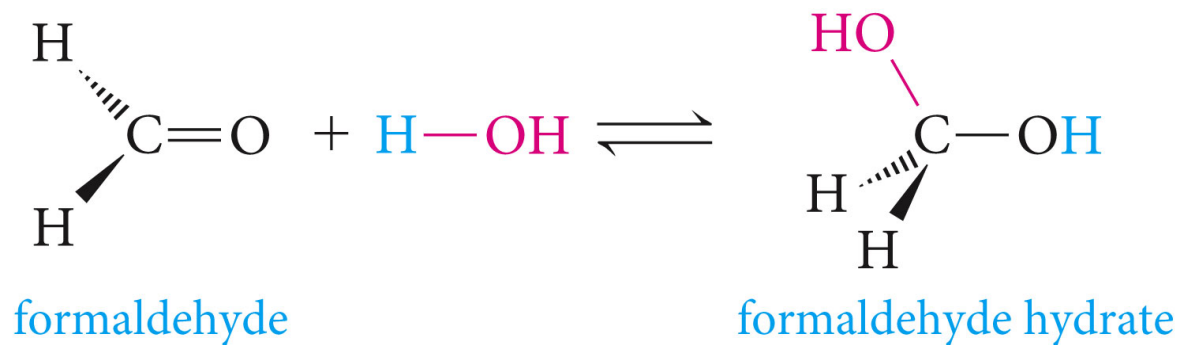
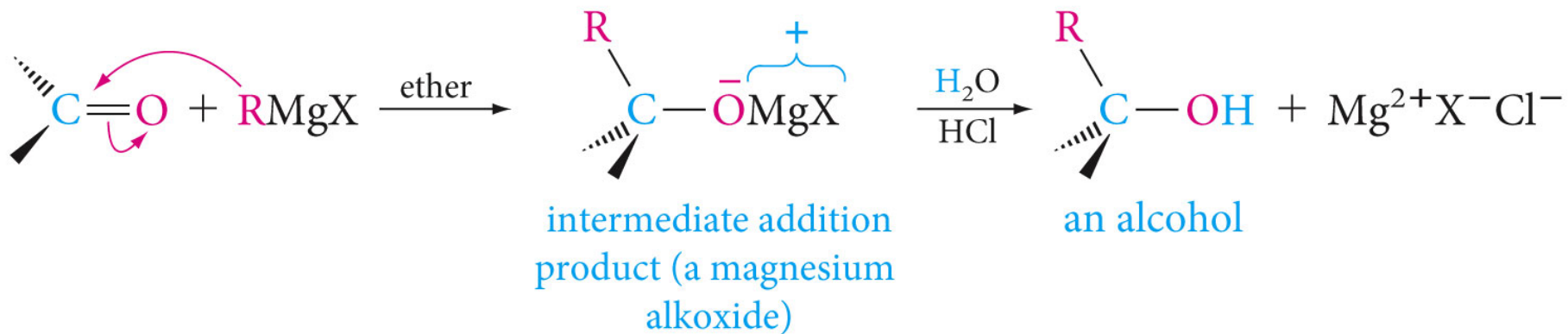
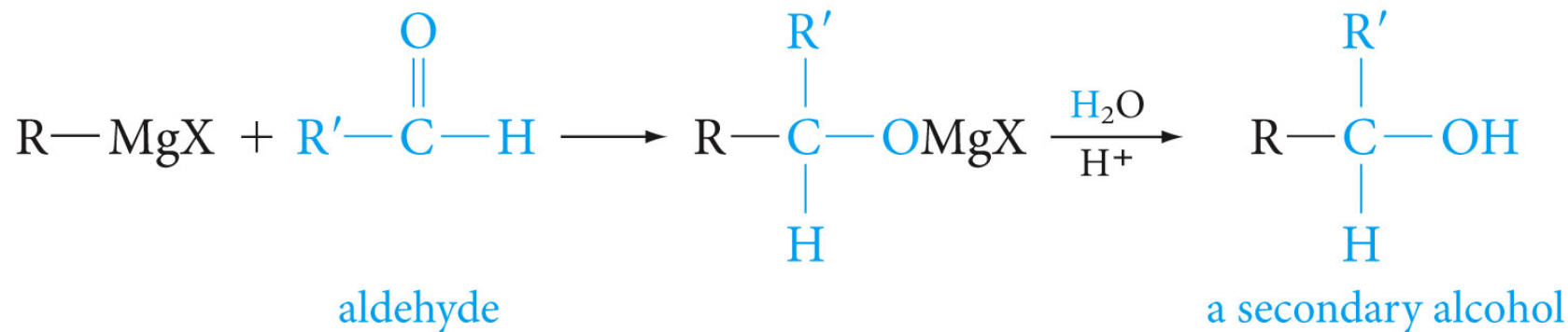
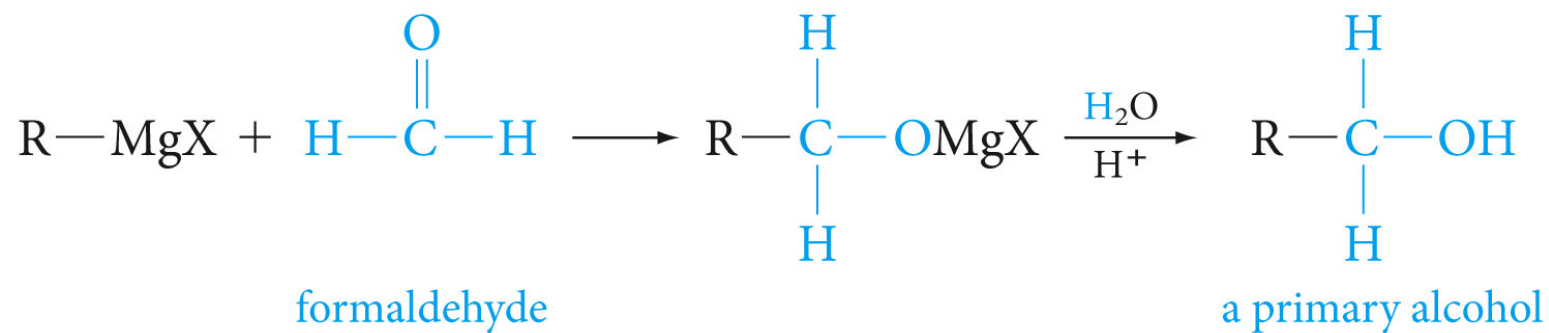


