red quinone that was used to dye the red coats of the British army during the American Revolution. Vitamin K is a quinone that is required for the normal clotting of blood.



alizarin  
mp 290°C



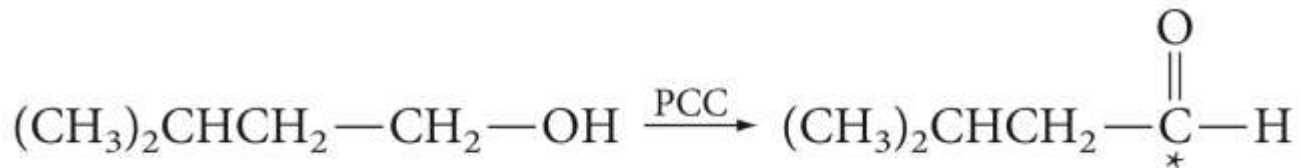
vitamin K  
mp -20°C

# Synthesis of Aldehydes and Ketones

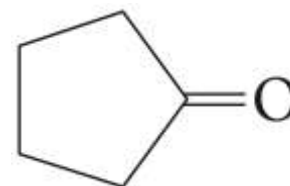
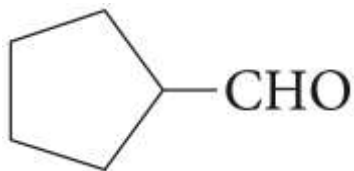


Aldehydes and ketones are mostly prepared by the oxidation of primary and secondary alcohols respectively. Chromium reagents such as pyridinium chlorochromate (PCC), are commonly used in the laboratory.

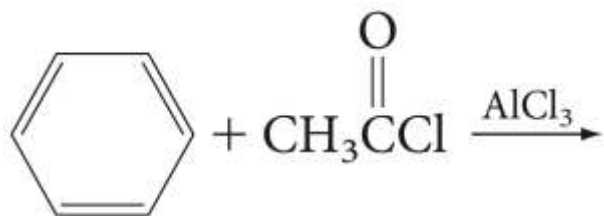
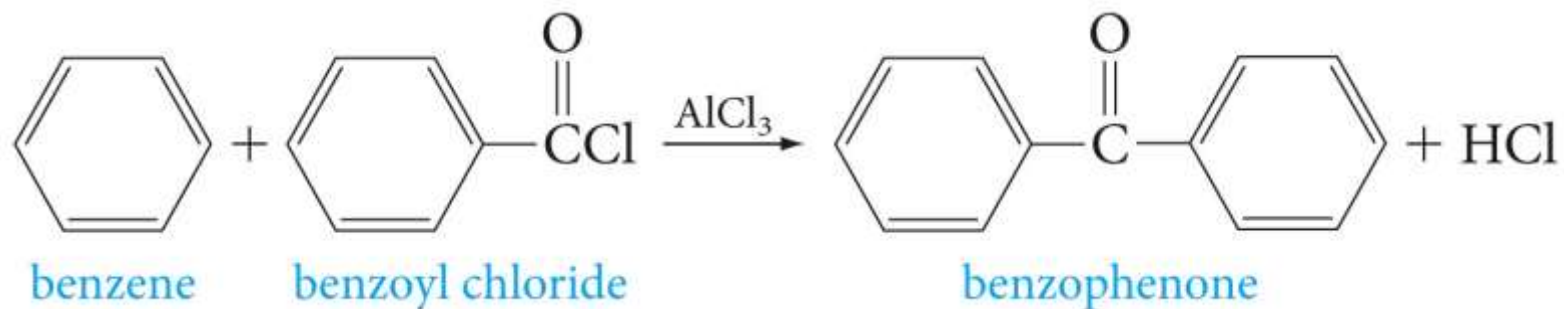
**example**



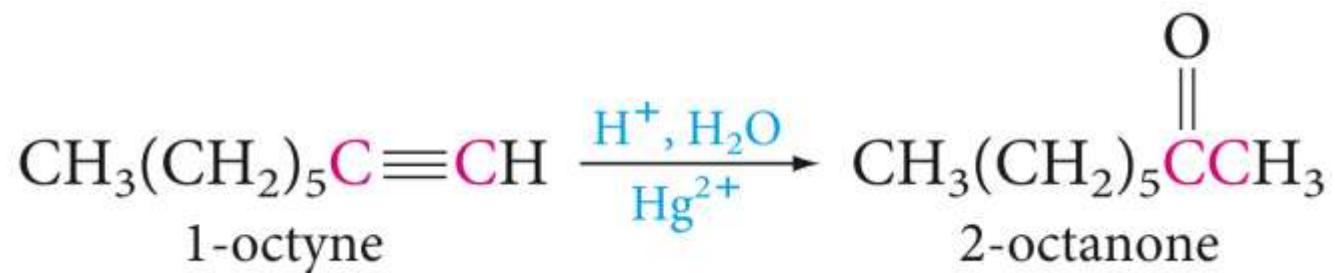
Using an appropriate alcohol, write an equation to show how the following compounds can be made by oxidation.



Aromatic ketones can be prepared by Friedel-Crafts acylation of an aromatic ring



Methyl ketones can be prepared by the hydration of terminal alkynes, catalyzed by acid and mercury ion.

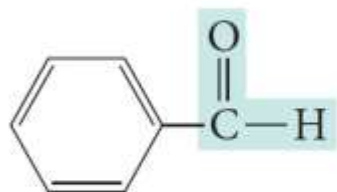




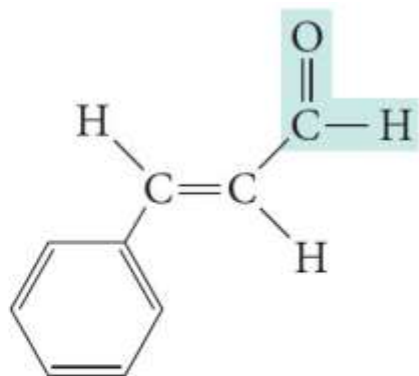
What alkyne would be useful for the synthesis of 2-heptanone (oil of cloves)? Write the synthesis reaction.



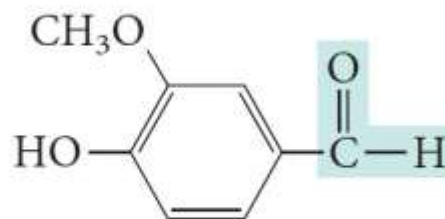
# Aldehydes and Ketones in Nature



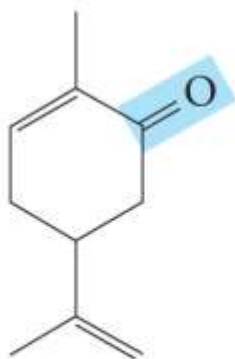
**benzaldehyde**  
(oil of almonds)  
bp 178.1°C



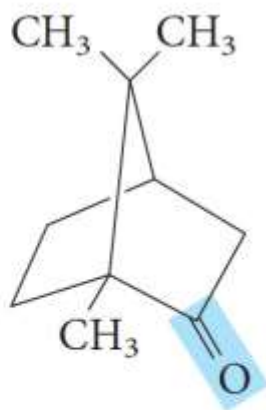
**cinnamaldehyde**  
(cinnamon)  
bp 253°C



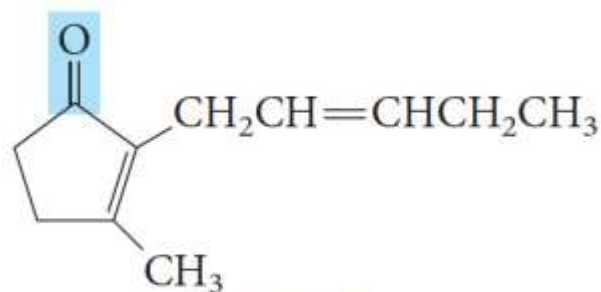
**vanillin**  
(vanilla bean)  
mp 80°C, bp 285°C



**carvone**  
(spearmint oil)  
bp 231°C

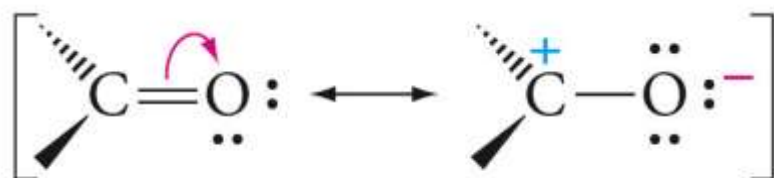


**camphor**  
mp 179°C



**jasmone**  
(from oil of jasmine)

# The Carbonyl Group



resonance contributors  
to the carbonyl group



polarization of the  
carbonyl group

The carbonyl carbon is  $sp^2$ –hybridized, the carbon-oxygen double bond consists of a sigma bond and a pi bond.

