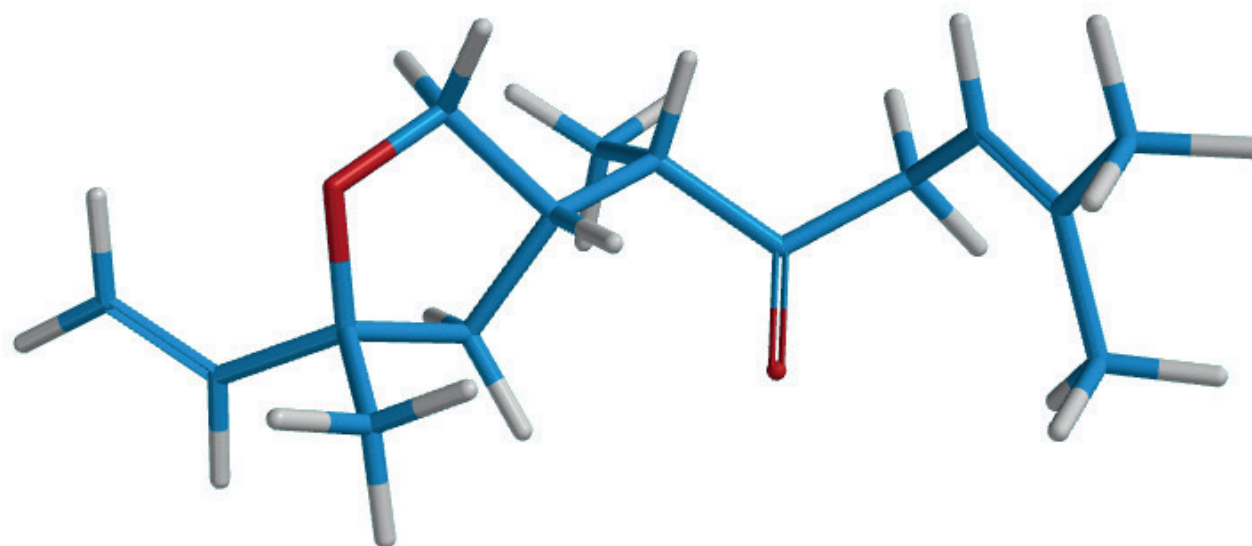


# 10

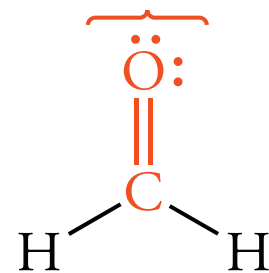
## ALDEHYDES AND KETONES



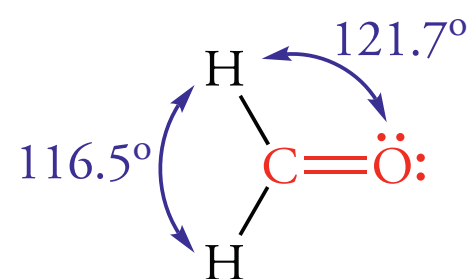
DAVANONE (A COMPONENT OF SOME PERFUMES)

## 10.1 THE CARBONYL GROUP

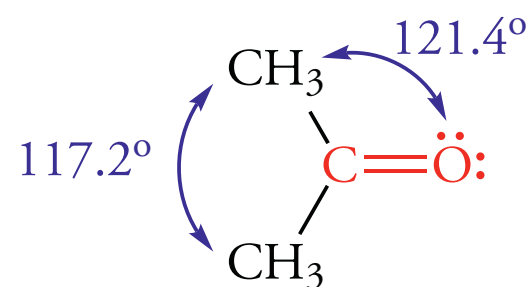
nonbonding electron pairs



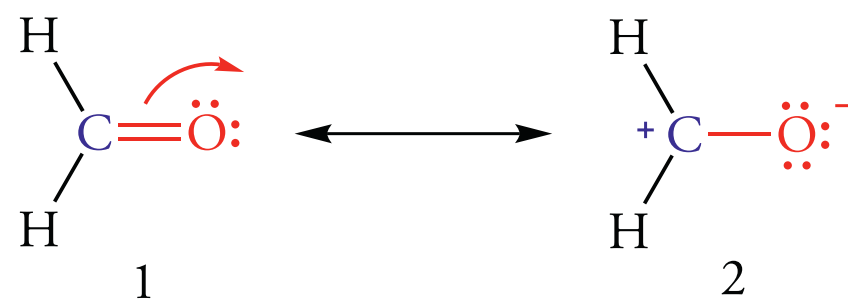
formaldehyde

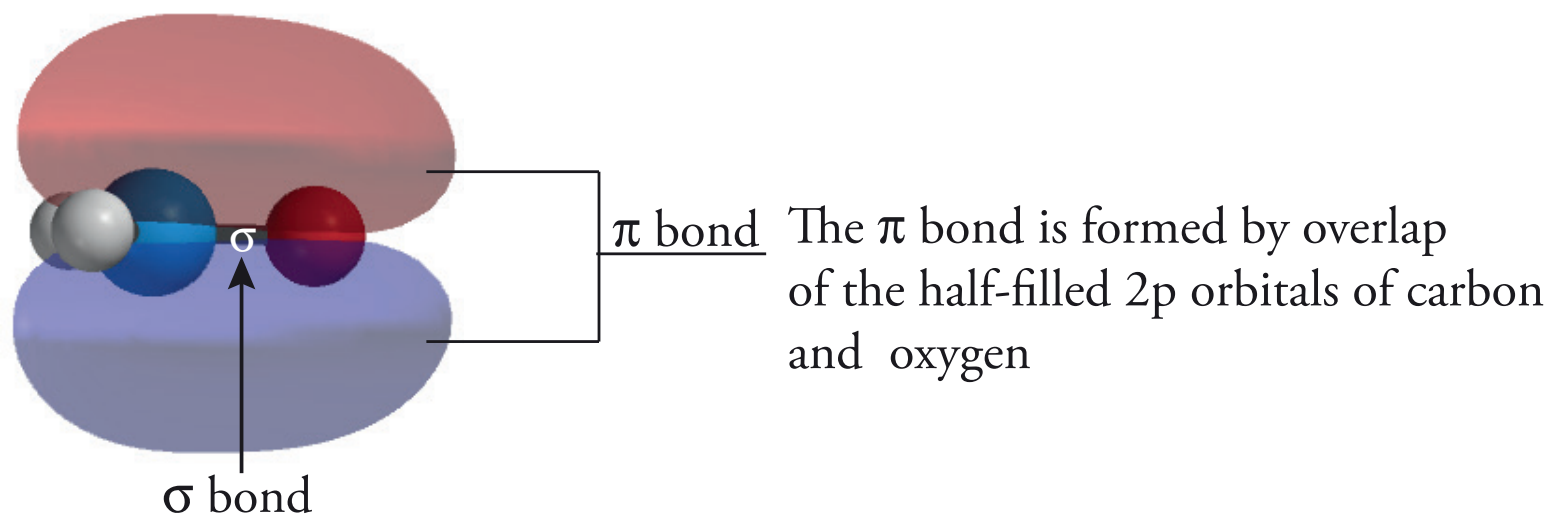


formaldehyde



acetone



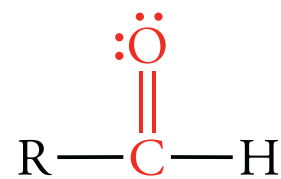
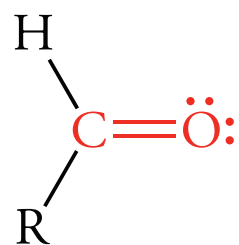


An electron of the  $sp^2$  hybrid orbital of the carbonyl carbon atom and an electron of the  $sp^2$  hybrid orbital of the oxygen atom form a  $\sigma$  bond

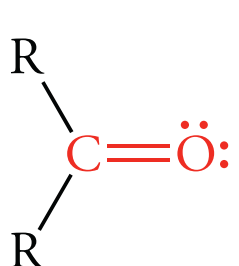
### Figure 10.1 Structure of Formaldehyde

The carbonyl carbon and oxygen atoms of formaldehyde are  $sp^2$ -hybridized. The H—C—H bond angle is close to  $120^\circ$ .

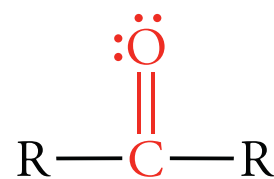
## Carbonyl Compounds



general formulas for an aldehyde



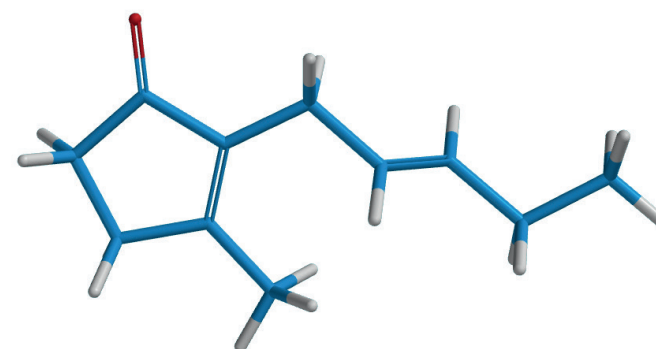
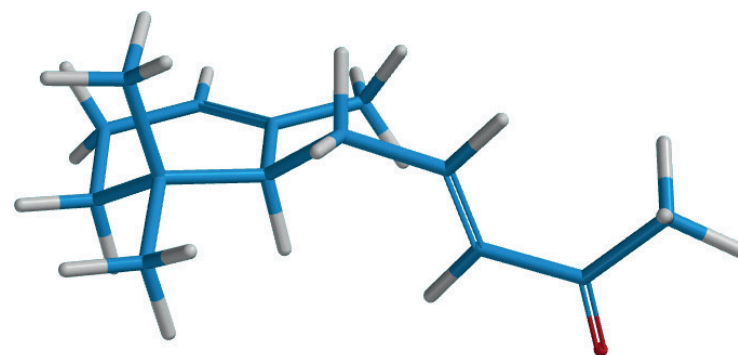
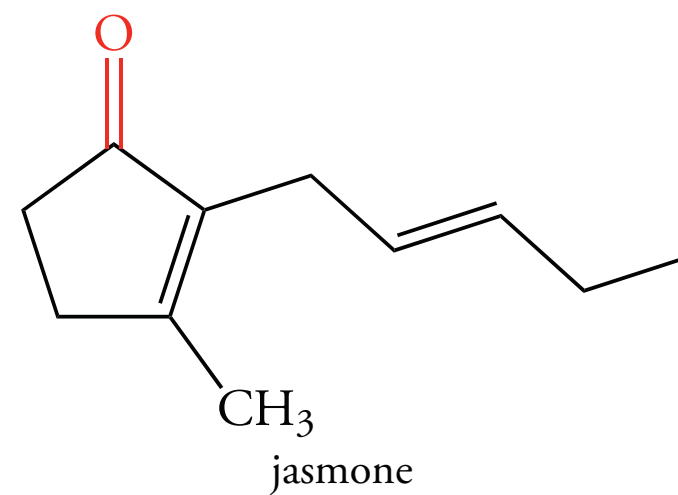
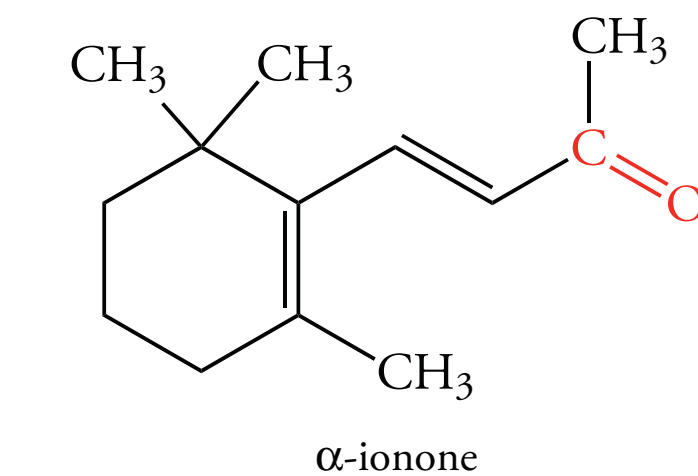
or



general formulas for a ketone

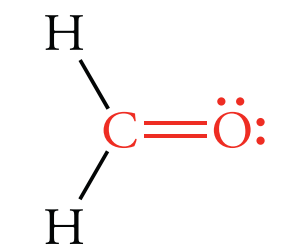
## Naturally Occurring Aldehydes and Ketones

Figure 10.2  
Structures of Naturally  
Occurring Aldehydes and  
Ketones

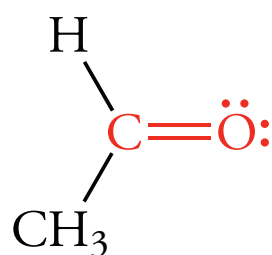


## 10.2 NOMENCLATURE OF ALDEHYDES AND KETONES

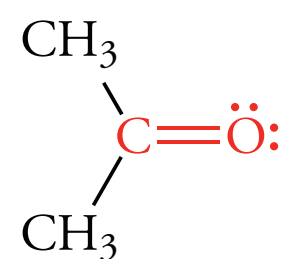
### Common Names of Aldehydes and Ketones