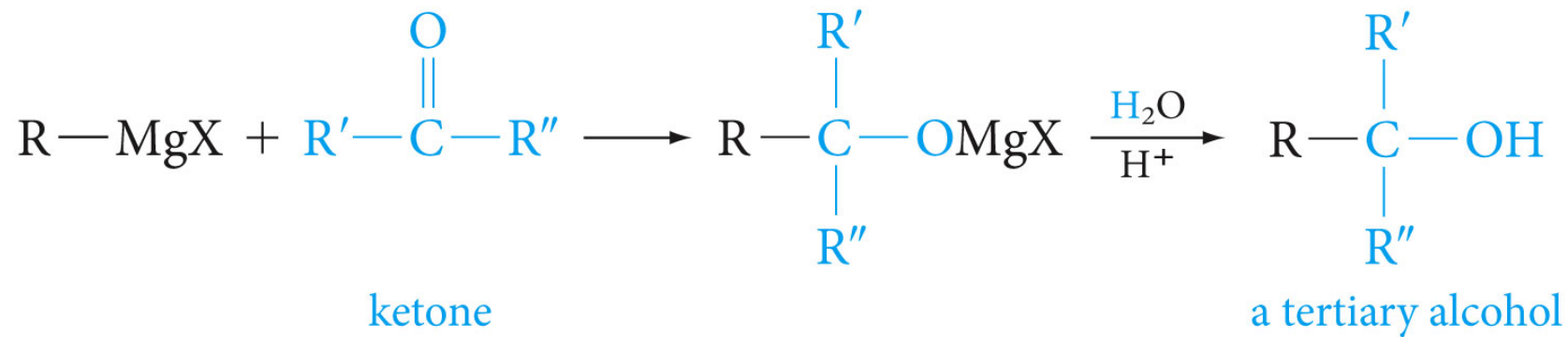
## Addition of Water: Hydration of Aldehydes and Ketones



## Addition of Grignard Reagents and Acetylides

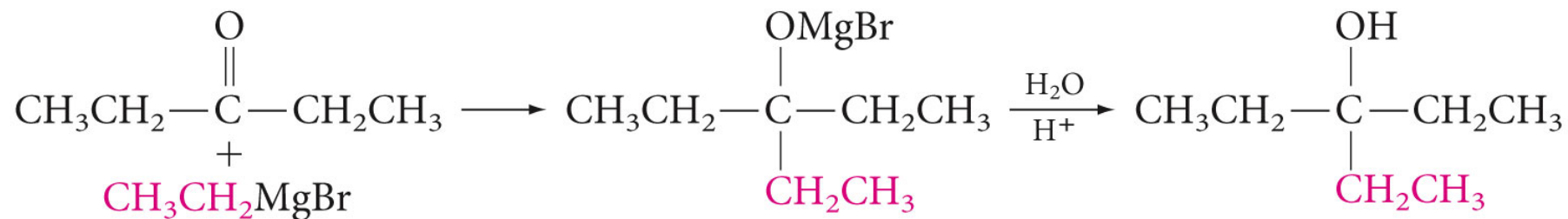




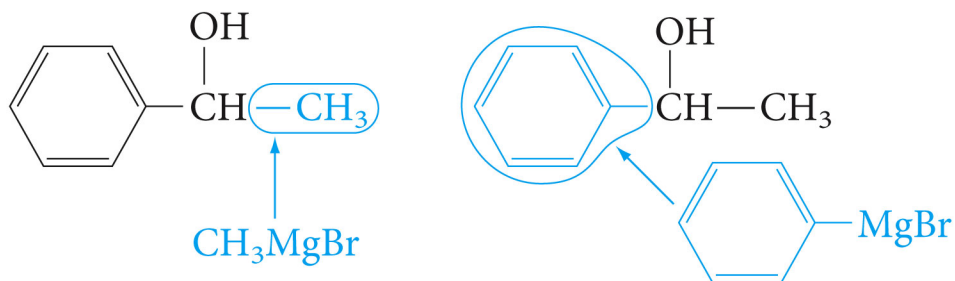
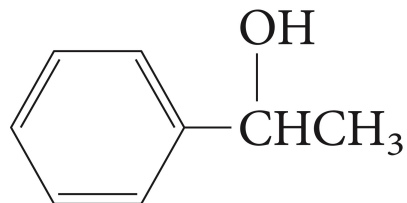


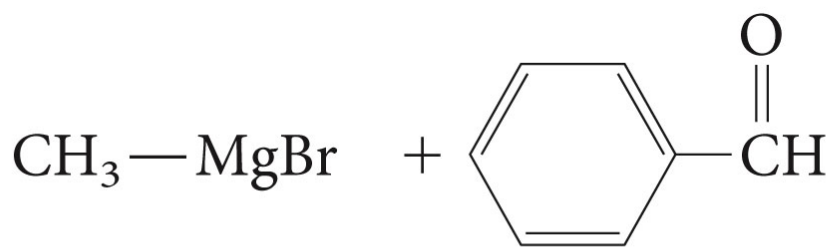
Example;

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



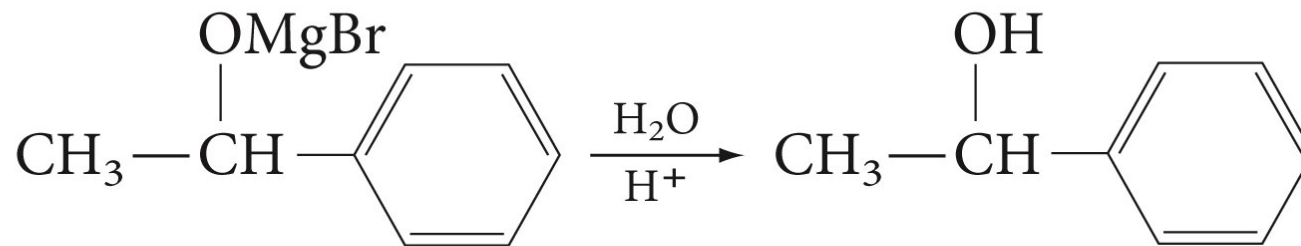
Show how the following alcohol can be made from a Grignard reagent and a carbonyl compound:



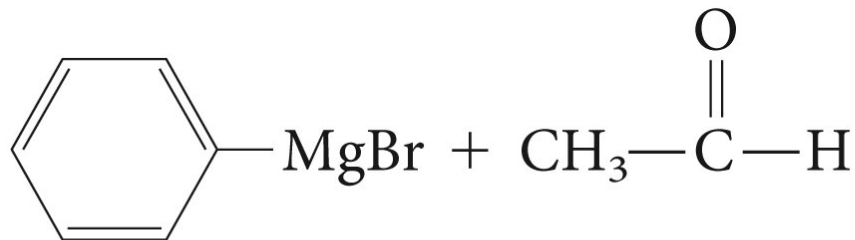


methylmagnesium  
bromide

benzaldehyde



alkoxide

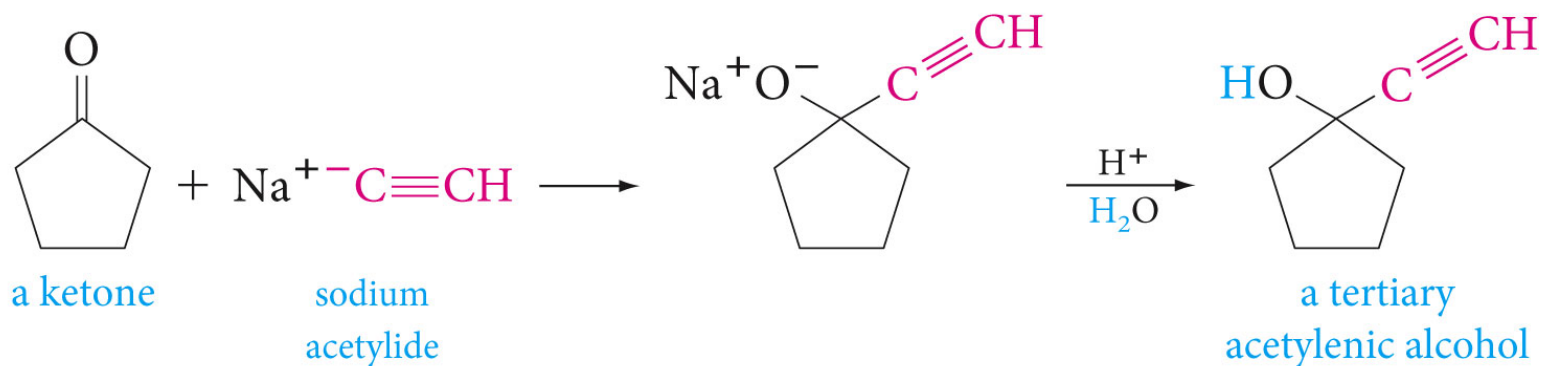


phenylmagnesium  
bromide

acetaldehyde

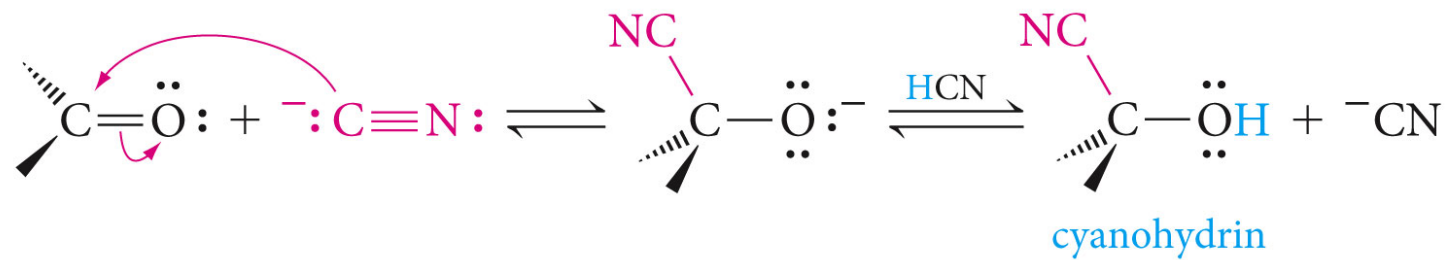
Other organometallic reagents, such as organolithium compounds and acetylides, react with carbonyl compounds in a similar fashion to Grignard reagents.

### Example

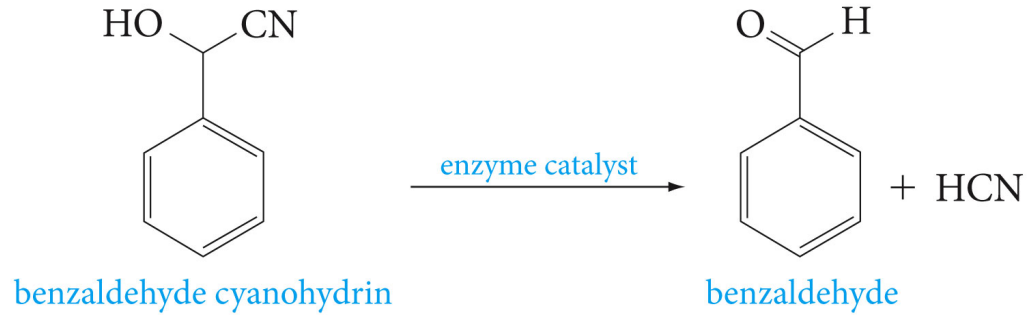




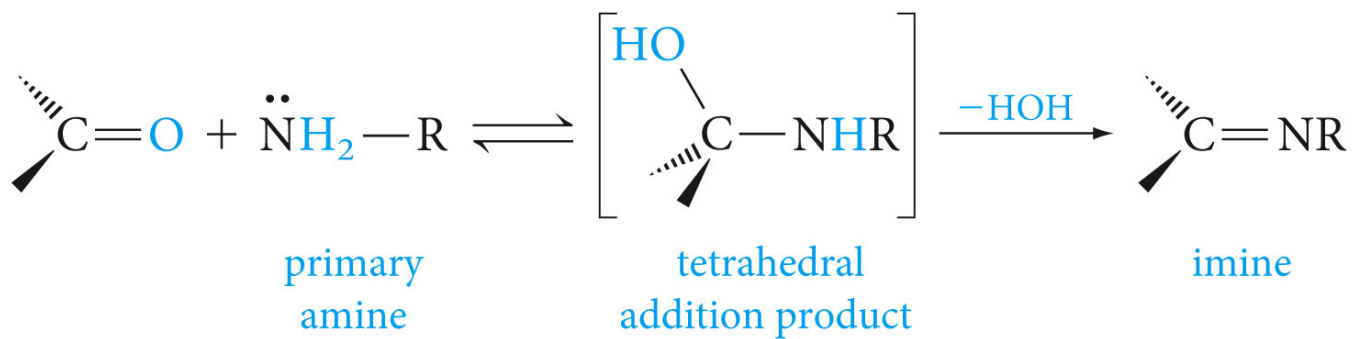




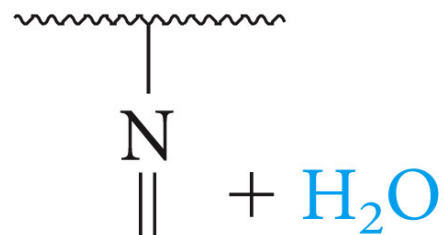
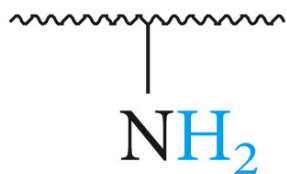
*Apheloria corrugata* (millipede) uses the cyanohydrin reaction for defense and as a deterrent of predators.