The three atoms attached to the carbonyl carbon lie on the same plane with bond angle of  $120^\circ$ .

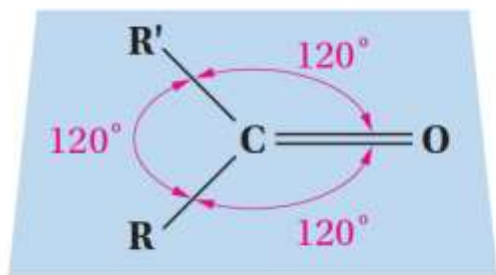
The C=O bond distance is  $1.24 \text{ \AA}$ , shorter than a C-O single bond in ethers and alcohols ( $1.43 \text{ \AA}$ )

The C=O bond is polarized

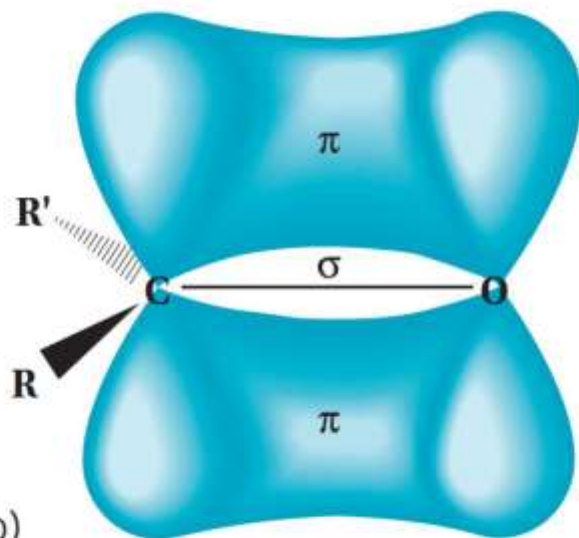
attack here by a nucleophile



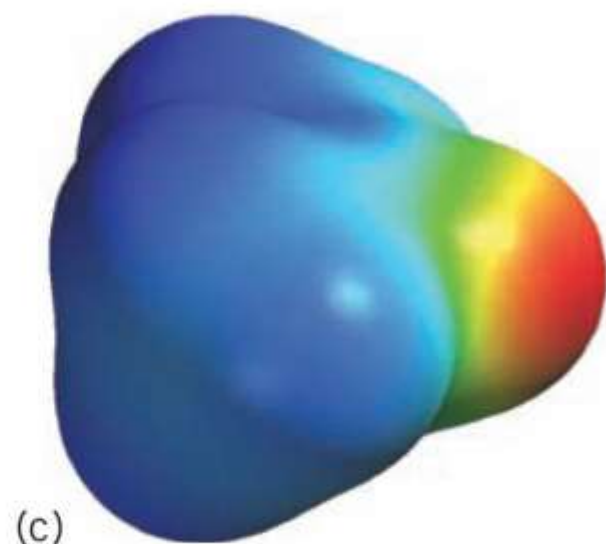
may react with a proton



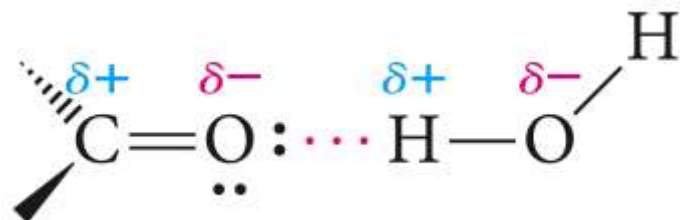
(a)



(b)



(c)



Aldehydes and ketones that have a C=O bond , but no O-H bond, cannot form hydrogen bonds with one another, as alcohols.

Aldehyde and ketones therefore have relatively higher boiling points than hydrocarbons, but less than alcohols.

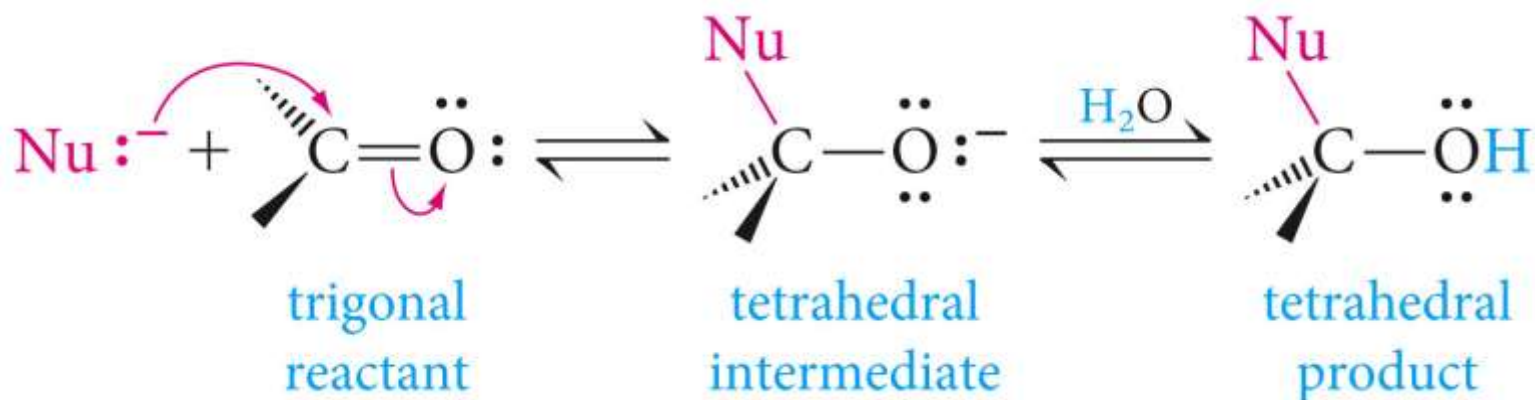
Low molecular weight aldehydes and ketones are water soluble as they can form hydrogen bonds with the water molecules but not with themselves.

# Clicker Question

Arrange Benzaldehyde (MW=106), Benzyl alcohol (MW=108) and p-Xylene (MW=106) in order of increasing boiling point?