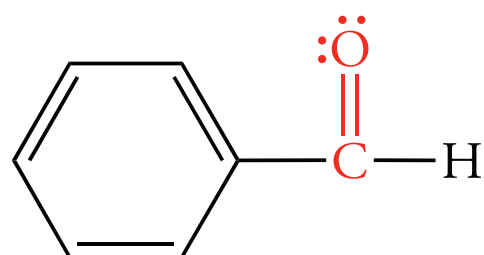
formaldehyde



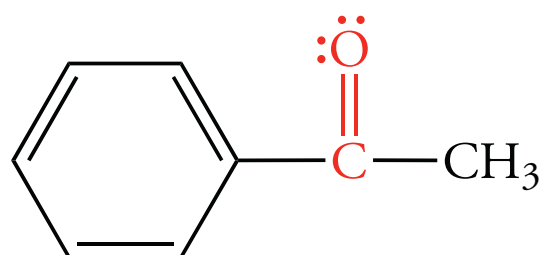
acetaldehyde



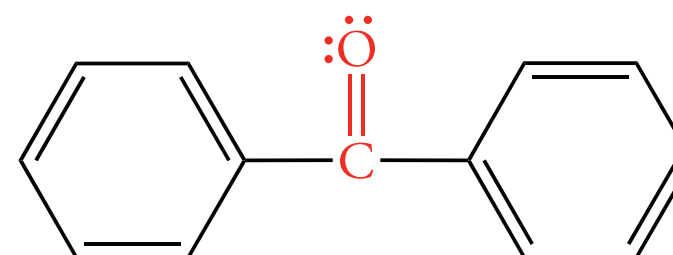
acetone



benzaldehyde



acetophenone

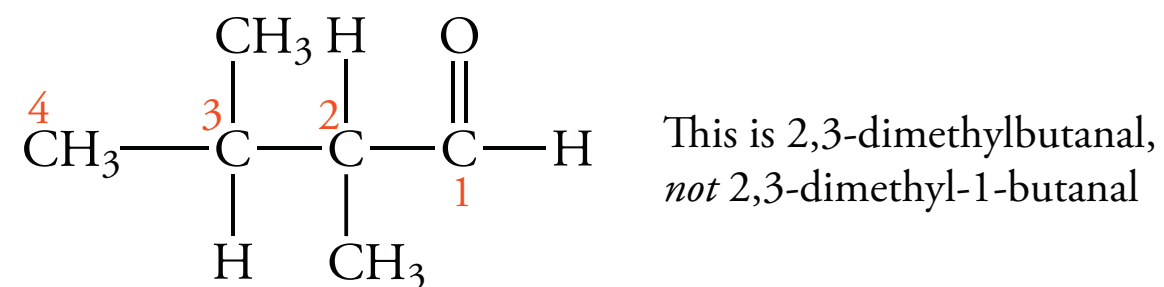


benzophenone

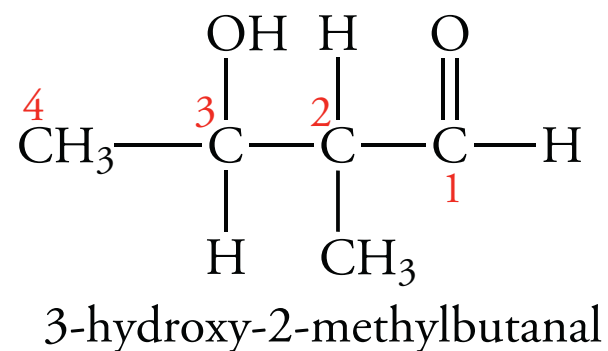
## IUPAC Names of Aldehydes and Ketones

The IUPAC rules for naming aldehydes are similar to those outlined for alcohols.

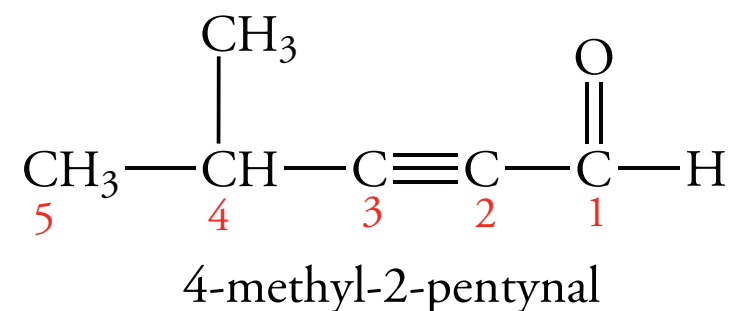
1. Aldehydes are named by IUPAC rules similar to those outlined for alcohols. The final *-e* of the parent hydrocarbon corresponding to the aldehyde is replaced by the ending *-al*. The IUPAC rules are as follows:



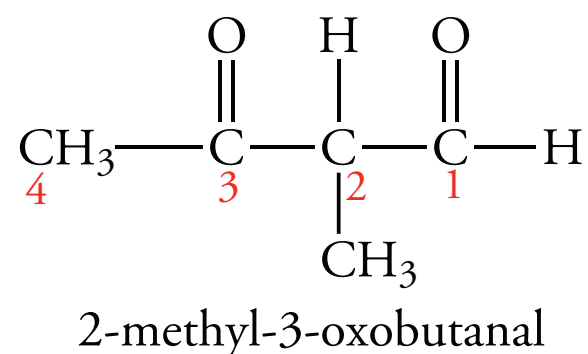
2. The aldehyde functional group has a higher priority than alkyl, halogen, hydroxyl, and alkoxy groups. The names and positions of these groups are indicated as prefixes to the name of the parent aldehyde.



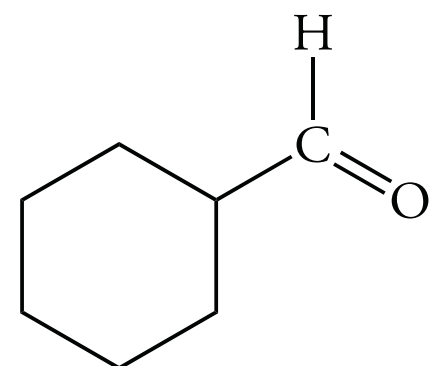
3. The aldehyde functional group has a higher priority than double or triple bonds. When the parent chain contains a double or triple bond, replace the final *-e* of the name of the parent alkene or alkyne with the suffix *-al*. Indicate the position of the multiple bond with a prefix.



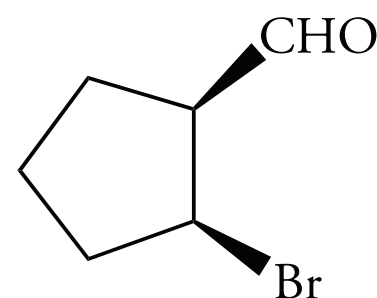
4. If an aldehyde or ketone contains other groups with a higher priority, such as carboxylic acids, give the carbonyl group the prefix *-oxo*. Use a number to indicate the position of the *-oxo* group. The priority order is carboxylic acid > aldehyde > ketone.



5. If an aldehyde group is attached to a ring, use the suffix *-carbaldehyde*.



cyclohexanecarbaldehyde



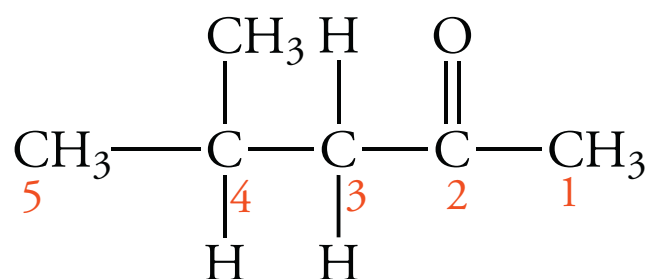
*cis*-2-bromocyclopentanecarbaldehyde



## IUPAC Names of Ketones

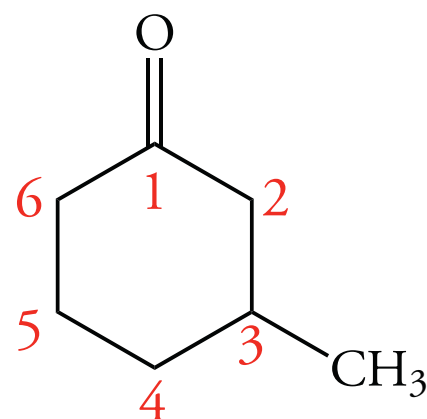
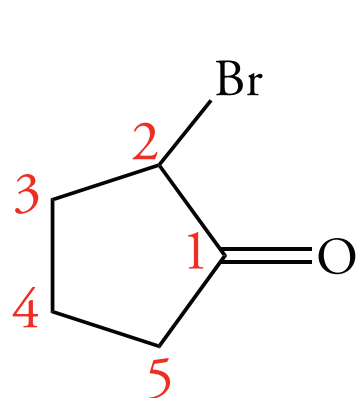
The IUPAC rules for naming ketones are similar to those used for aldehydes. The final -e of the parent hydrocarbon is replaced with the ending *-one*. However, the carbonyl group in a ketone is not on a terminal carbon atom, and we must indicate its position.

1. Number the carbon chain so that the carbonyl carbon atom has the lower number. This number appears as a prefix to the parent name. The identity and location of substituents are indicated with a prefix to the parent name.



This is 4-methyl-2-pentanone,  
*not* 2-methyl-4-pentanone

2. Name cyclic ketones as cycloalkanones. The carbonyl carbon is C-1. Number the ring in the direction that gives the lower number to the first substituent encountered.



3. Halogen, hydroxyl, alkoxy groups, and multiple bonds have lower priorities than the ketone group. These substituted ketones are named using the same method described for aldehydes.

## 10.3 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

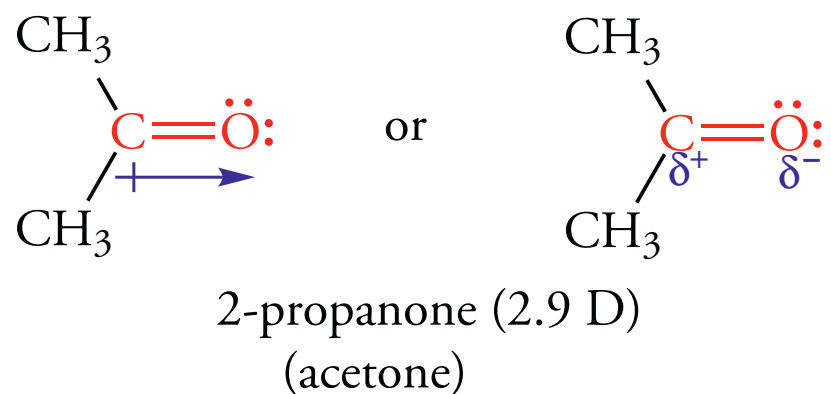
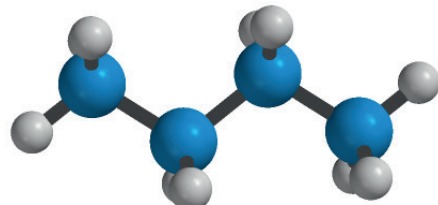
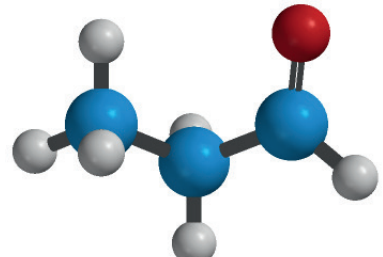
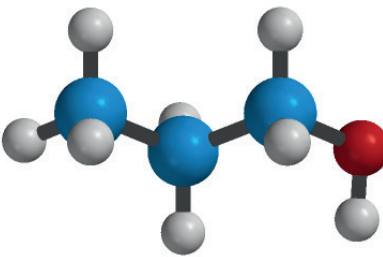
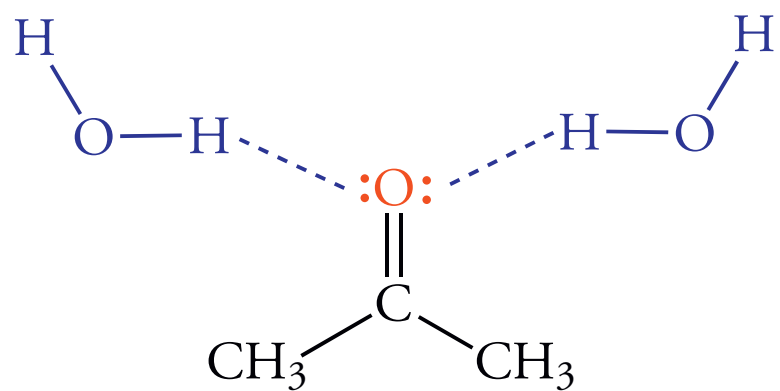