## Addition of Nitrogen Nucleopiles



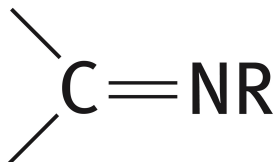
enzyme



substrate

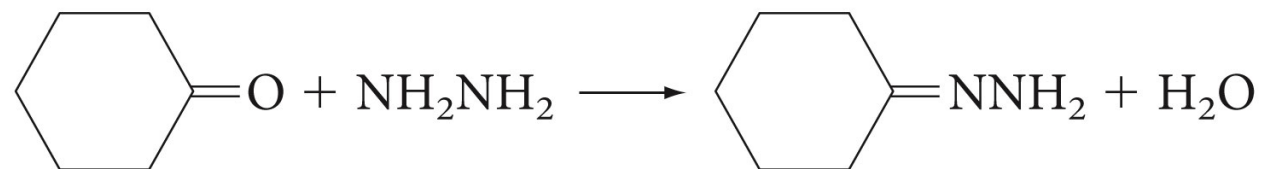


enzyme-substrate  
compound

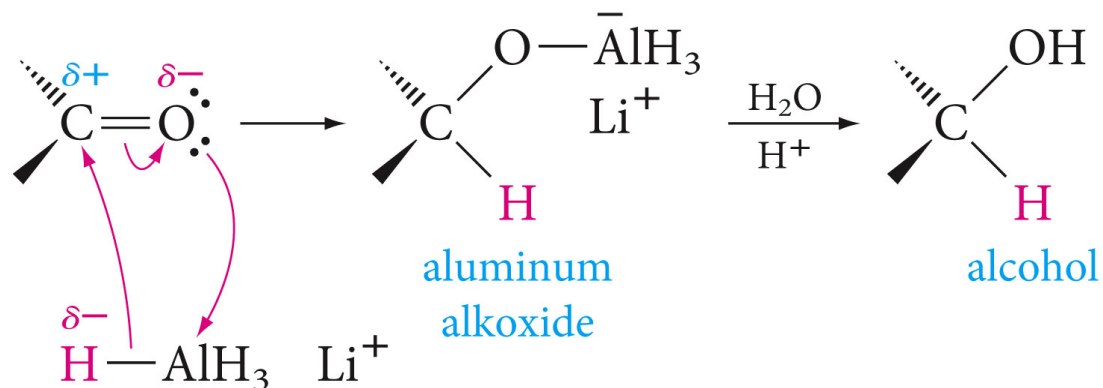


**Table 9.1** ▀ Nitrogen Derivatives of Carbonyl Compounds

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



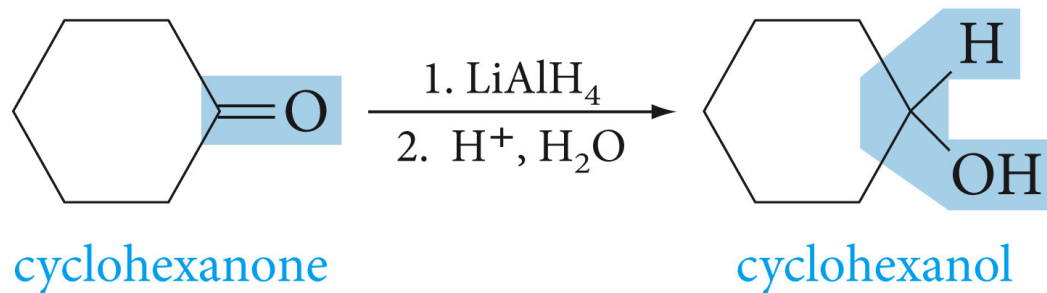
## Reduction of Carbonyl Compounds



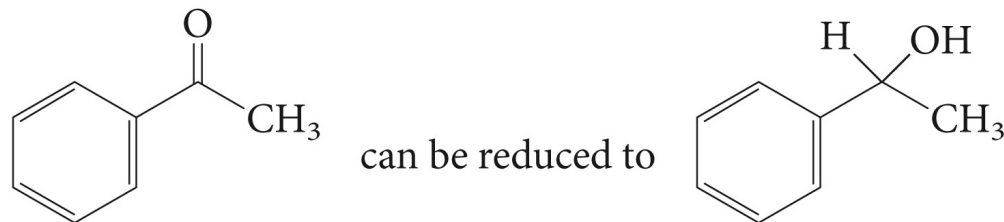
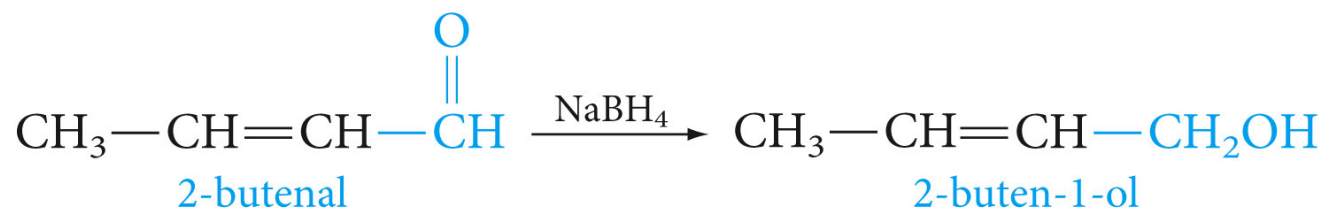
Aldehydes and ketones are easily reduced to primary and secondary alcohols respectively. Reduction can be accomplished in many ways, most commonly by metal hydrides.

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



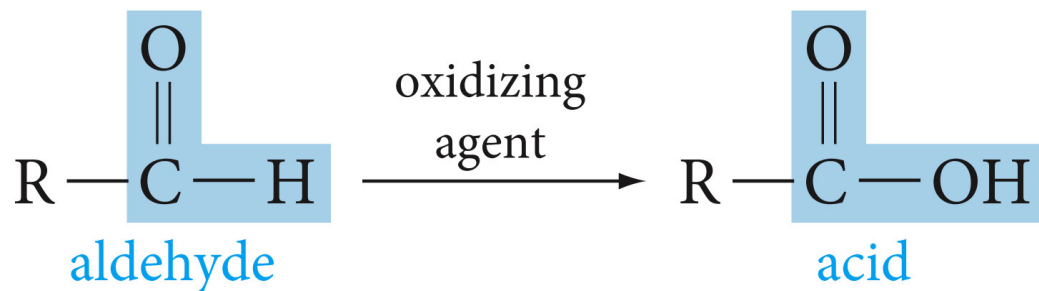


Because a carbon-carbon double bond is not readily attacked by nucleophiles, metal hydrides can be used to reduce a carbon-oxygen double bond to the corresponding alcohol without reducing the alkene.

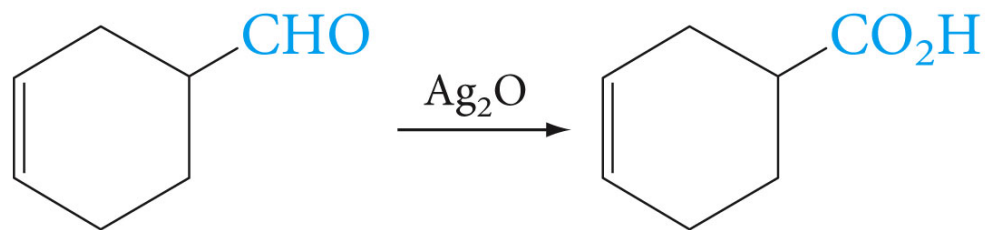
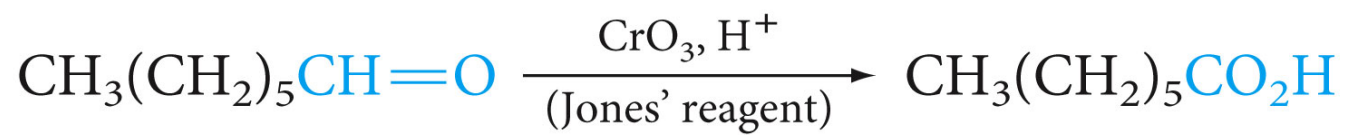


## Oxidation of Carbonyl Compounds

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

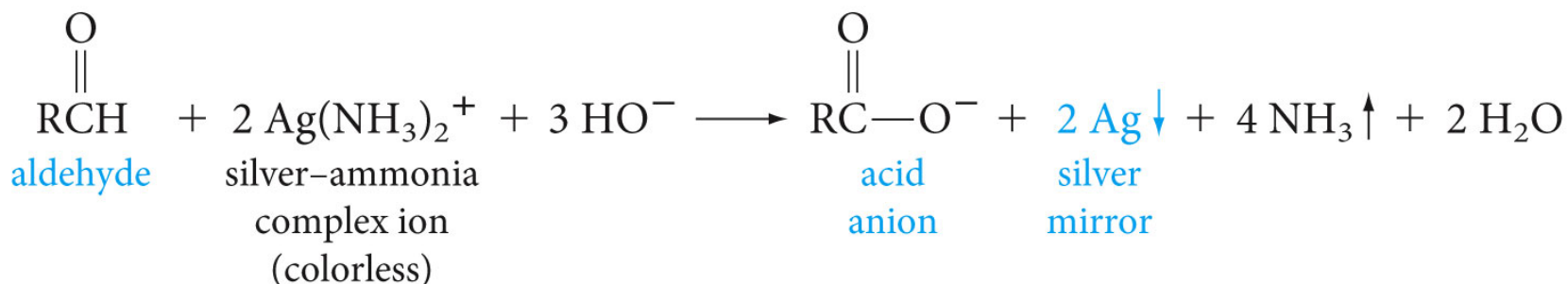


Oxidation may be achieved by many oxidizing agents, such as  $\text{KMnO}_4$ ,  $\text{CrO}_3$ ,  $\text{Ag}_2\text{O}$ , and peracids.