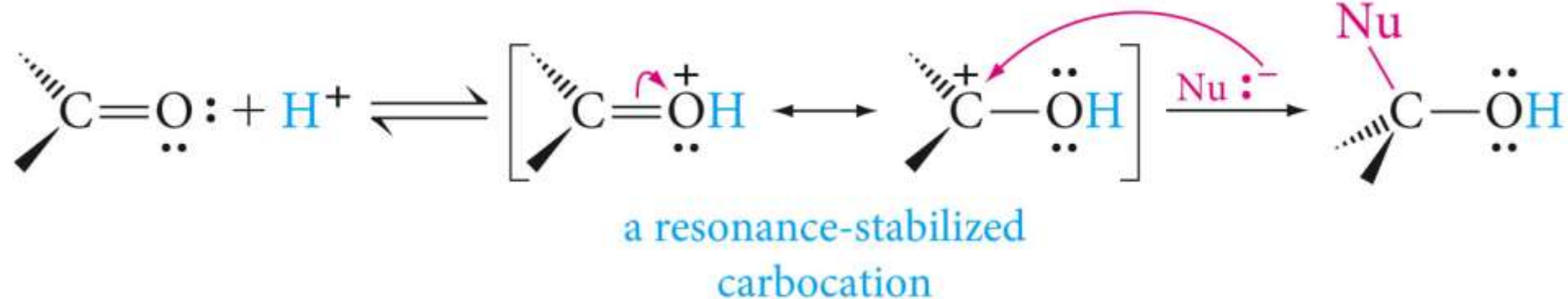
- A. Benzaldehyde < Benzyl alcohol < p-Xylene
- B. Benzyl alcohol < Benzaldehyde < p-Xylene
- C. p-Xylene < Benzaldehyde < Benzyl alcohol
- D. p-Xylene < Benzyl alcohol < Benzaldehyde

# Nucleophilic Addition to Carbonyl Groups



Nucleophiles attack the carbon atom of a carbon-oxygen double bond because that carbon has a partial positive charge. The pi-electrons of the  $\text{C}=\text{O}$  bond move to the oxygen atom

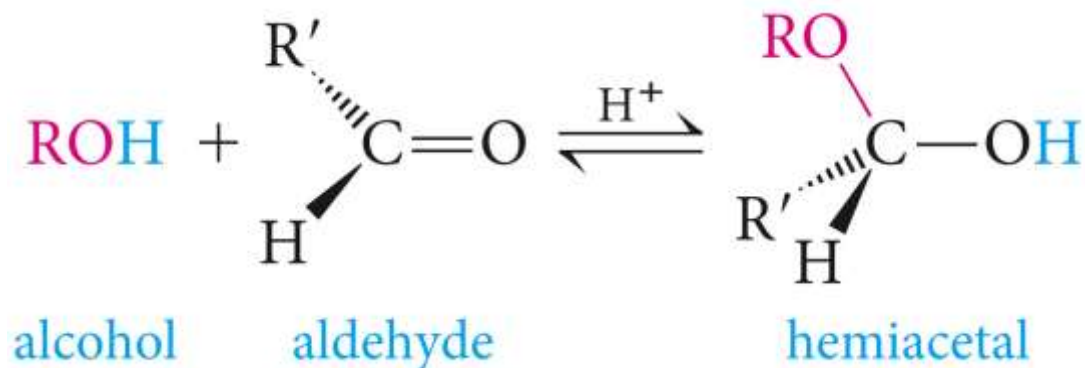
Acids can catalyze the addition of weak nucleophiles to carbonyl compounds by protonating the carbonyl oxygen atom. This makes the carbonyl carbon more electrophilic and reactive by converting it to a carbocation thereby enhancing its susceptibility to attack by nucleophiles.



### Classification of Nucleophiles;

- Those that add reversibly are also good leaving groups and are conjugate bases of relatively strong acids
- Those that add irreversibly are poor leaving groups, and are conjugate bases of weak acids.

# Addition of Alcohols: Formation of Hemiacetals and Acetals



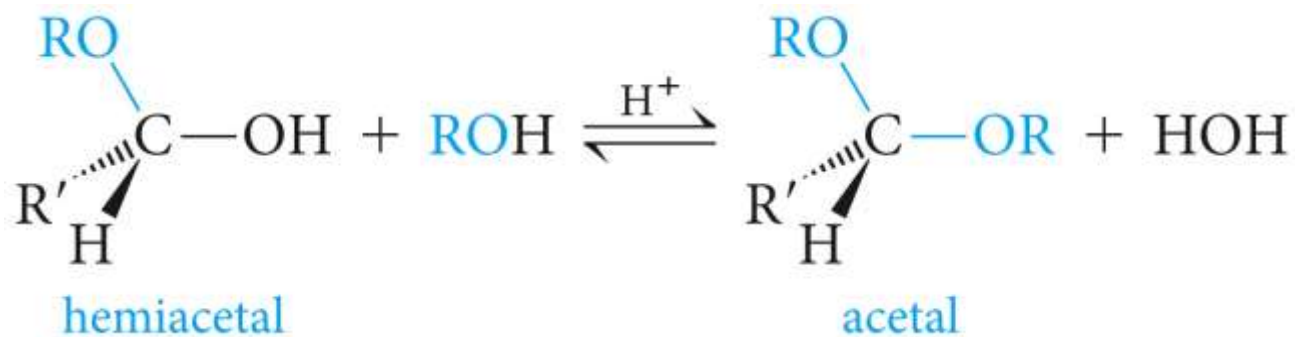
Alcohols are oxygen nucleophiles, they add to the C=O bond, the OR group becoming attached to the carbon and the proton becoming attached to the oxygen.

The product is a **hemiacetal** which contains both alcohol and ether groups on the same carbon.