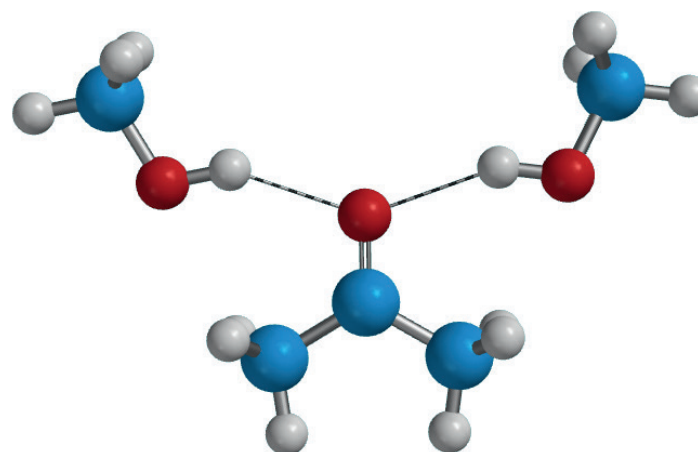
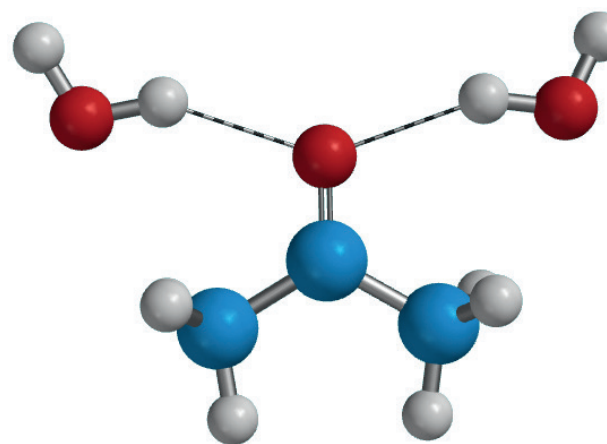
Table 10.1  
Comparisons of Physical Properties

			
Property	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CHO	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH
Dipole moment	Butane	Propanal	1-Propanol
Dipole moment	0.05 D	2.52 D	1.68 D
Boiling point	-1 °C	48.8 °C	97.1 °C

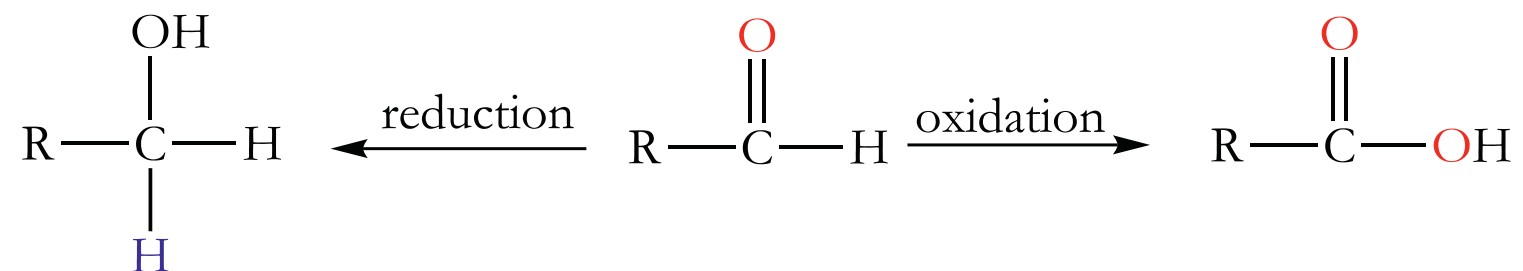
## Solubility of Aldehydes and Ketones in Water and Ethanol



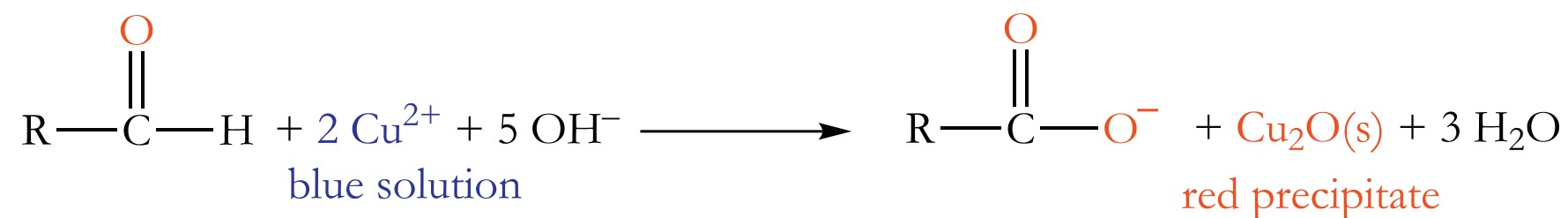
The lone pair electrons of the carbonyl group act as hydrogen bond acceptors



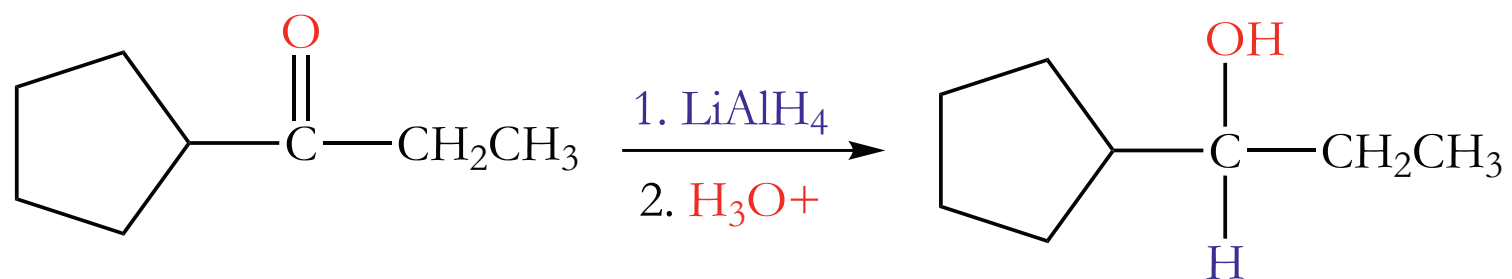
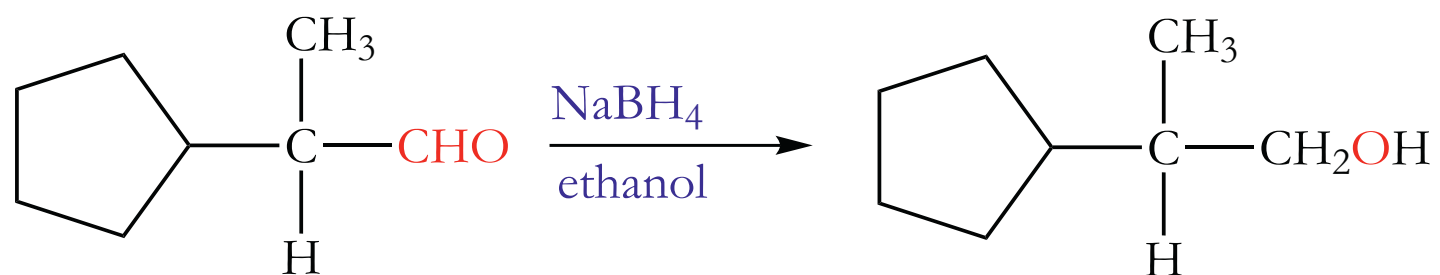
## 10.4 OXIDATION-REDUCTION REACTIONS OF CARBONYL COMPOUNDS