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.

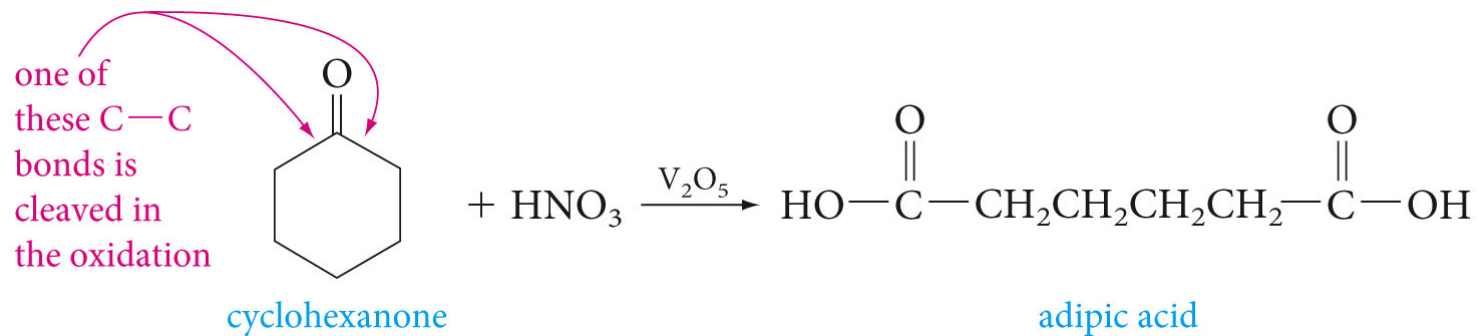
A laboratory test that distinguishes aldehydes from ketones takes advantage of their different ease of oxidation. In the Tollen's silver mirror test, the silver-ammonia complex ion is reduced by aldehydes (but not ketones) to metallic silver according to the equation below.



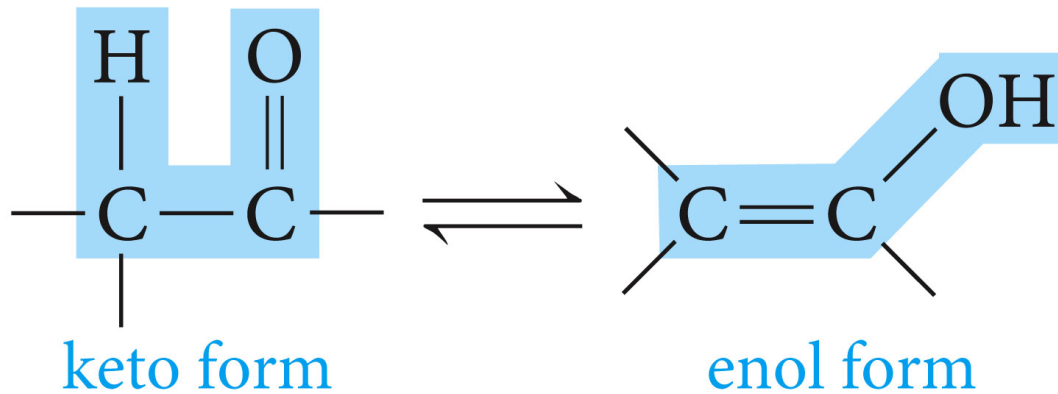
If the glass vessel in which the test is performed is thoroughly clean, the silver deposits as a mirror on the glass surface.



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

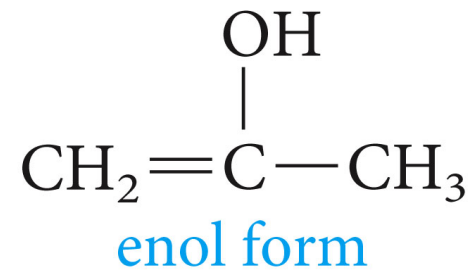
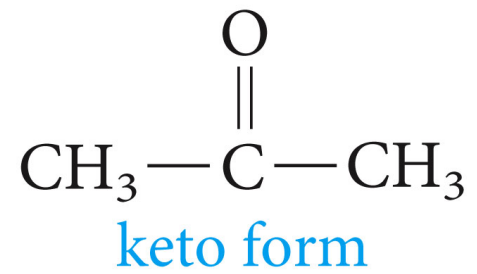


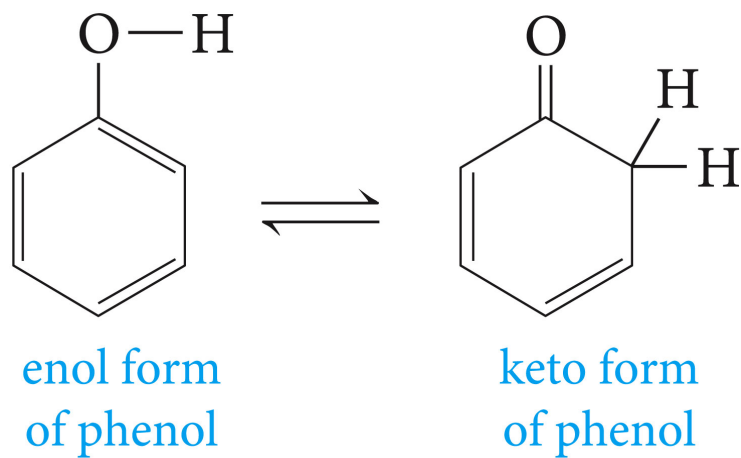
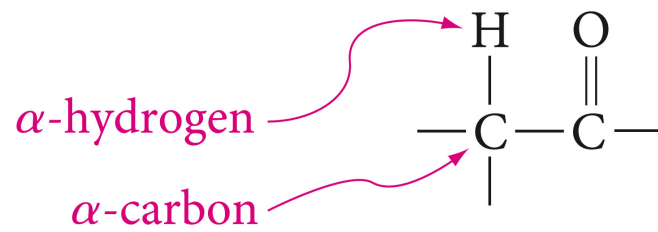
# Keto-Enol Tautomerism