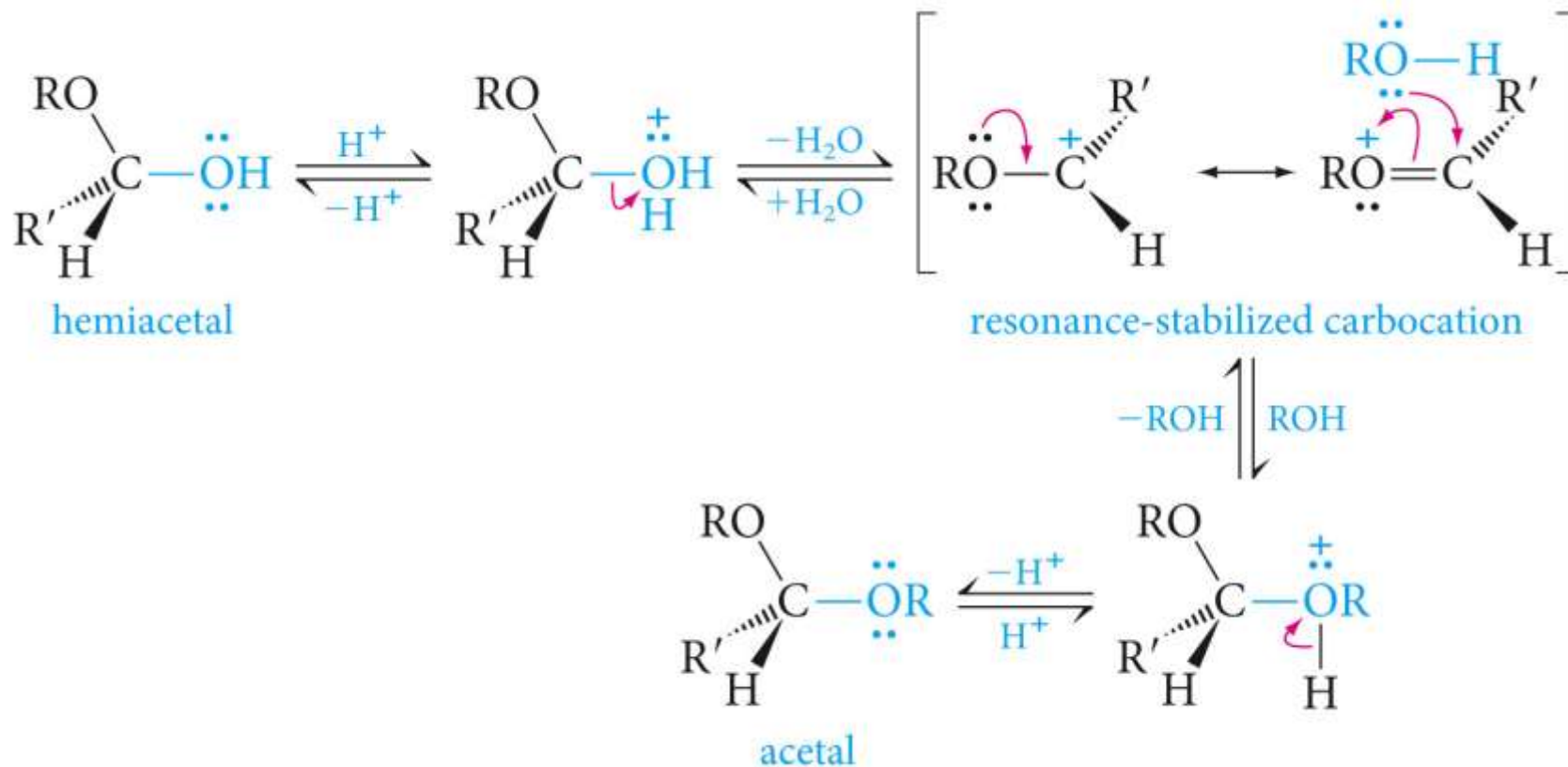
The addition process is reversible



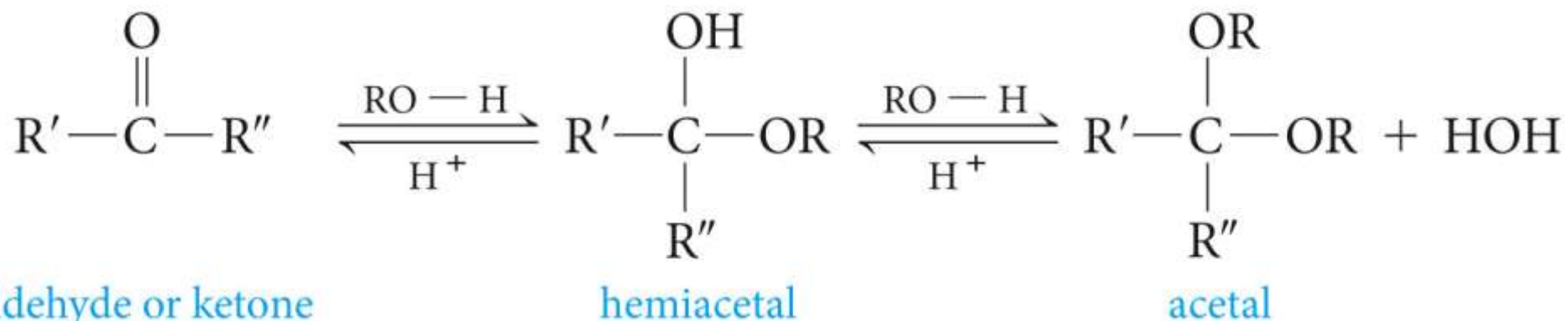
In the presence of excess alcohol, hemiacetals react to form **acetals**. acetals have two ether functional groups at the same carbon atom.



# Mechanism of acetal formation



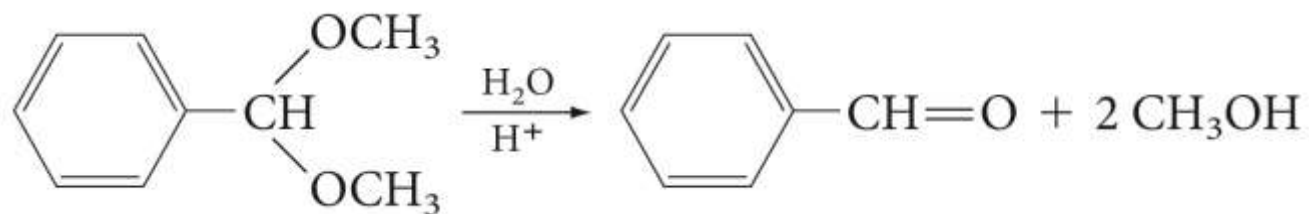
## Reaction summary



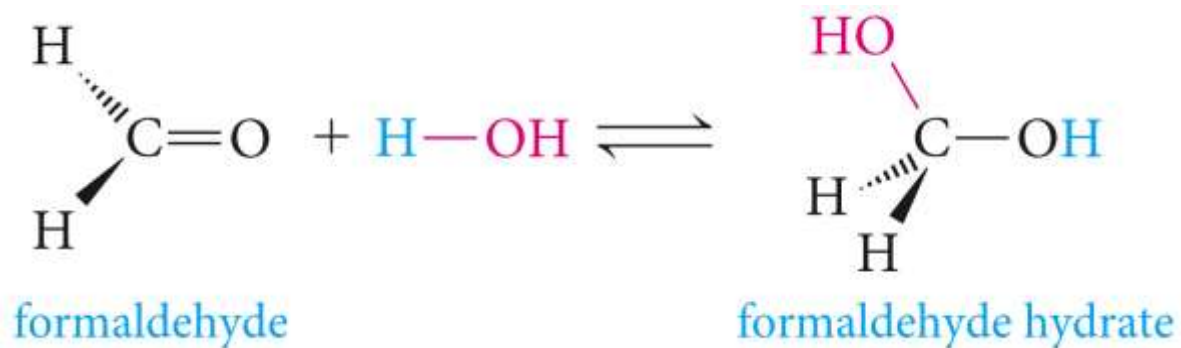
### Question

Write the equation for the reaction of benzaldehyde with excess methanol and an acid catalyst.

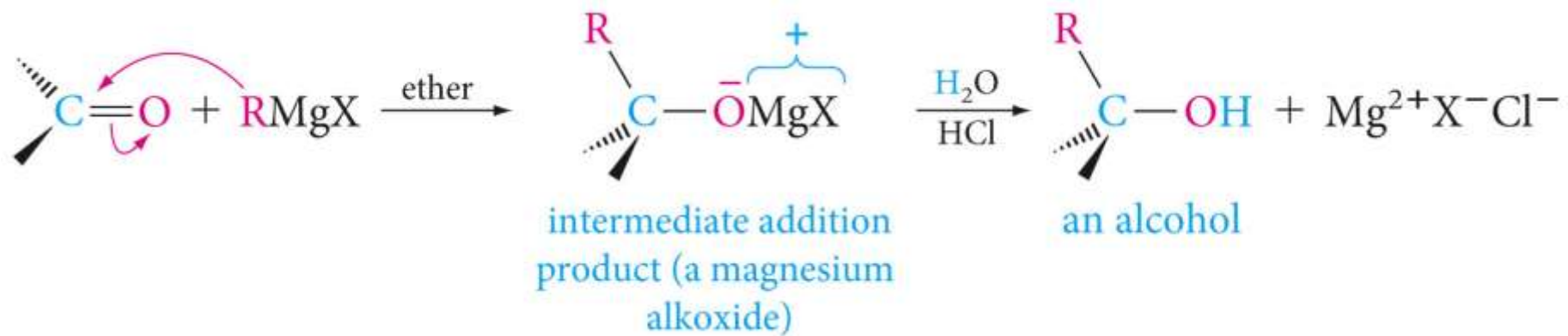
The reverse of acetal formation is acetal hydrolysis. This is achieved by excess water in the presence of an acid catalyst.