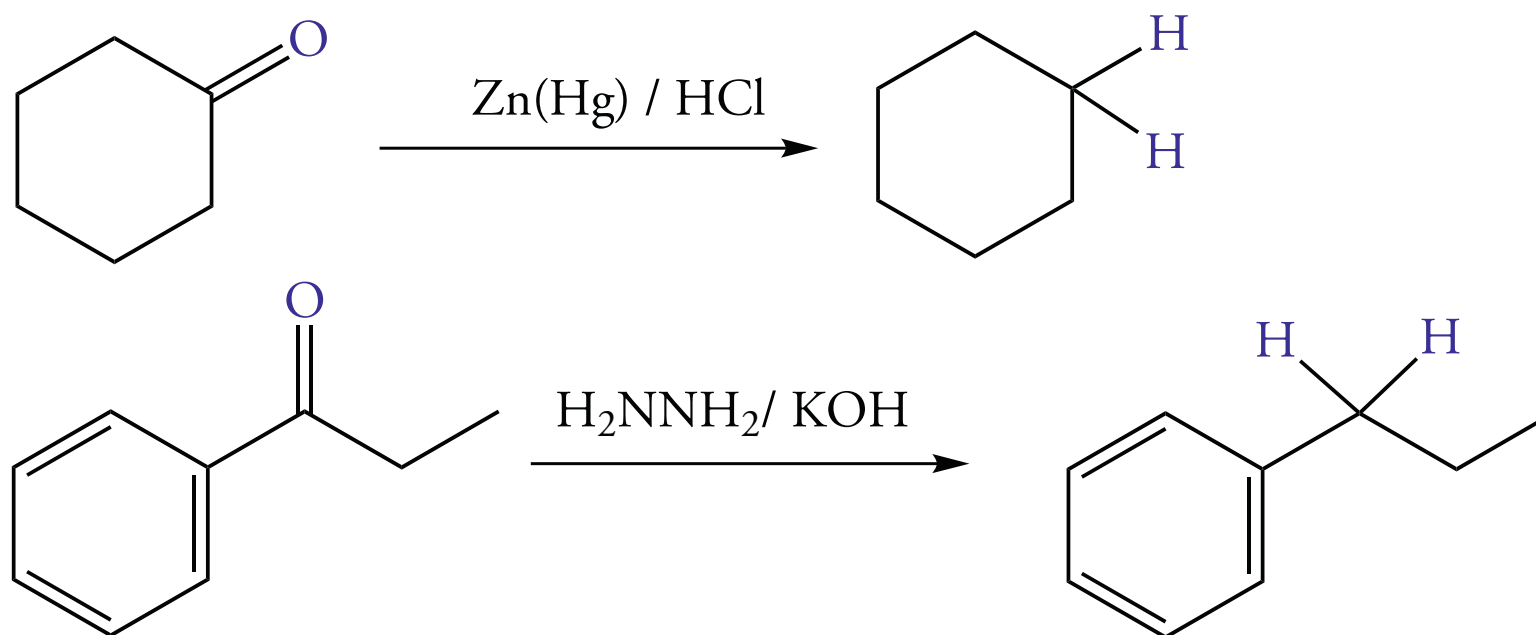
### Oxidation of Aldehydes



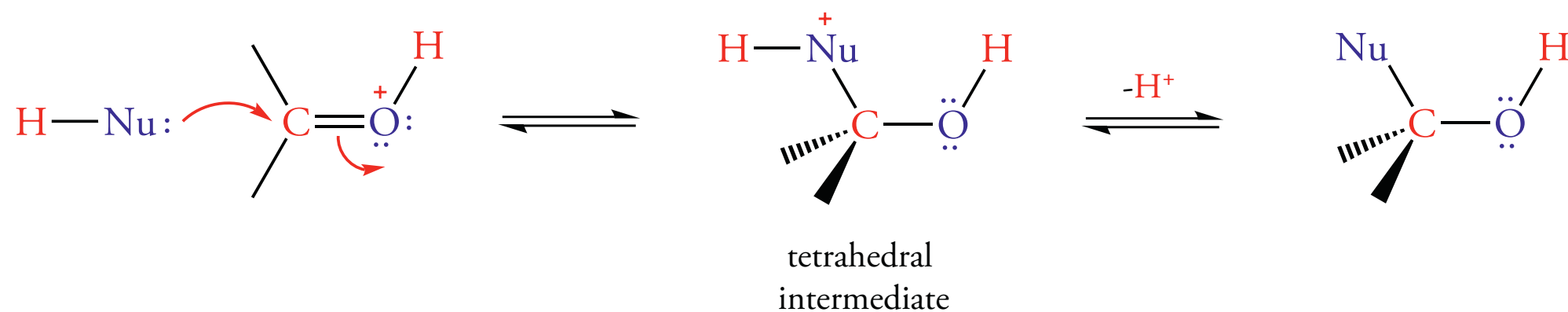
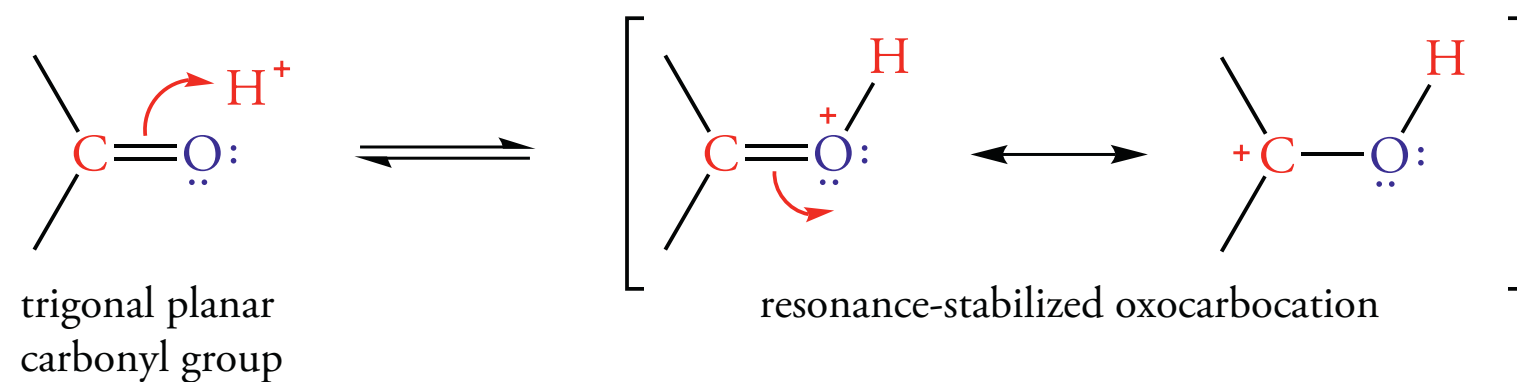
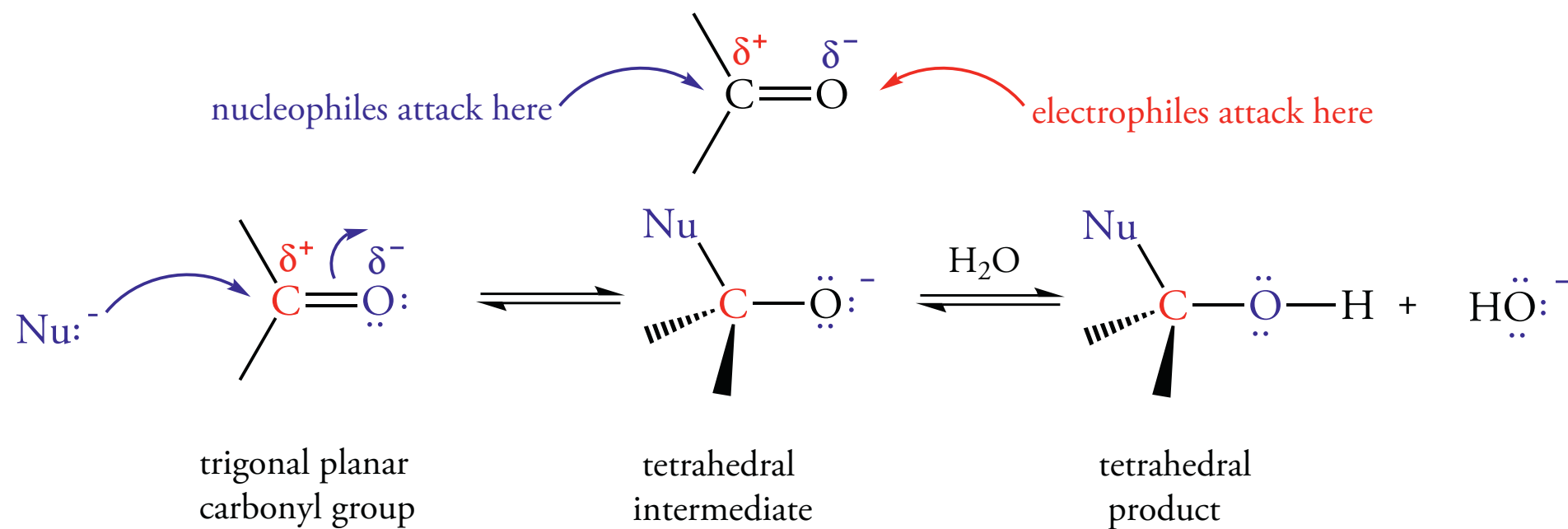
## Reduction of Aldehydes and Ketones to Alcohols



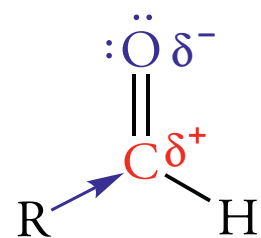
## Reduction of a Carbonyl Group to a Methylene Group



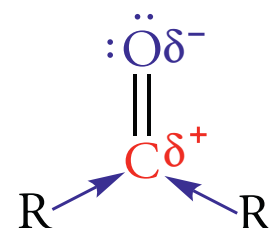
## 10.5 ADDITION REACTIONS OF CARBONYL COMPOUNDS



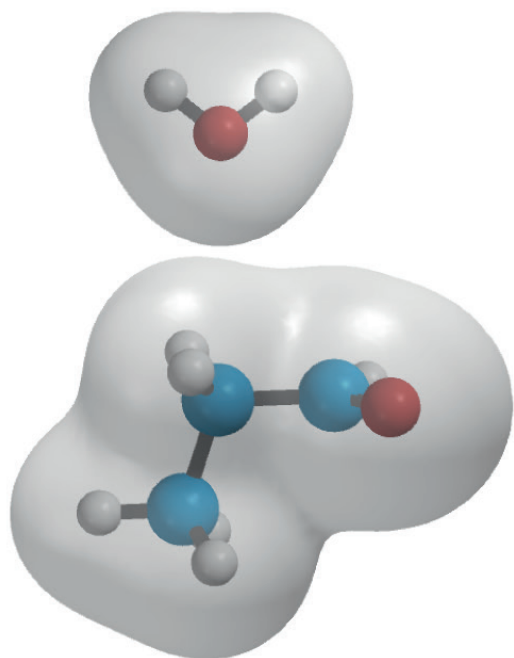
## Relative Reactivities of Aldehydes and Ketones



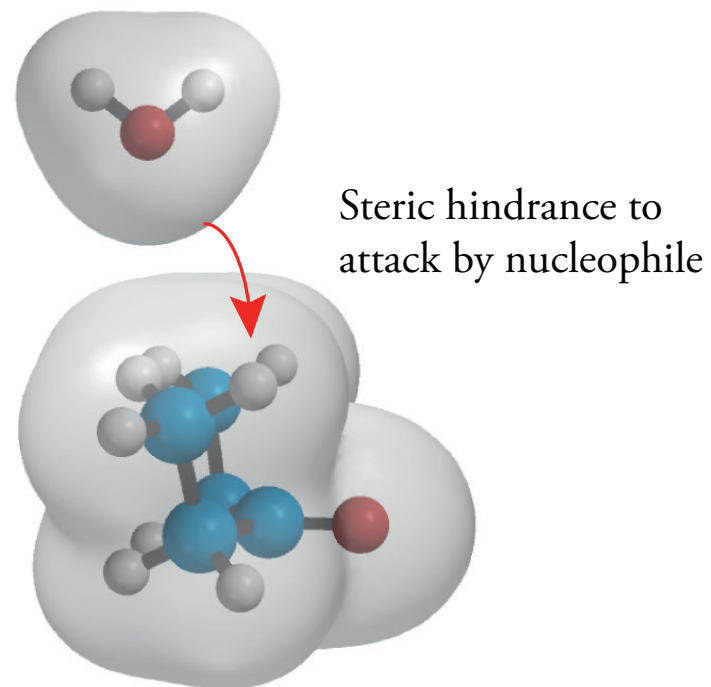
less stabilization  
more reactive



more stabilization  
less reactive



(a) Hydration of an aldehyde



(b) Hydration of a ketone

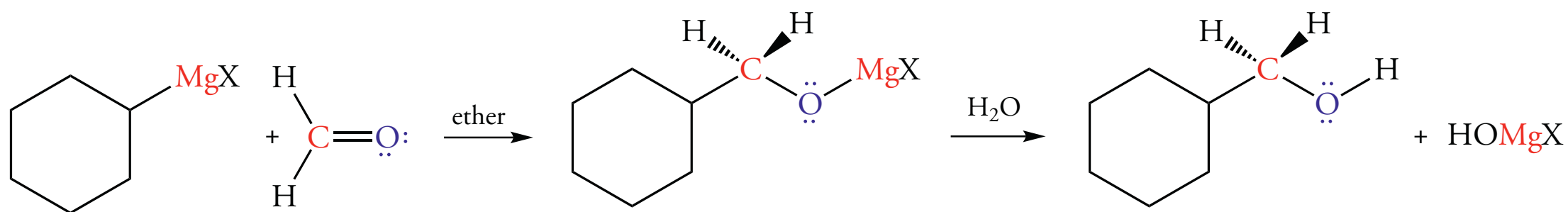
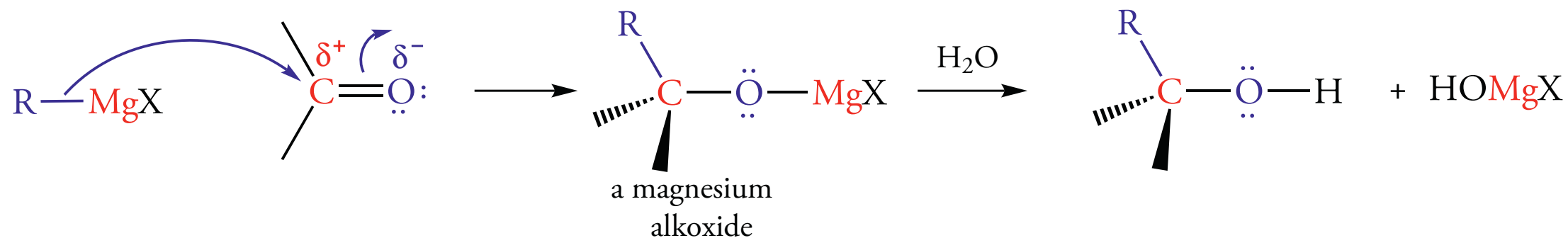
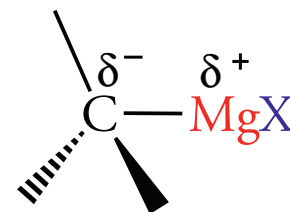
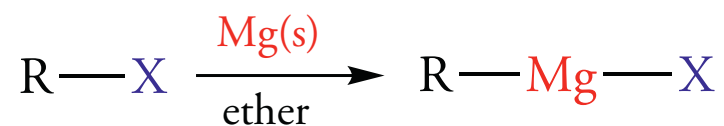
### Figure 10.3 Steric Effects on Addition Reactions

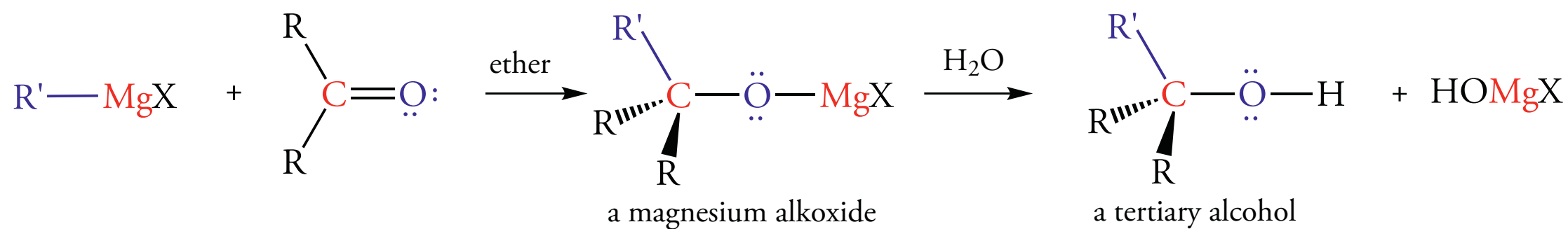
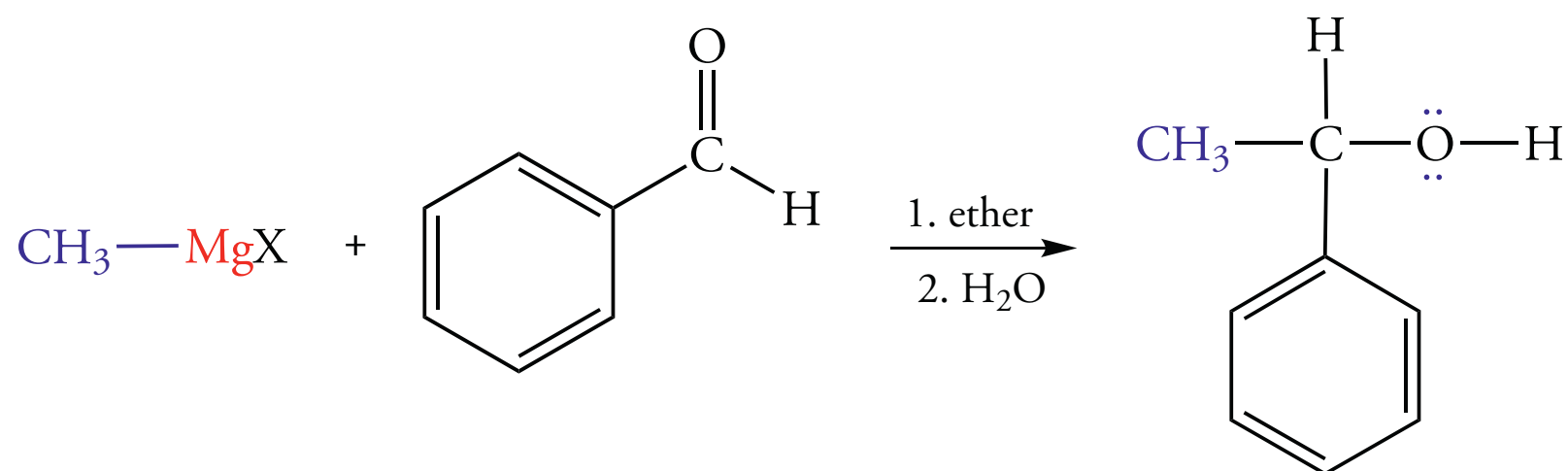
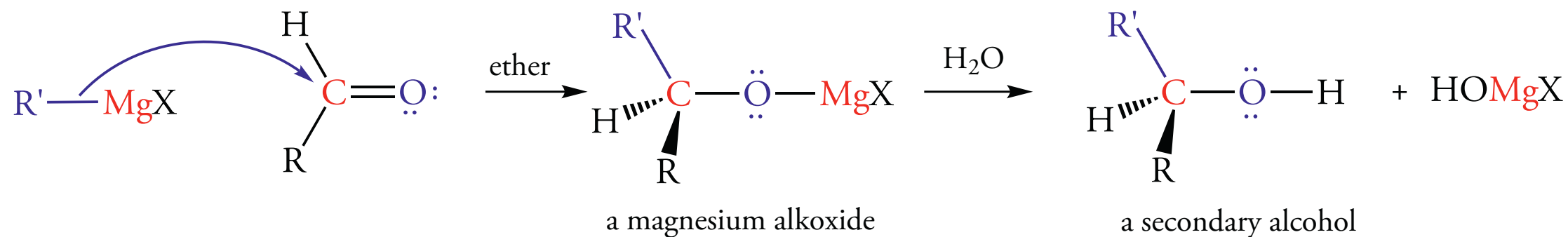
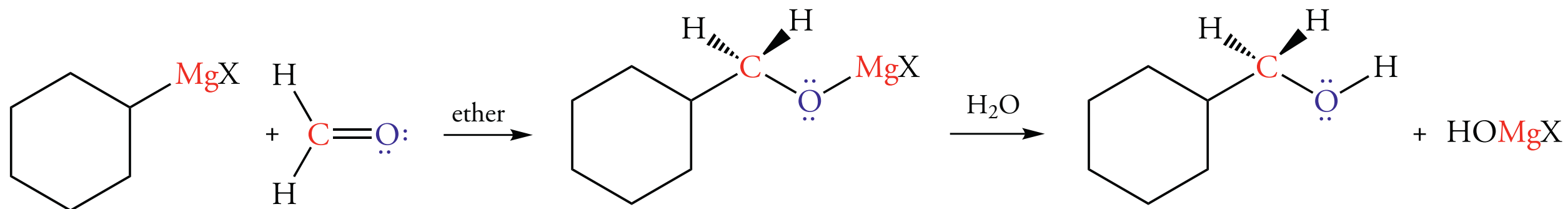
The carbonyl group of an aldehyde (a) is less sterically hindered than the carbonyl group of a ketone (b). Therefore, ketones react more slowly than aldehydes in nucleophilic addition reactions. The nucleophile here is water.