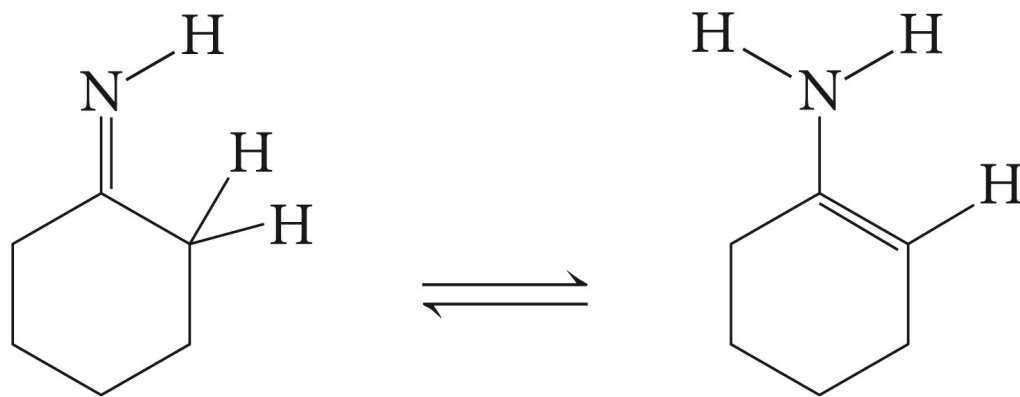
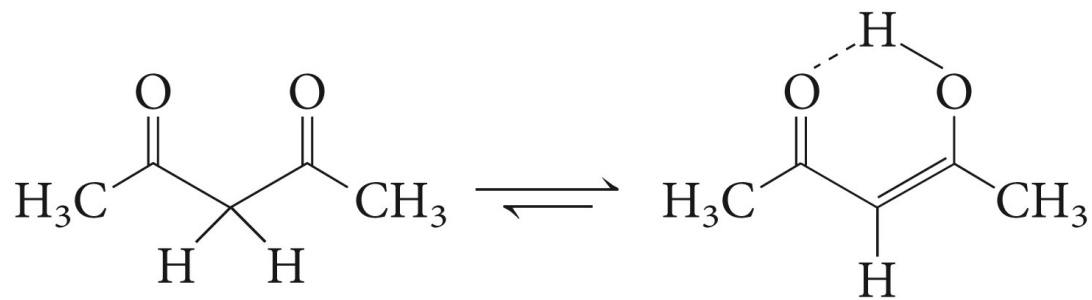


**Tautomers** are structural isomers that differ in the location of a proton and a double bond. The keto and enol forms of aldehyde or ketone are tautomers

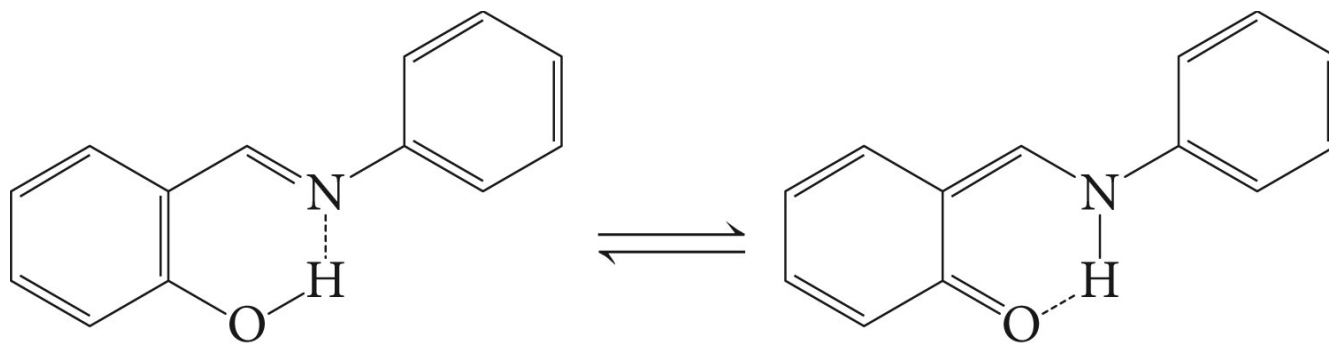




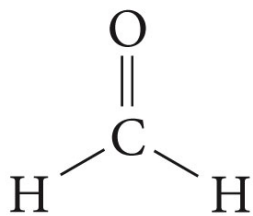




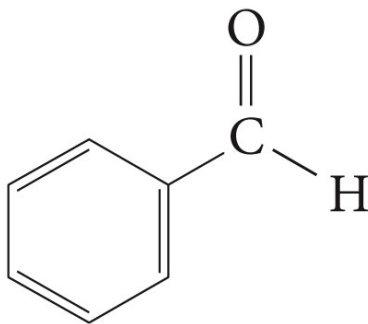
# photochromism



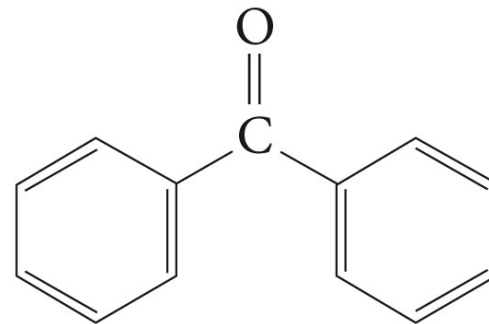
Carbonyl compounds that do not have an alpha-hydrogen cannot form enols and exist only in the keto form. Examples include



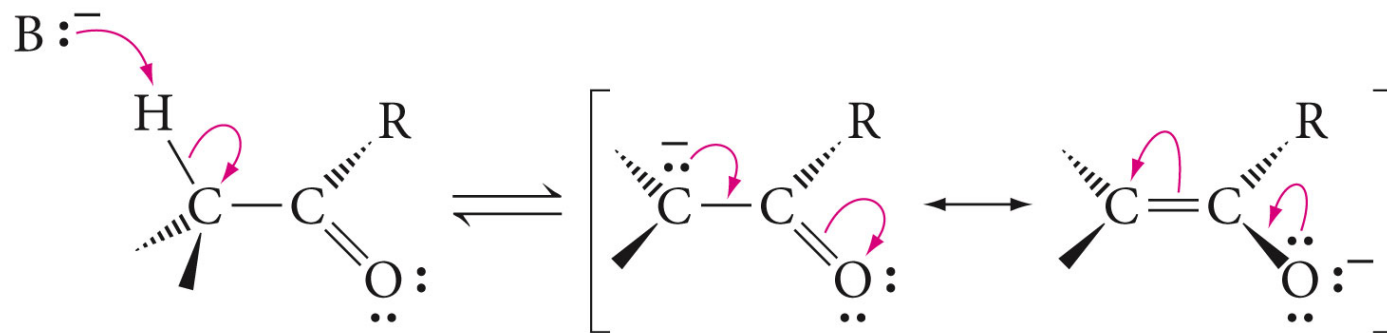
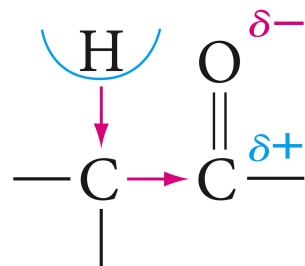
formaldehyde