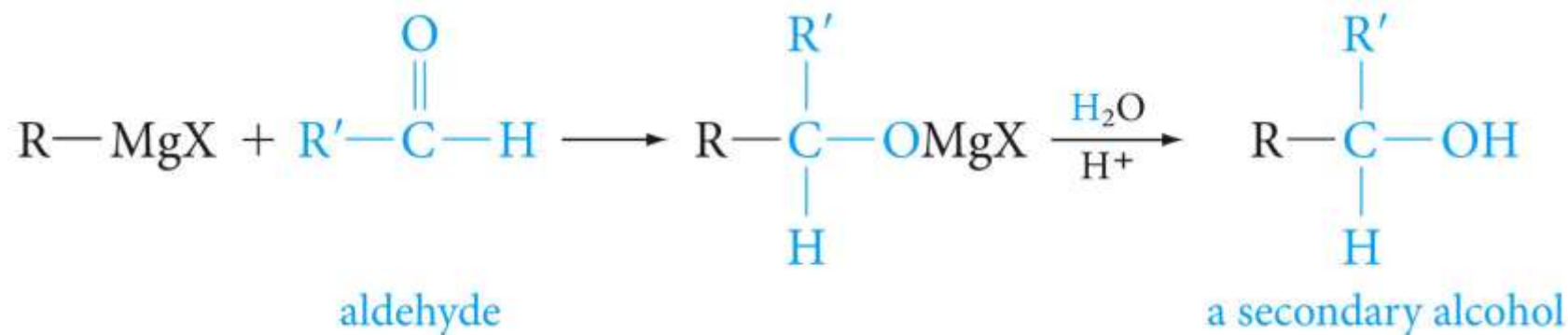
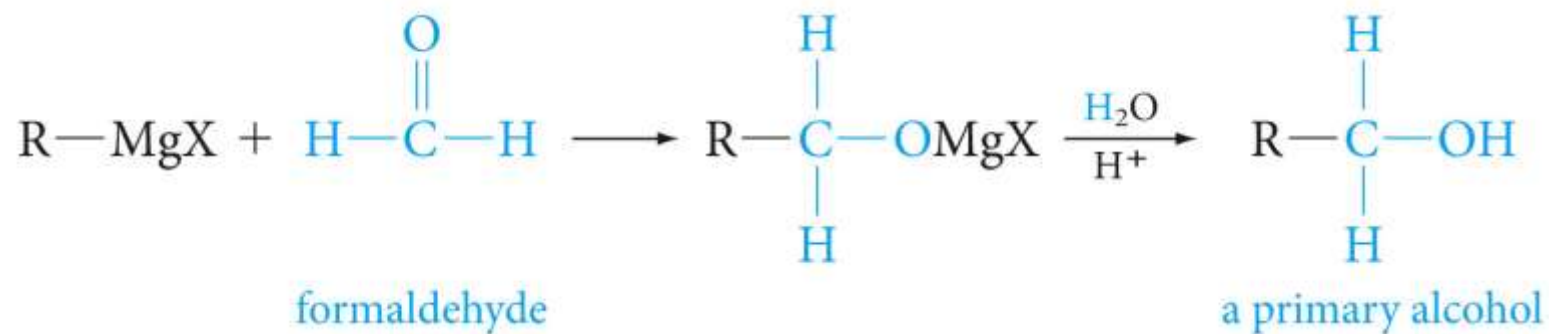


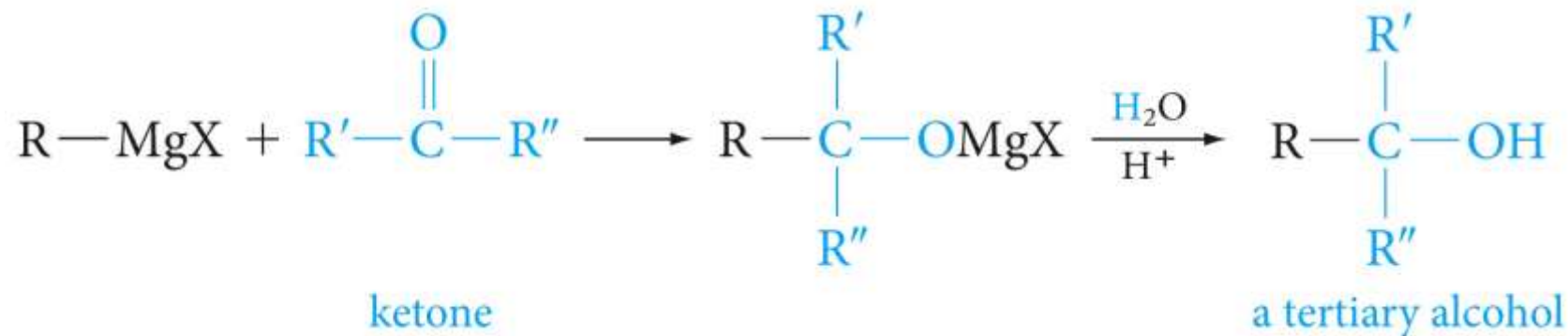
## Addition of Water: Hydration of Aldehydes and Ketones



## Addition of Grignard Reagents and Acetylates







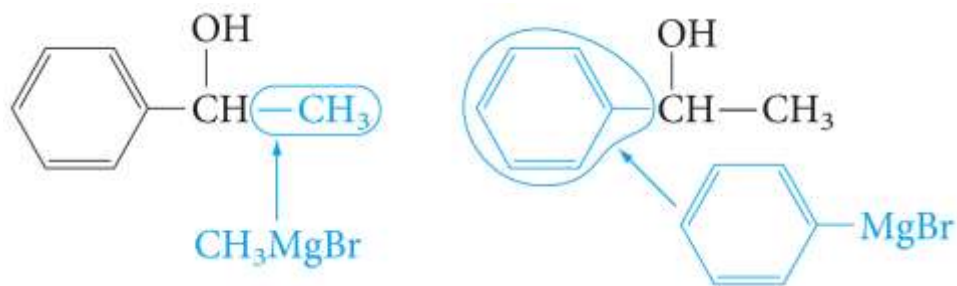
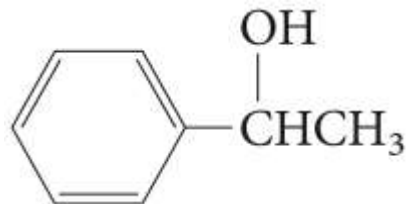


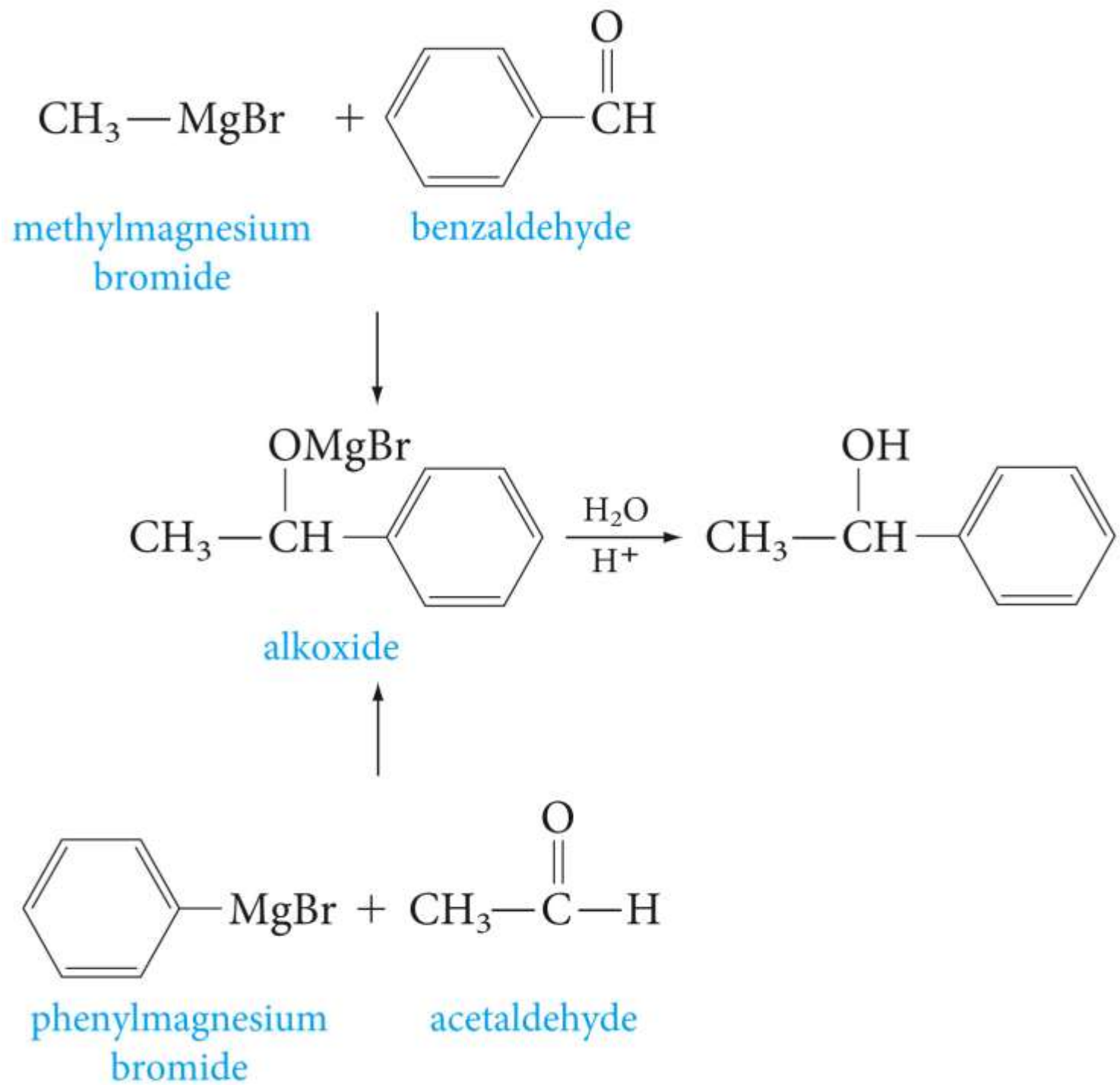
Example;