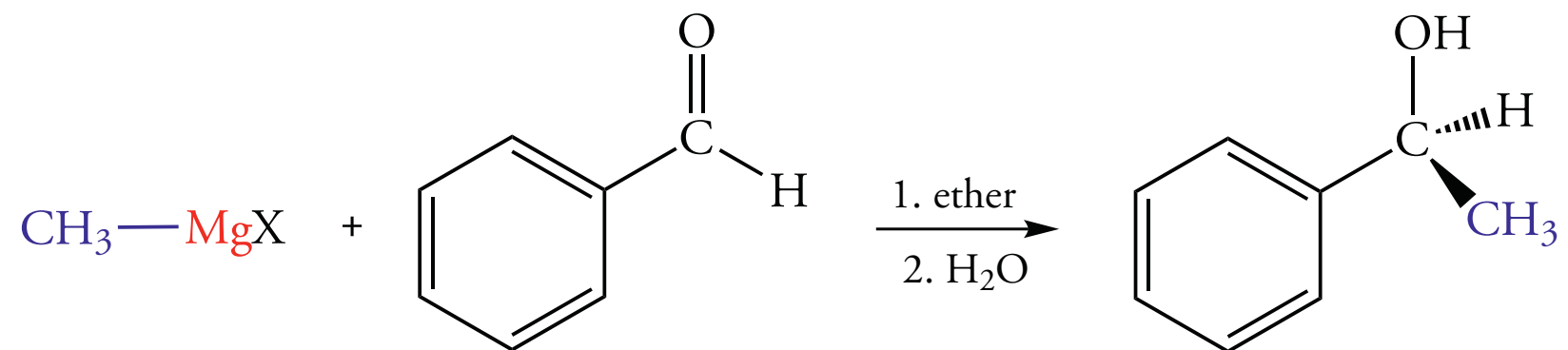


## 10.6 SYNTHESIS OF ALCOHOLS FROM CARBONYL COMPOUNDS

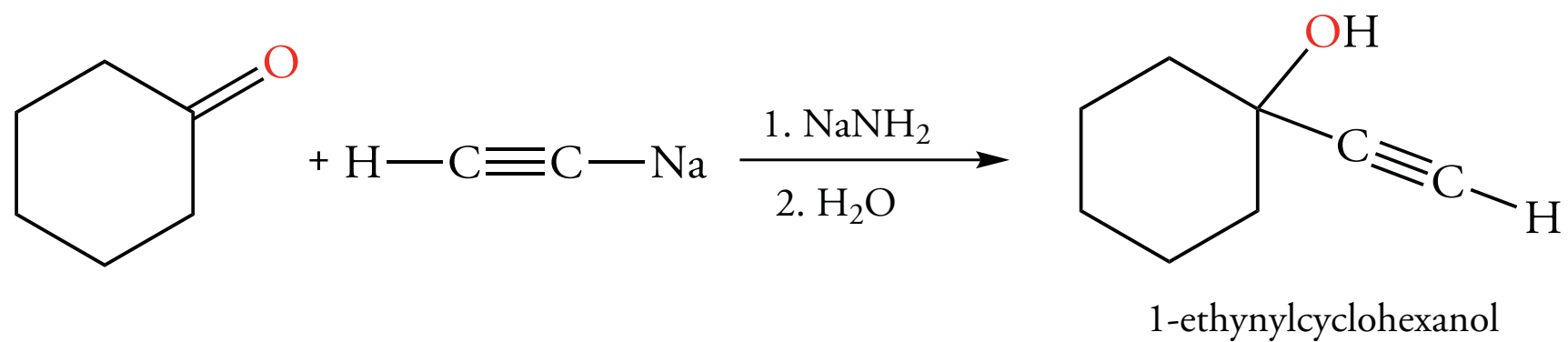
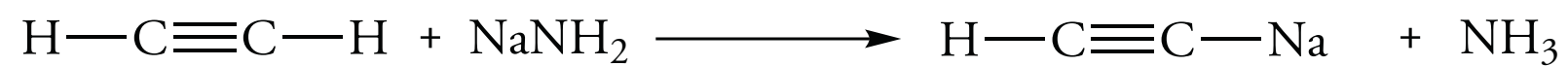
### Reactions of Aldehydes and Ketones with Grignard Reagents



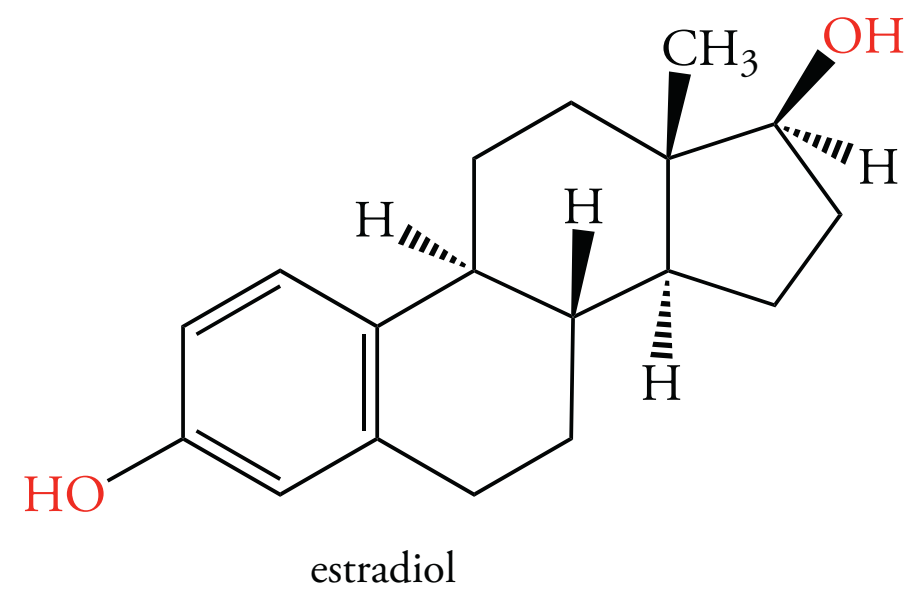
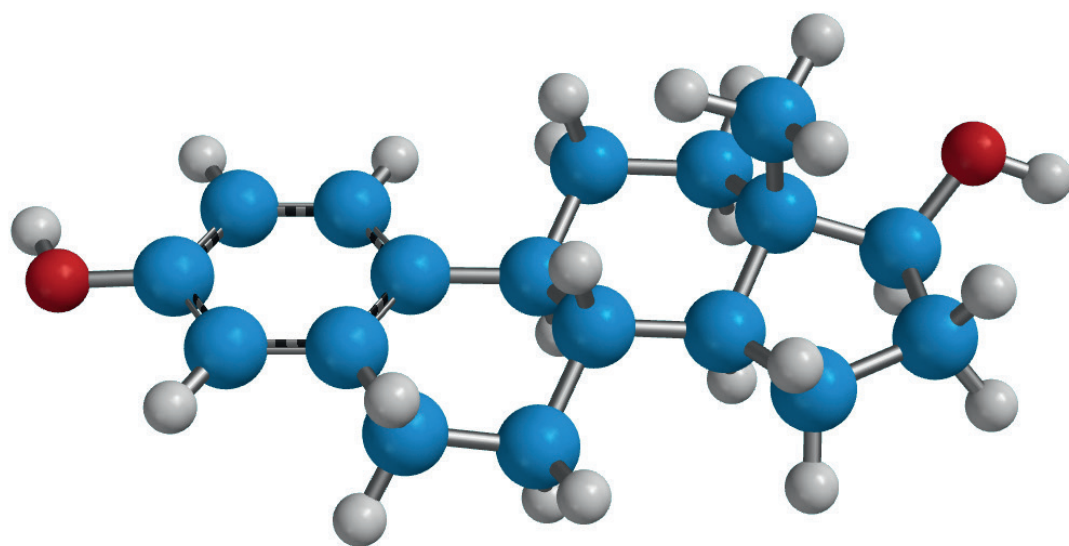


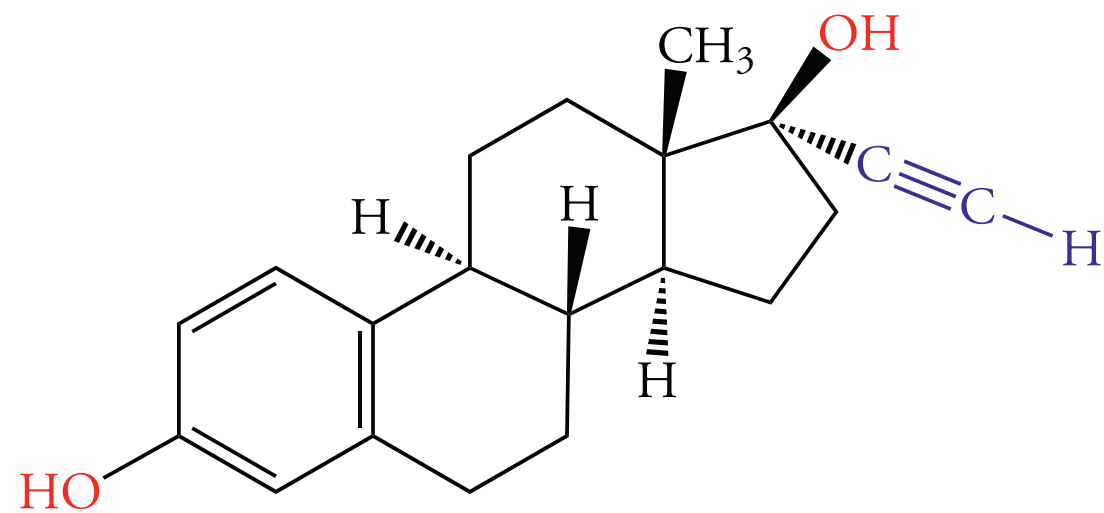
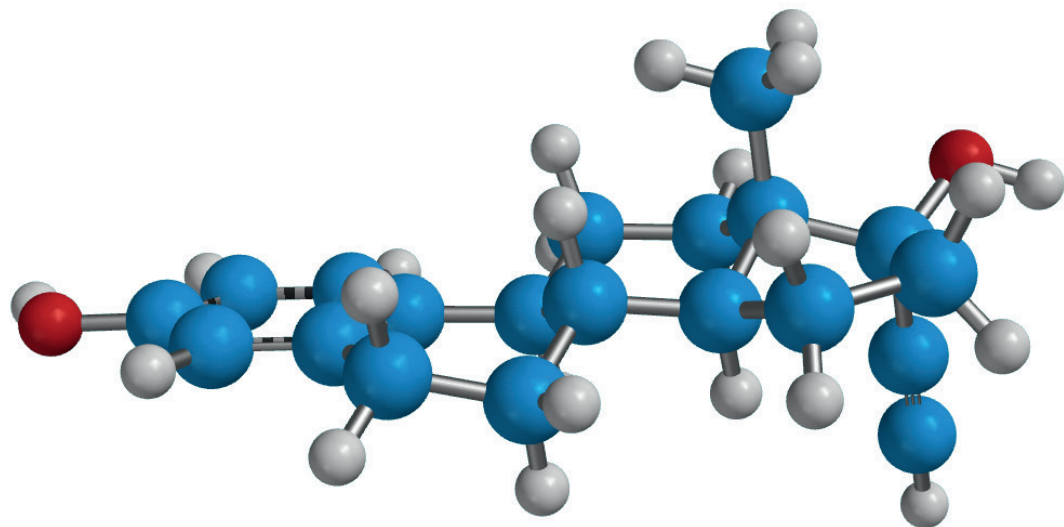