benzaldehyde



benzophenone

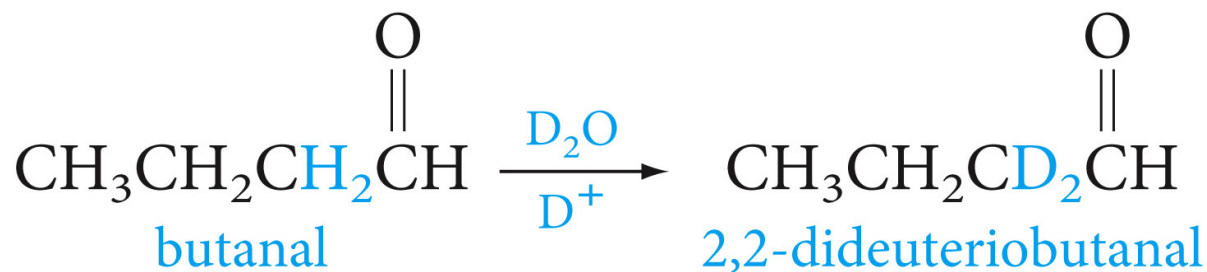
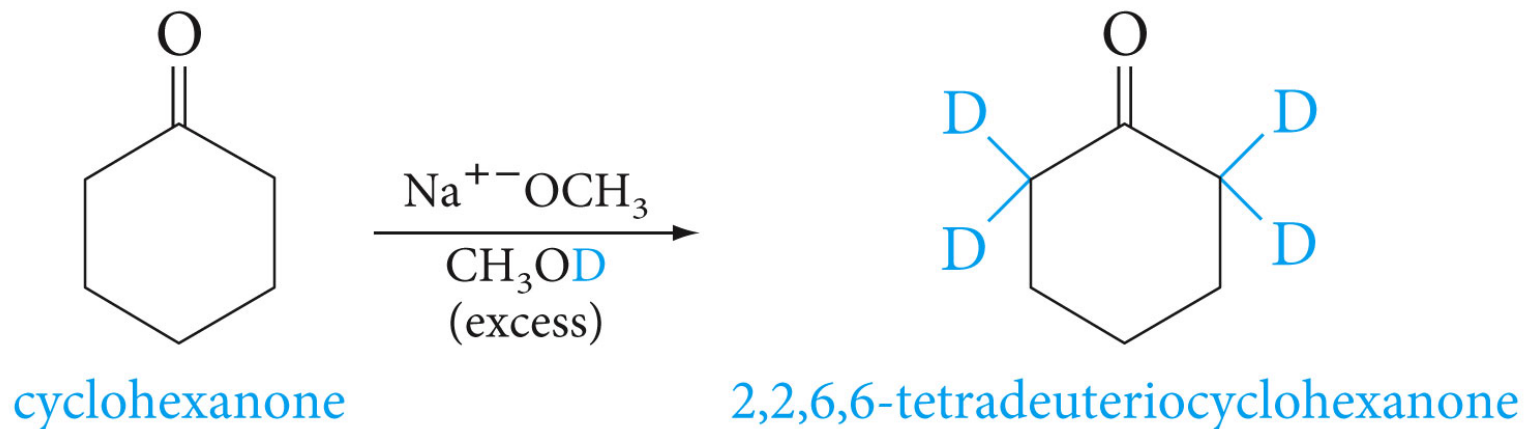


resonance structures of an enolate anion

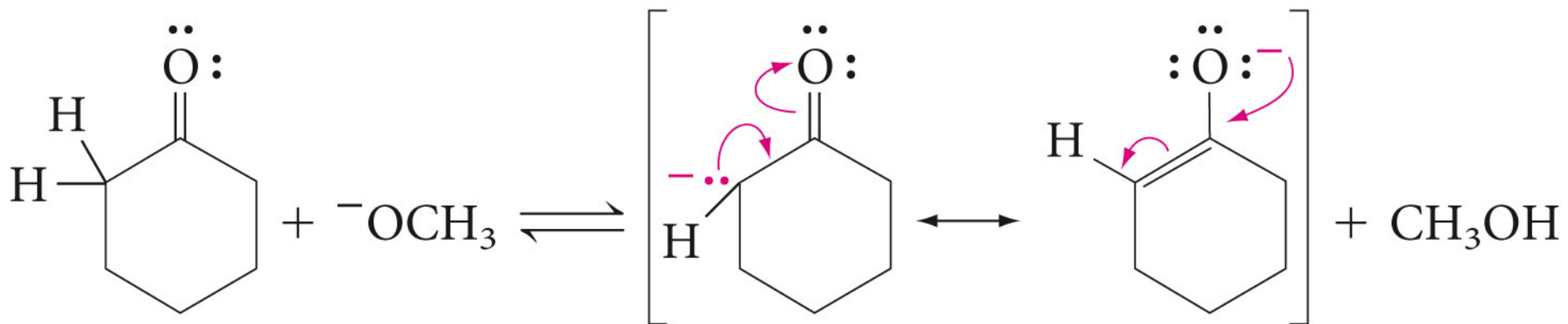
**Table 9.2**  **Acidity of  $\alpha$ -Hydrogens**

<b>Compound</b>	<b>Name</b>	<b><math>pK_a</math></b>
$\text{CH}_3\text{CH}_2\text{CH}_3$	propane	$\sim 50$
$\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CCH}_3 \end{array}$	acetone	19
$\begin{array}{c} \text{O} \\    \\ \text{CH}_3\text{CH} \end{array}$	acetaldehyde	17
$\text{CH}_3\text{CH}_2\text{OH}$	ethanol	16

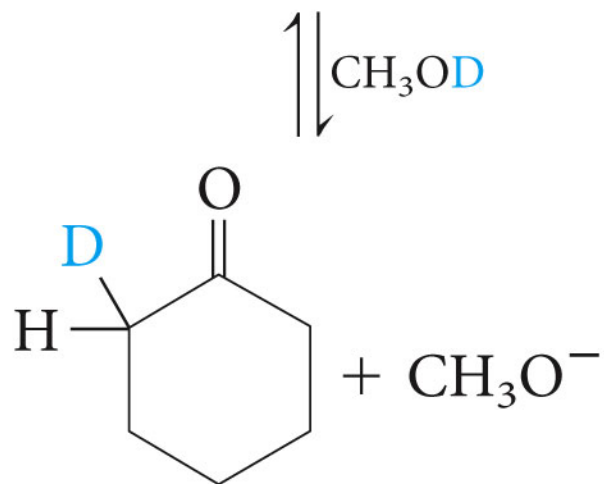
## Deuterium Exchange in Carbonyl compounds