What is the product expected from the reaction of ethylmagnesium bromide and 3-pentanone followed by hydrolysis?



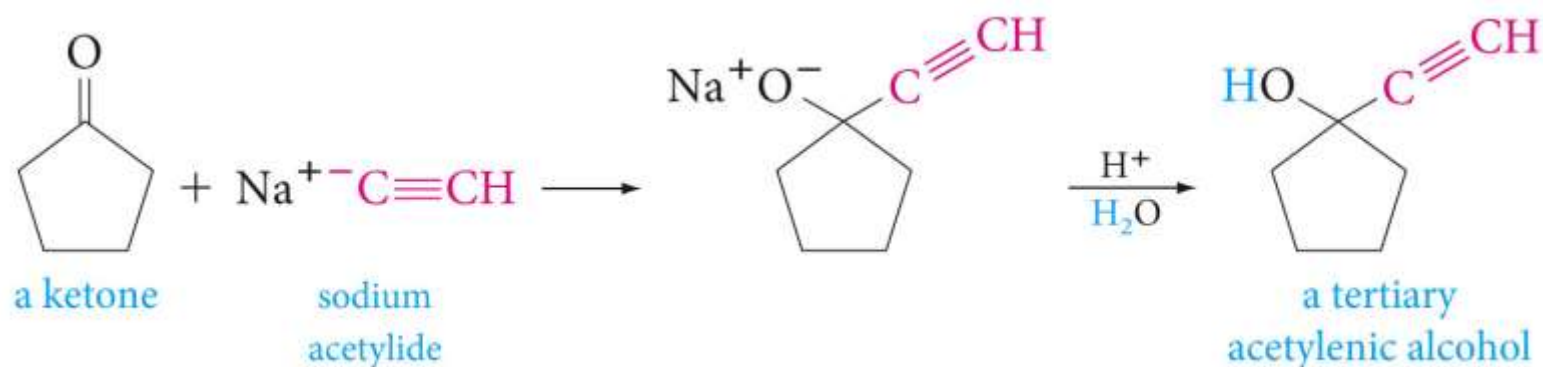
Show how the following alcohol can be made from a Grignard reagent and a carbonyl compound:



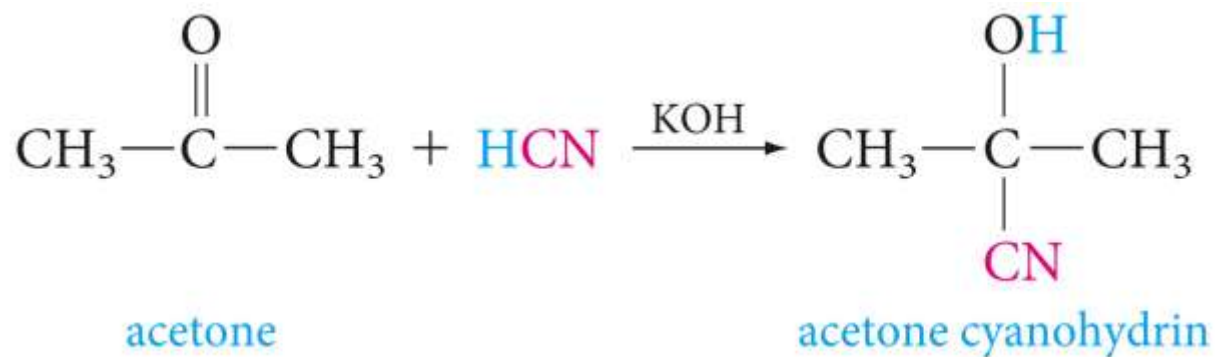
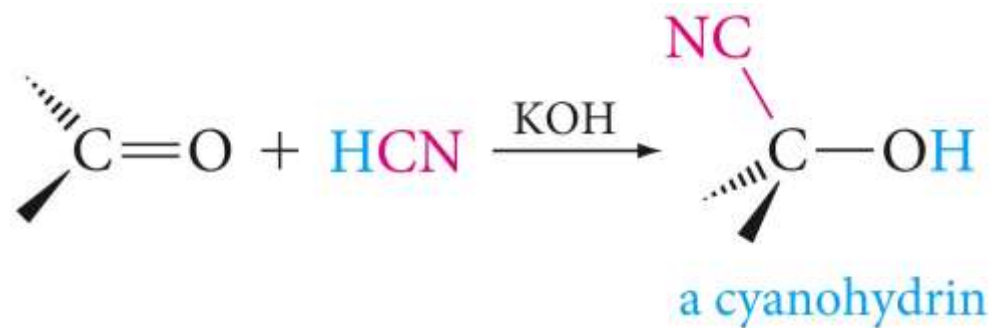


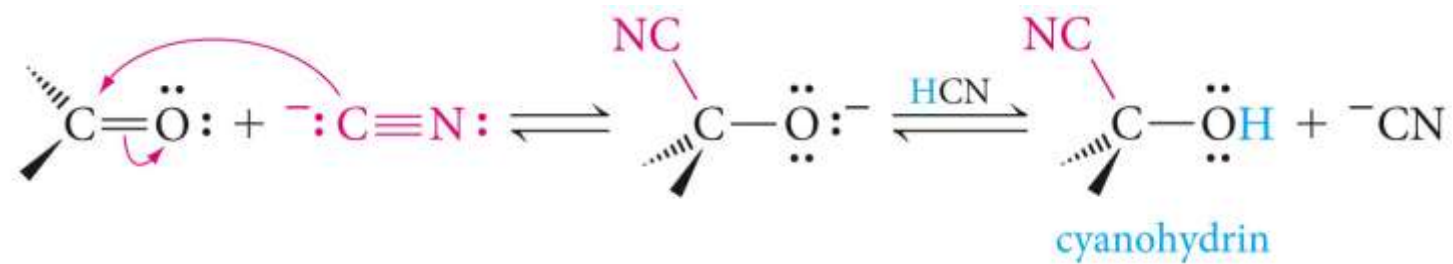
Other organometallic reagents, such as organolithium compounds and acetylides, react with carbonyl compounds in a similar fashion to Grignard reagents.