## Acetylenic Alcohols

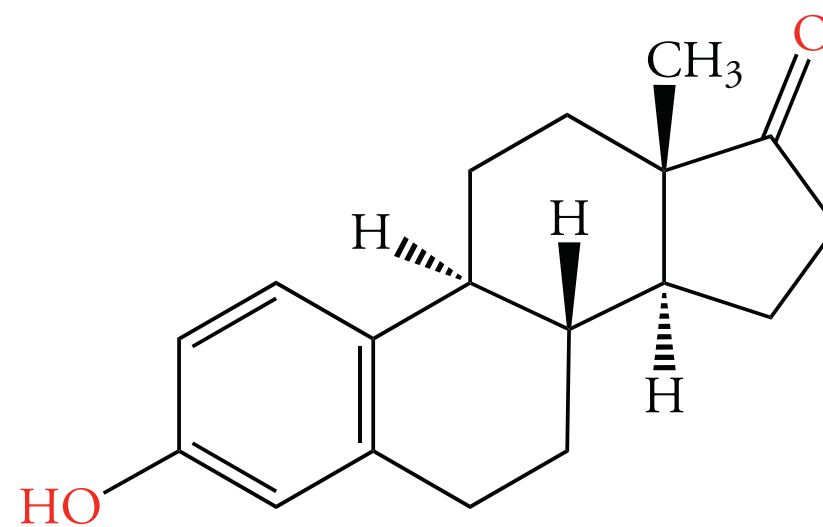
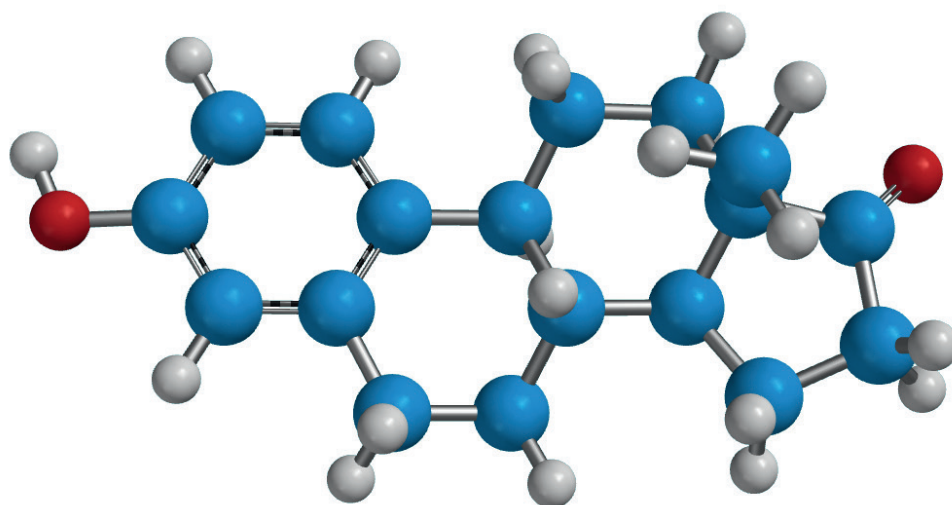


## Oral Contraceptives





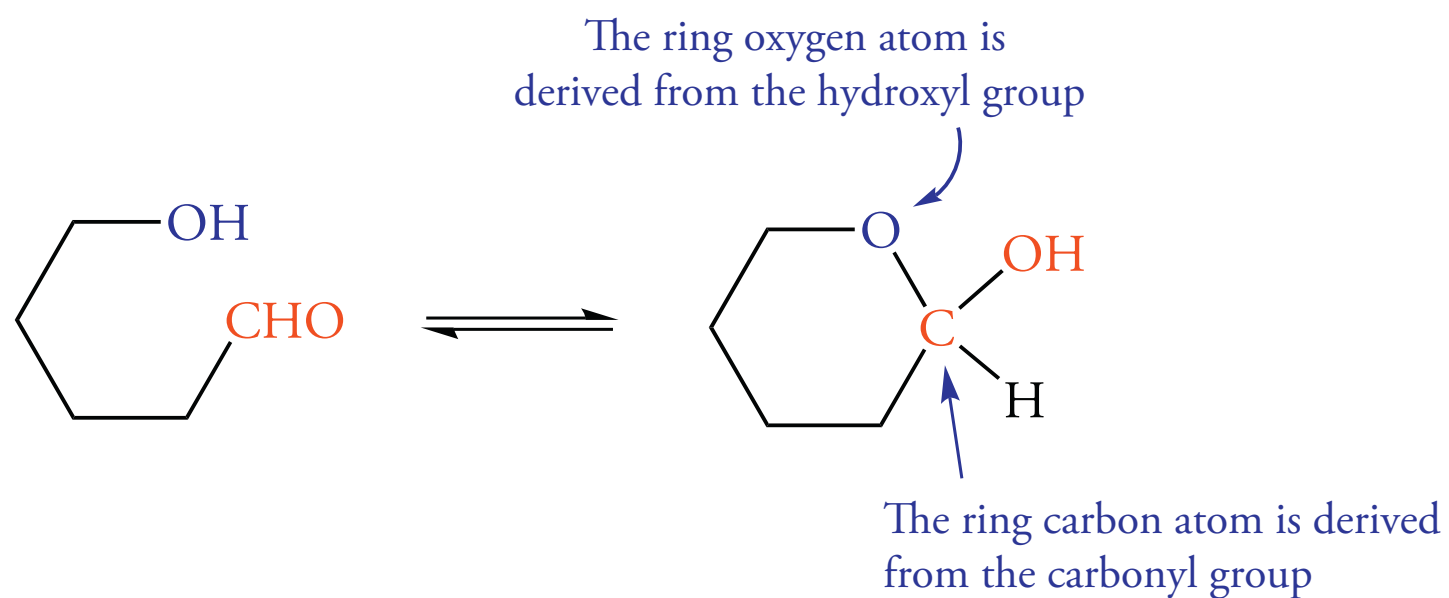
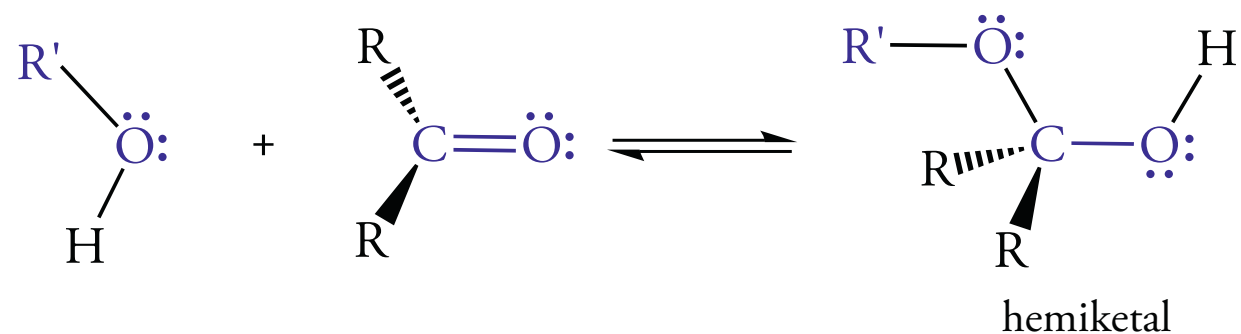
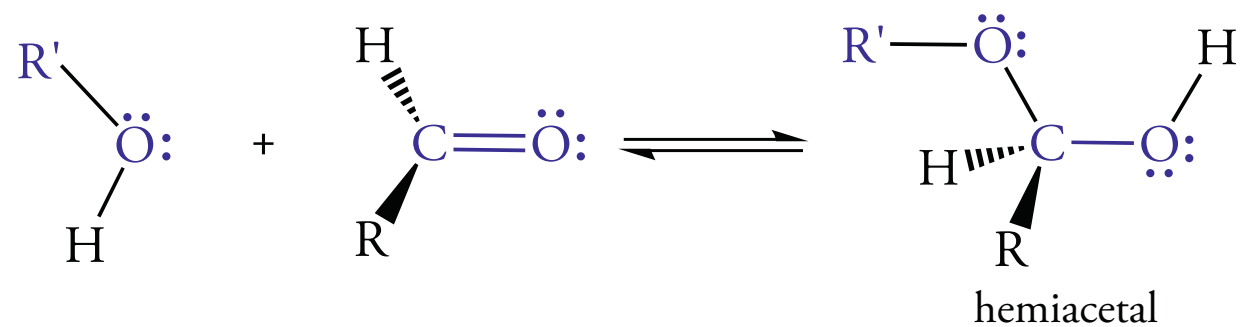
17-ethynylestradiol



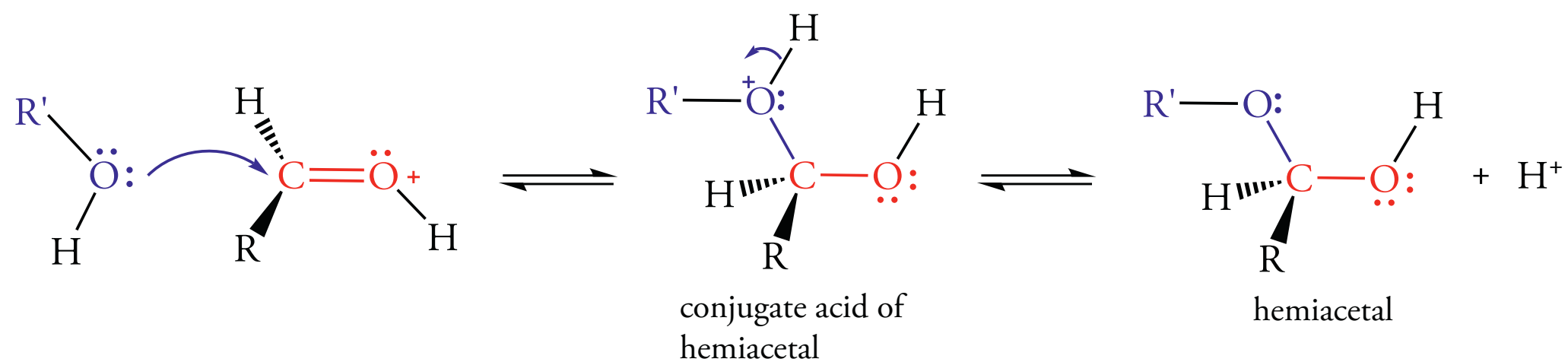
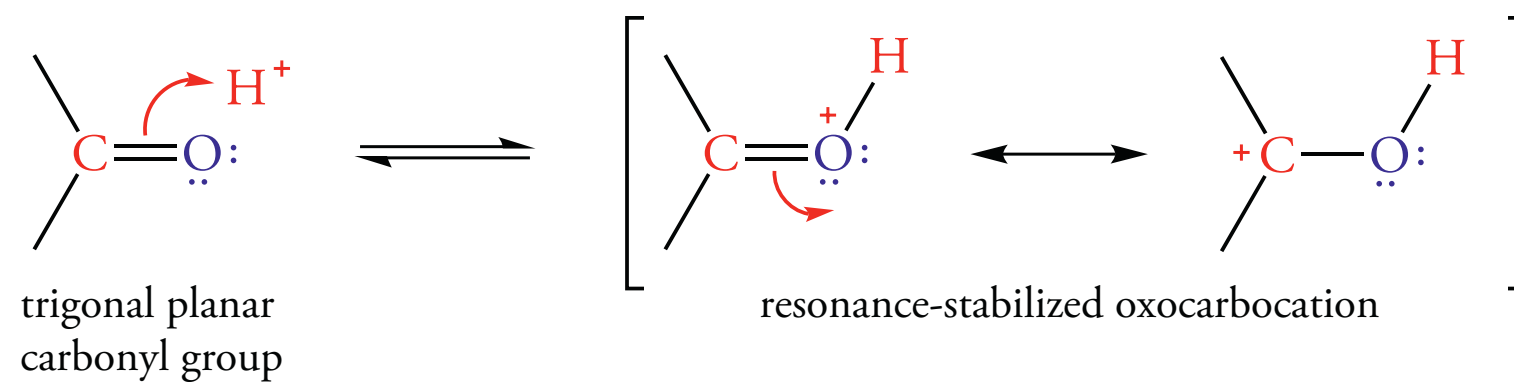
estrone