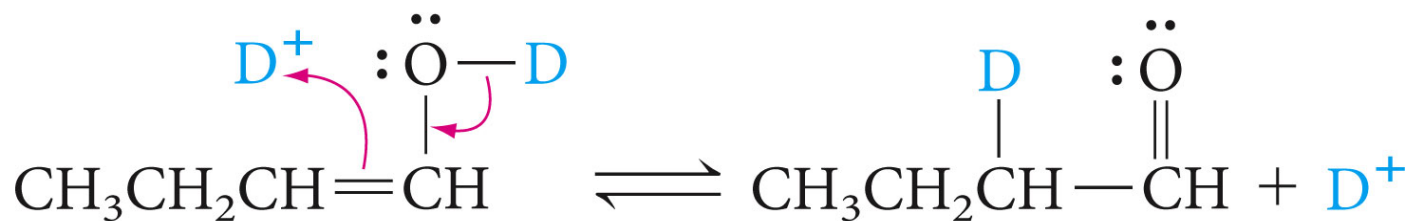
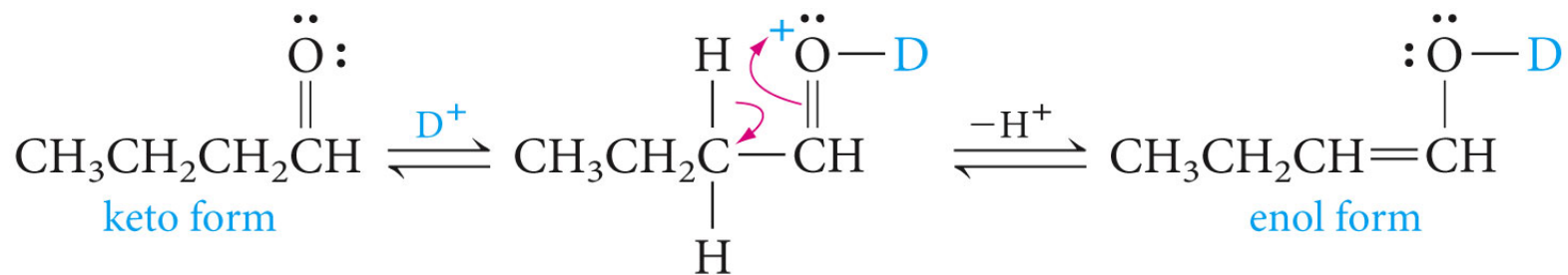




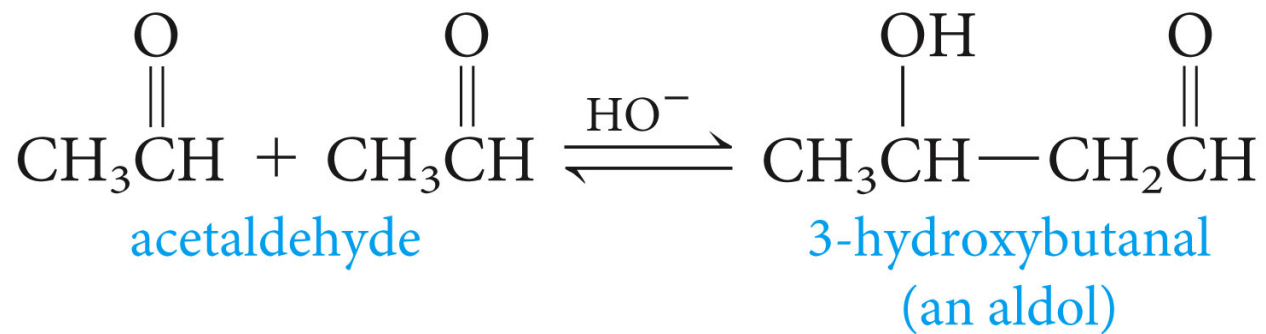


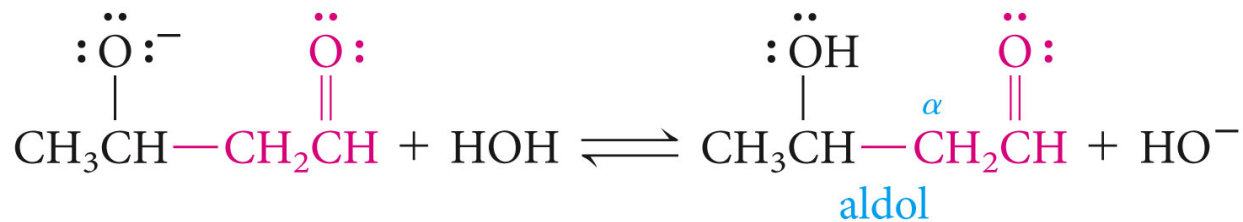
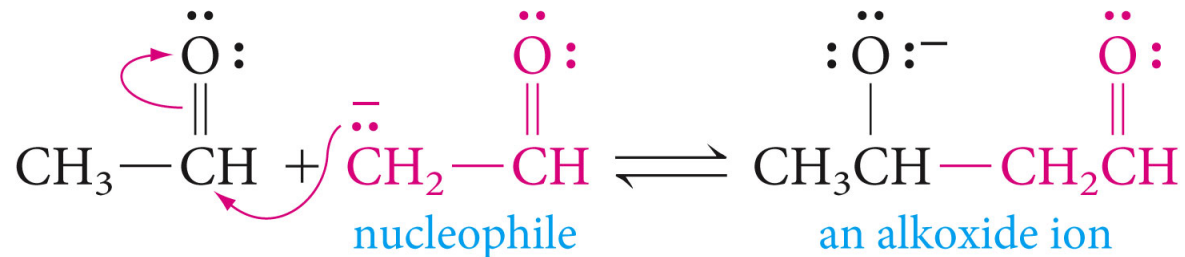
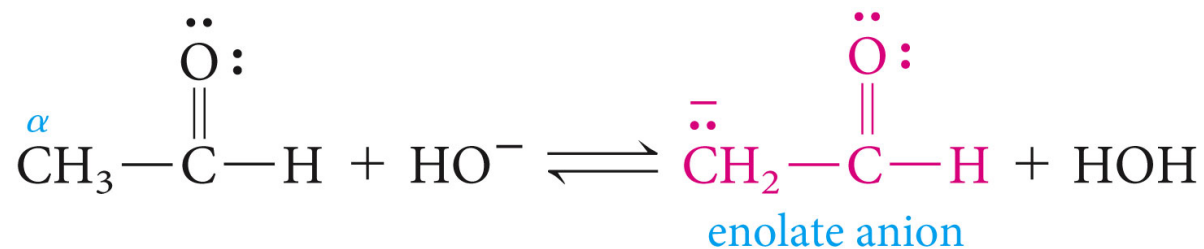
enolate anion

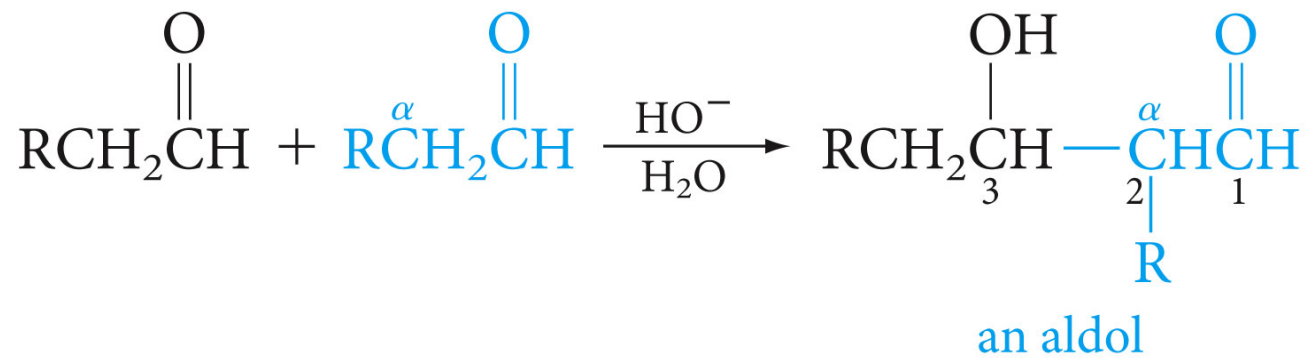




## The Aldol Condensation







# The Mixed Aldol Condensation