Example

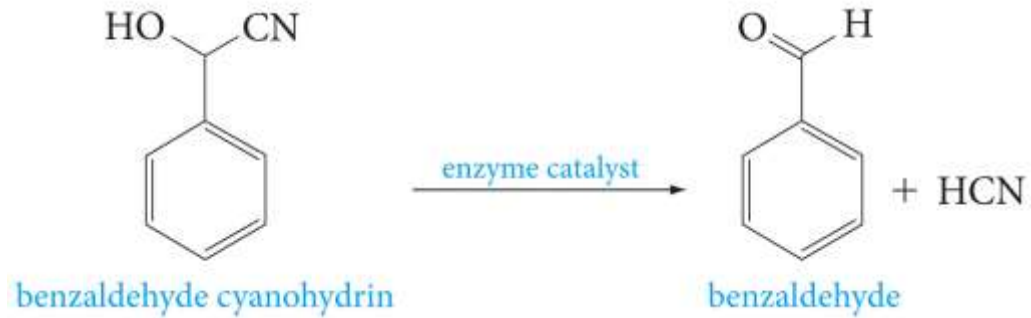


## Addition of Hydrogen Cyanide; Cyanohydrins

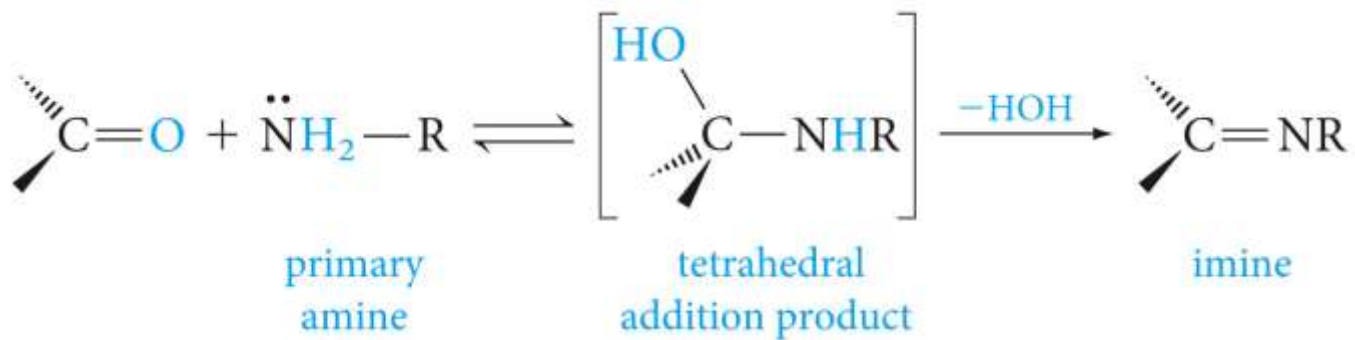




*Apheloria corrugata* (millipede) uses the cyanohydrin reaction for defense and as a deterrent of predators.



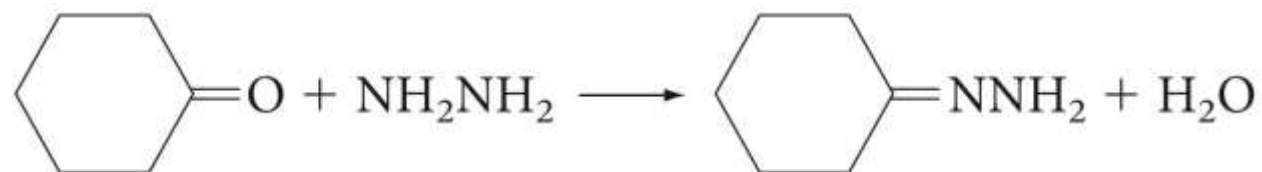
## Addition of Nitrogen Nucleophiles



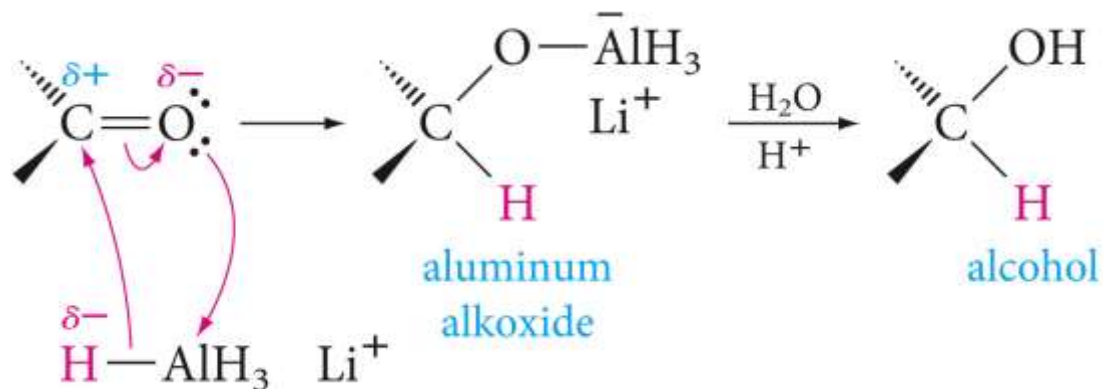


**Table 9.1** ▀ Nitrogen Derivatives of Carbonyl Compounds

Formula of ammonia derivative	Name	Formula of carbonyl derivative	Name
$\text{RNH}_2$ or $\text{ArNH}_2$	primary amine	$\text{>C=NR}$ or $\text{>C=NAr}$	imine
$\text{NH}_2\text{OH}$	hydroxylamine	$\text{>C=NOH}$	oxime
$\text{NH}_2\text{NH}_2$	hydrazine	$\text{>C=NNH}_2$	hydrazone
$\text{NH}_2\text{NHC}_6\text{H}_5$	phenylhydrazine	$\text{>C=NNHC}_6\text{H}_5$	phenylhydrazone

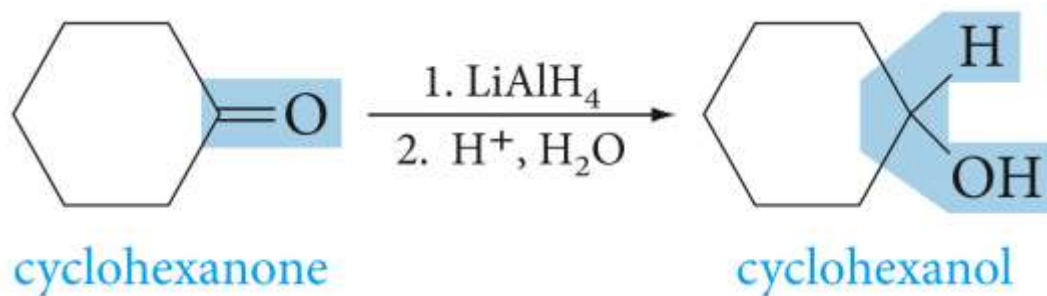


## Reduction of Carbonyl Compounds

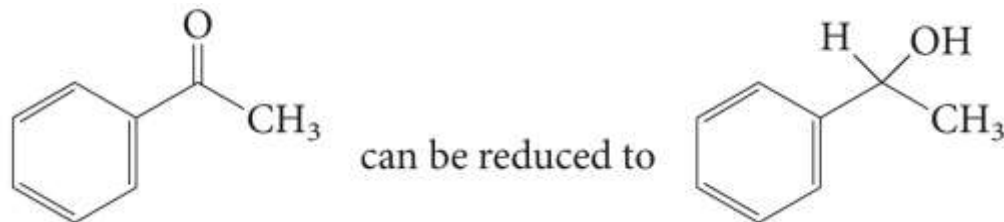
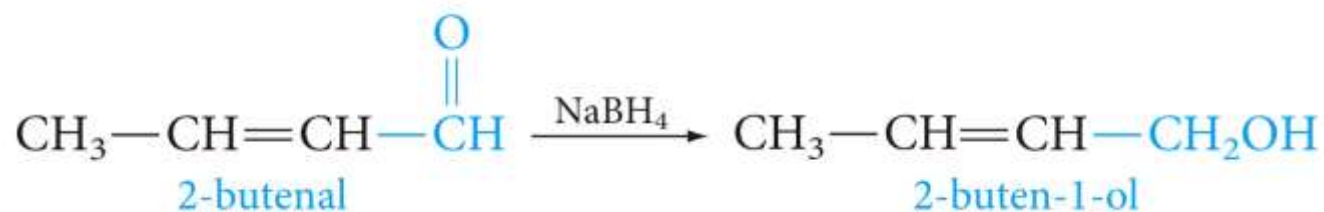