## 10.7 ADDITION REACTIONS OF OXYGEN COMPOUNDS

### Addition of Water

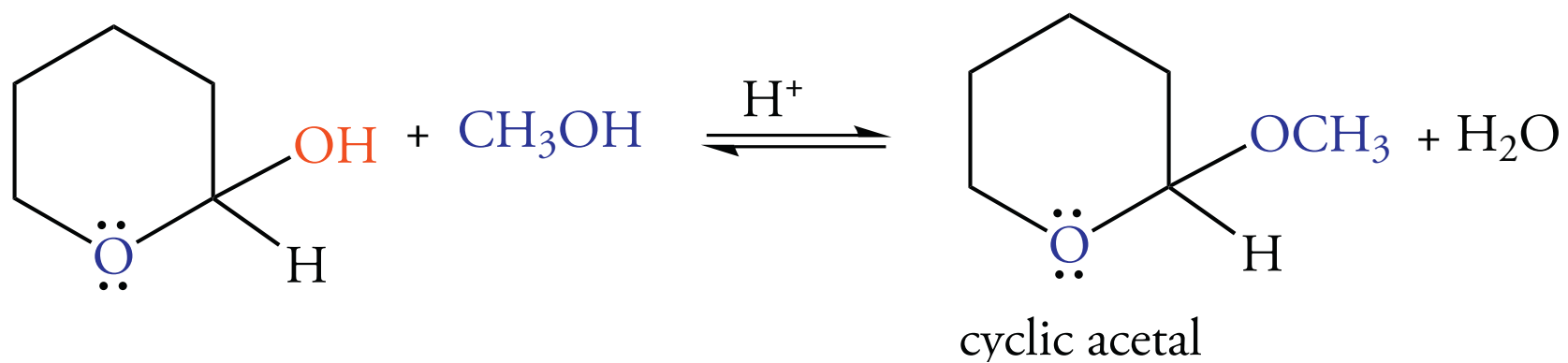
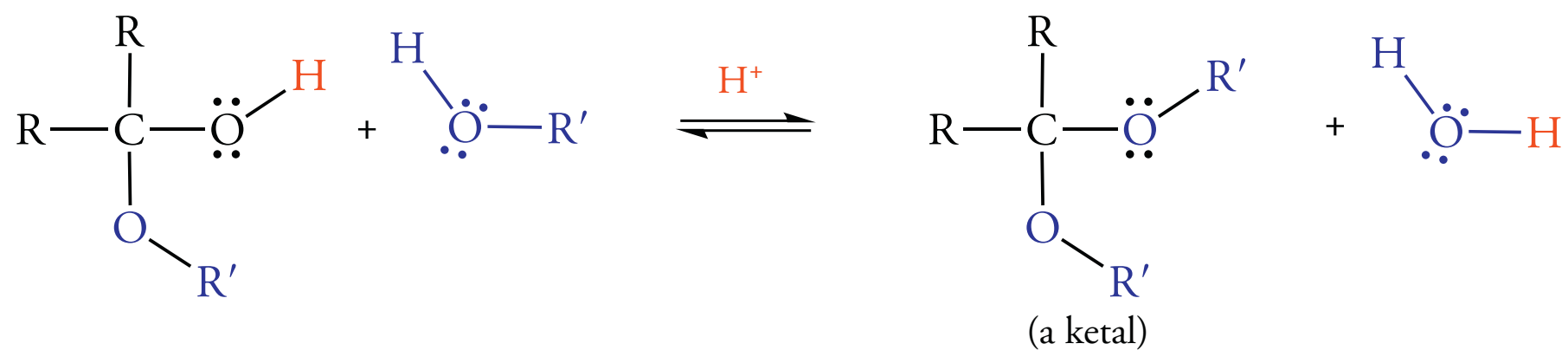
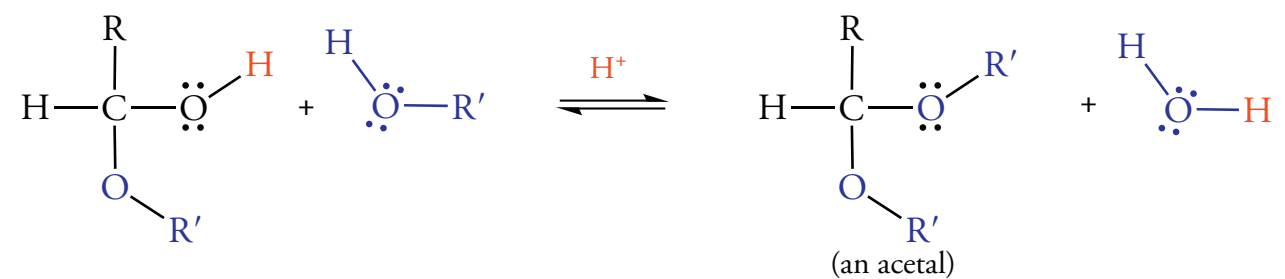


## Mechanism of Addition of Alcohols

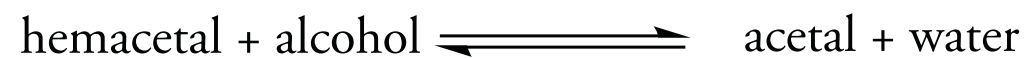




## 10.8 FORMATION OF ACETALS AND KETALS

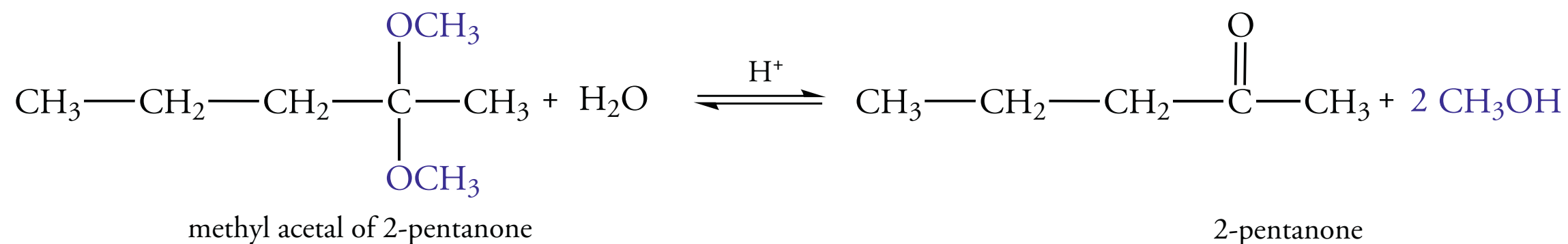


## Reactivity of Acetals and Ketals

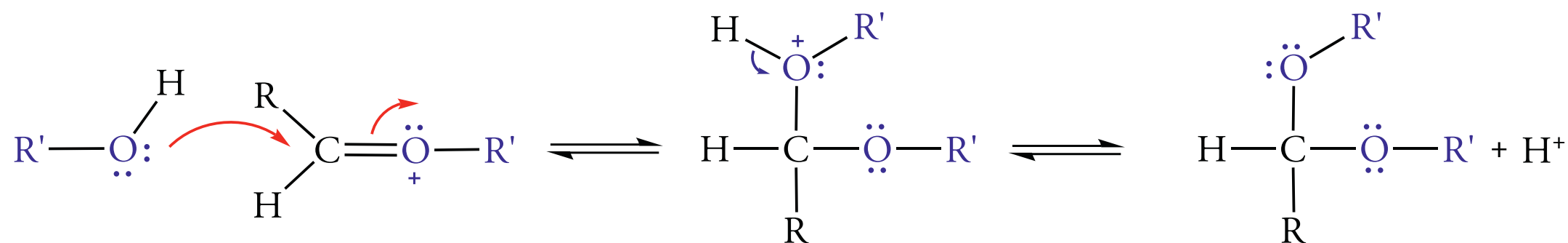
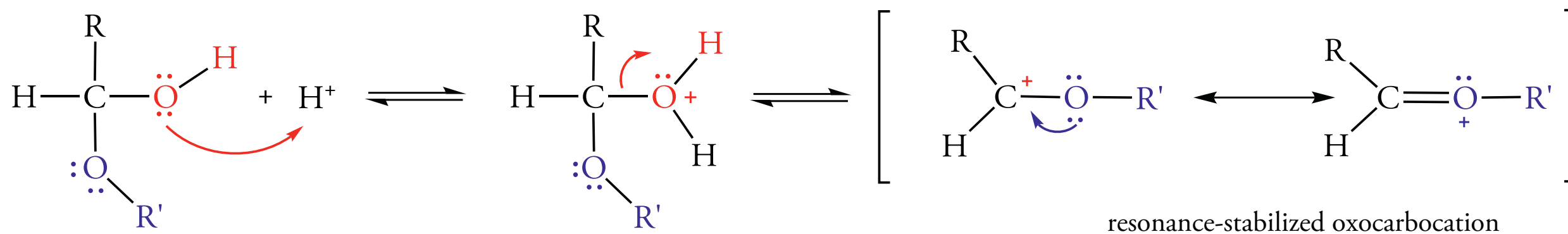


Adding alcohol pushes the equilibrium to the right

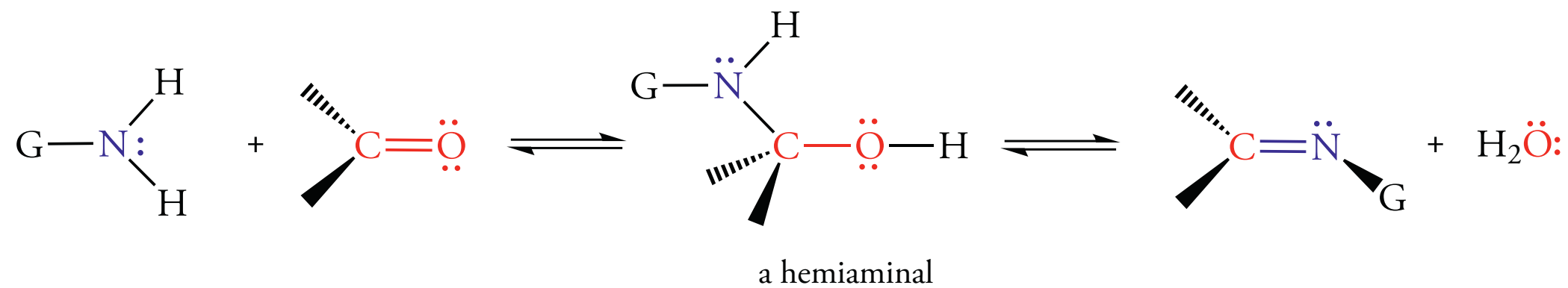
Removing water pulls the equilibrium to the right



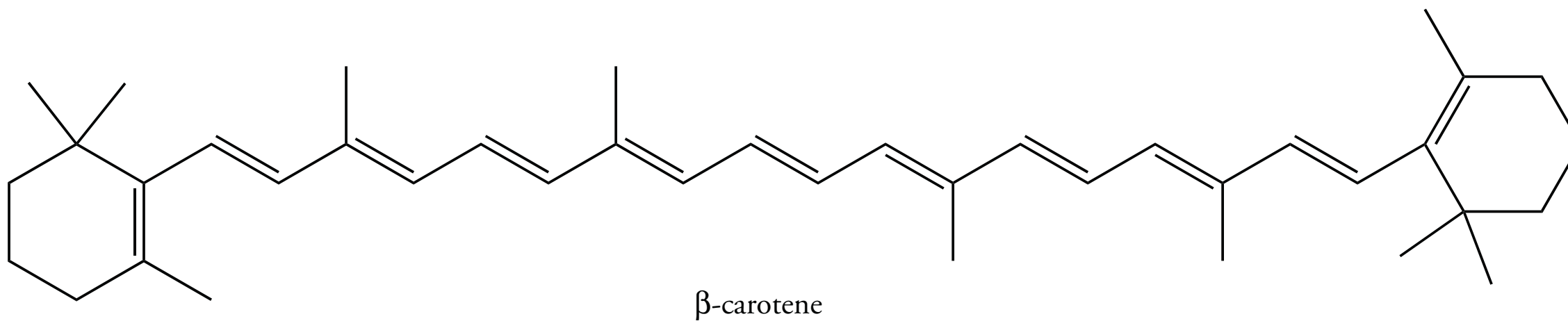
## Mechanism of Acetal and Ketal Formation