Aldehydes and ketones are easily reduced to primary and secondary alcohols respectively. Reduction can be accomplished in many ways, most commonly by metal hydrides.

Lithium aluminum hydride (LiAlH<sub>4</sub>) and sodium borohydride (NaBH<sub>4</sub>) are among the commonly used.

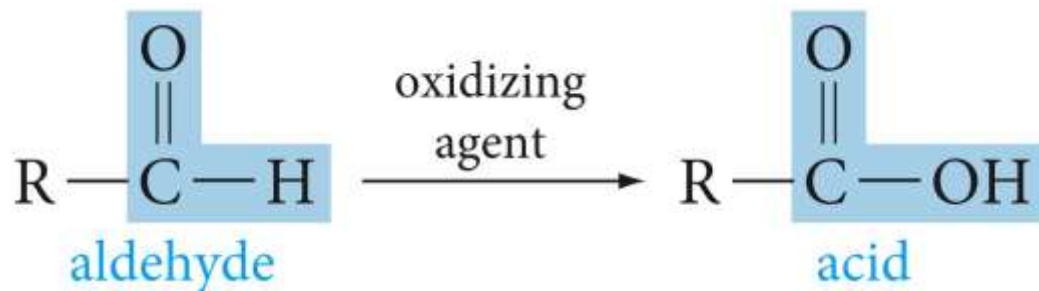


Because a carbon-carbon double bond is not readily attacked by nucleophiles, metal hydrides can be used to reduce a carbon-oxygen double bond to the corresponding alcohol without reducing the alkene.

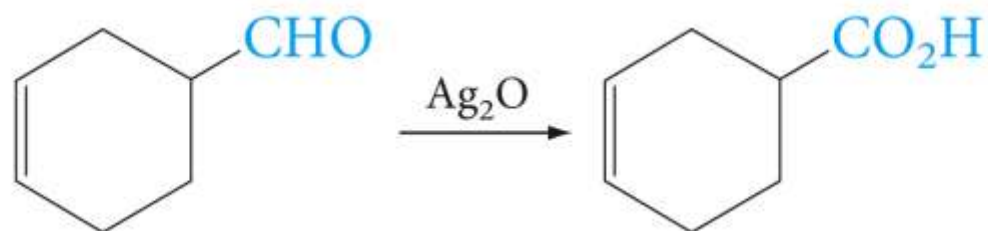
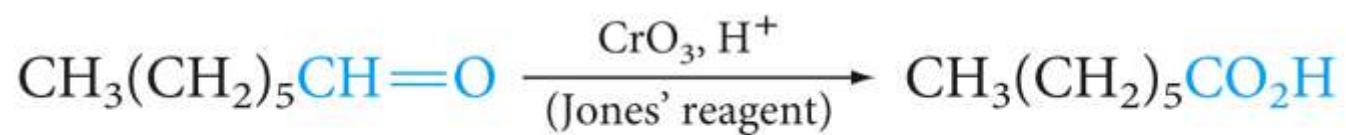


## Oxidation of Carbonyl Compounds

Aldehydes are more easily oxidized than ketones. Oxidation of an aldehyde gives a carboxylic acid with the same number of carbon atoms.

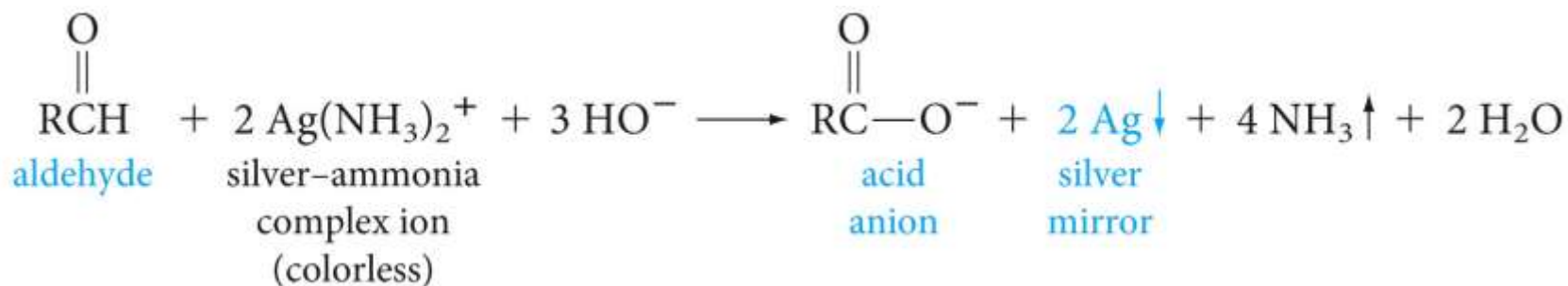


Oxidation may be achieved by many oxidizing agents, such as  $\text{KMnO}_4$ ,  $\text{CrO}_3$ ,  $\text{Ag}_2\text{O}$ , and peracids.



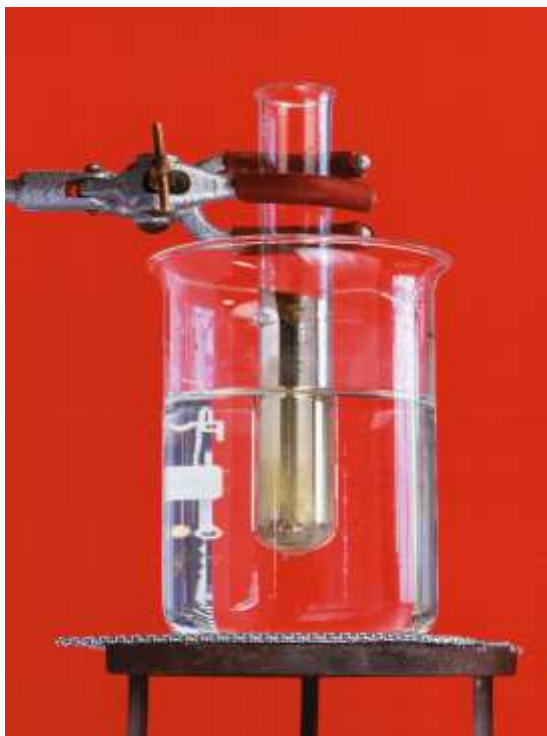
Silver ion as an oxidizing agent is expensive but has the virtue that it selectively oxidizes aldehydes to carboxylic acids in the presence of alkenes.

A laboratory test that distinguishes aldehydes from ketones takes advantage of their different ease of oxidation. In the Tollen's silver mirror test, the silver-ammonia complex ion is reduced by aldehydes (but not ketones) to metallic silver according to the equation below.





If the glass vessel in which the test is performed is thoroughly clean, the silver deposits as a mirror on the glass surface.



Ketones also can be oxidized, but require special oxidizing conditions.