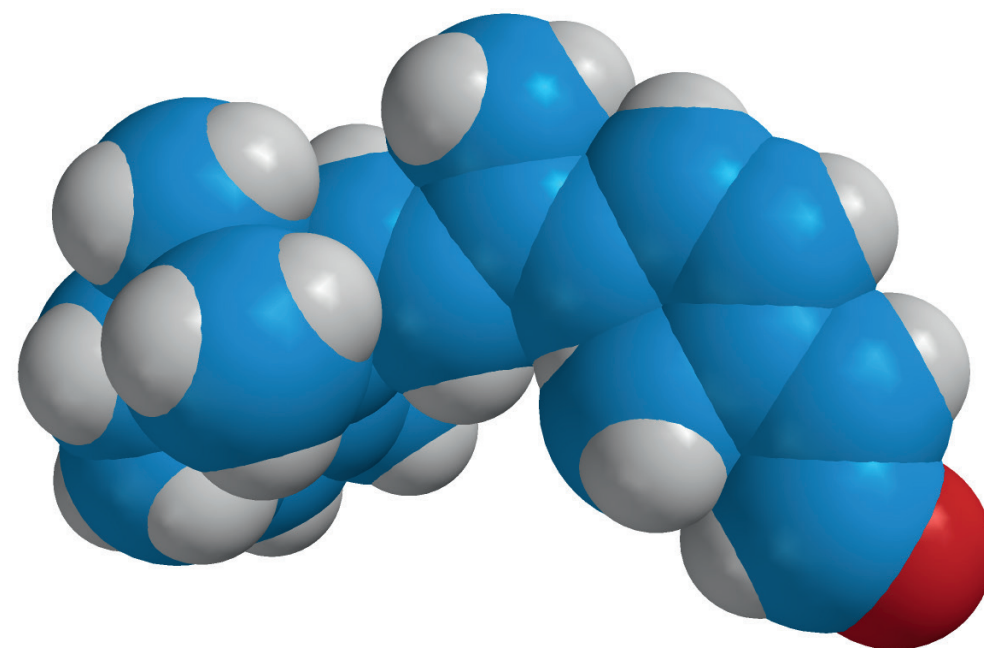
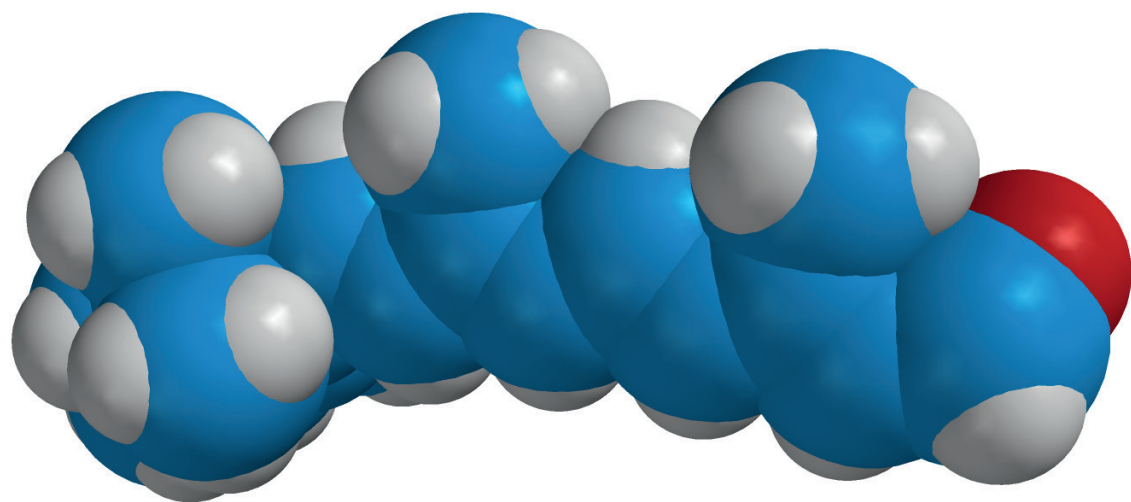
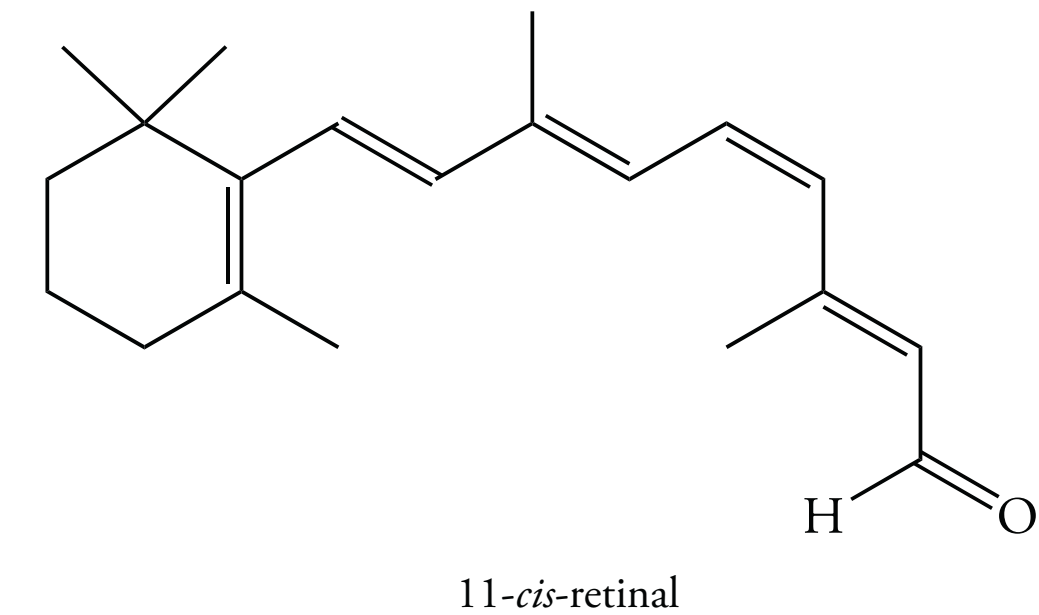
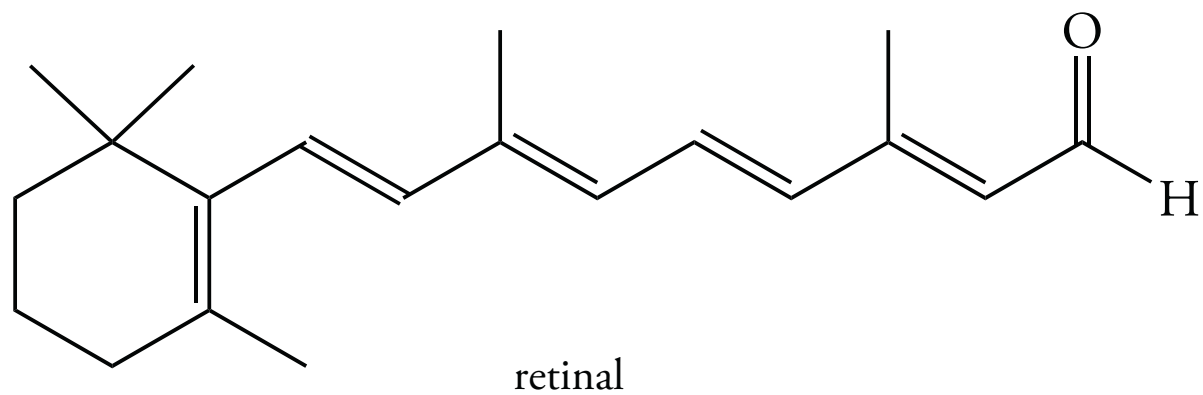


## 10. 9 ADDITION OF NITROGEN COMPOUNDS



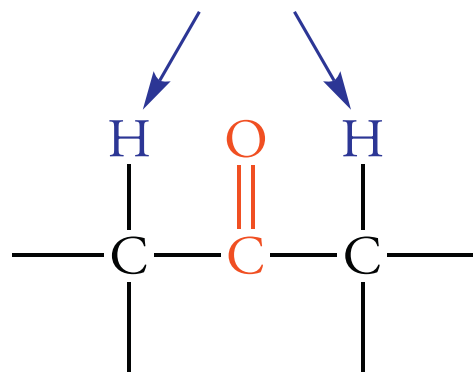
## Addition Reactions of Nitrogen Compounds and Vision





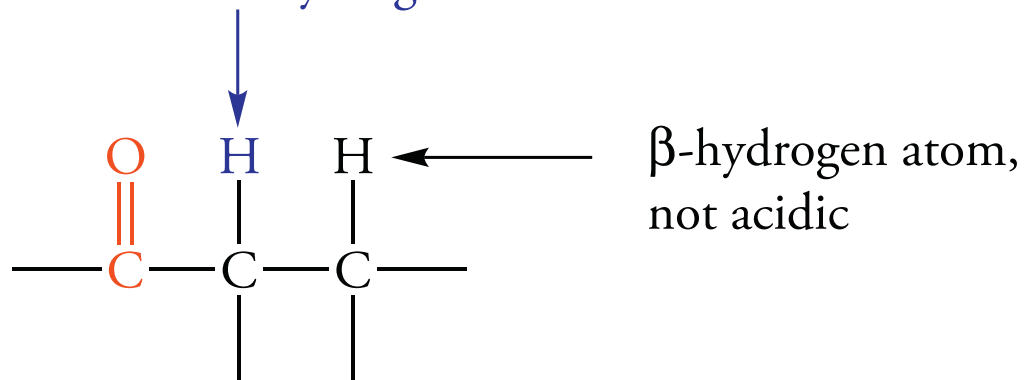
## 10.10 REACTIVITY OF THE $\alpha$ -CARBON ATOM

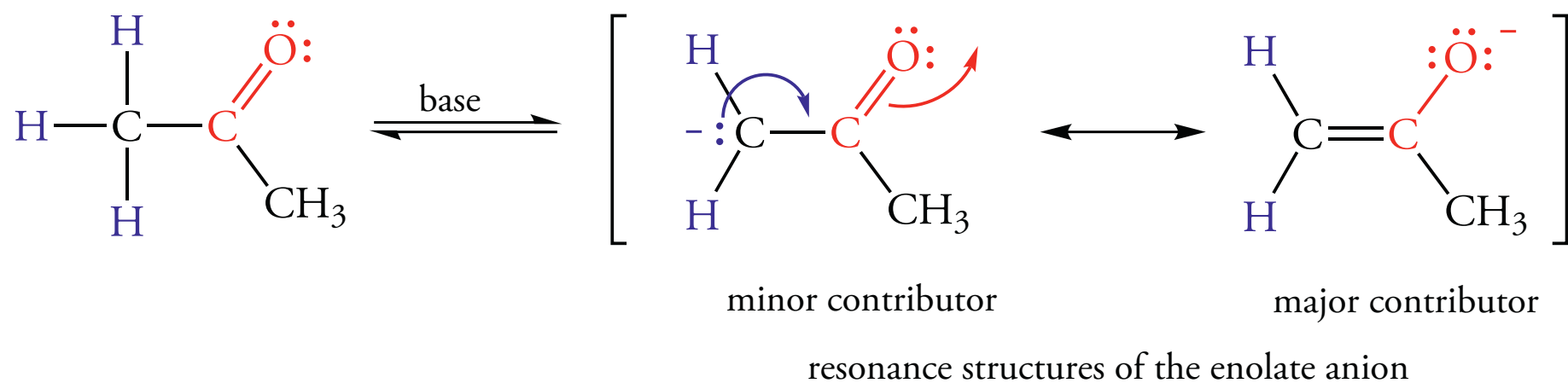
$\alpha$ -hydrogen atoms



Acidity of  $\alpha$  Hydrogens

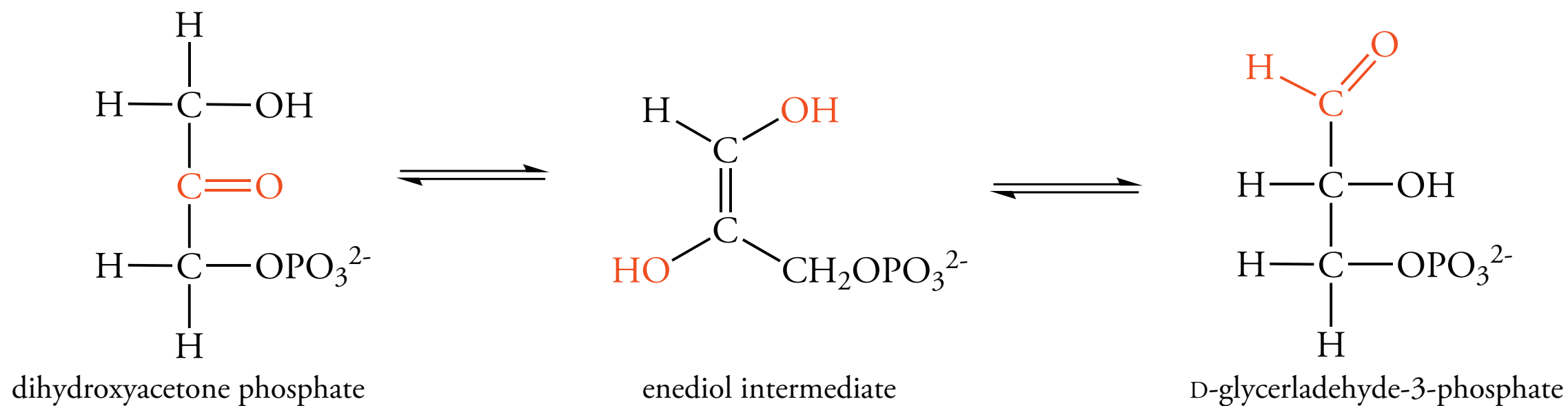
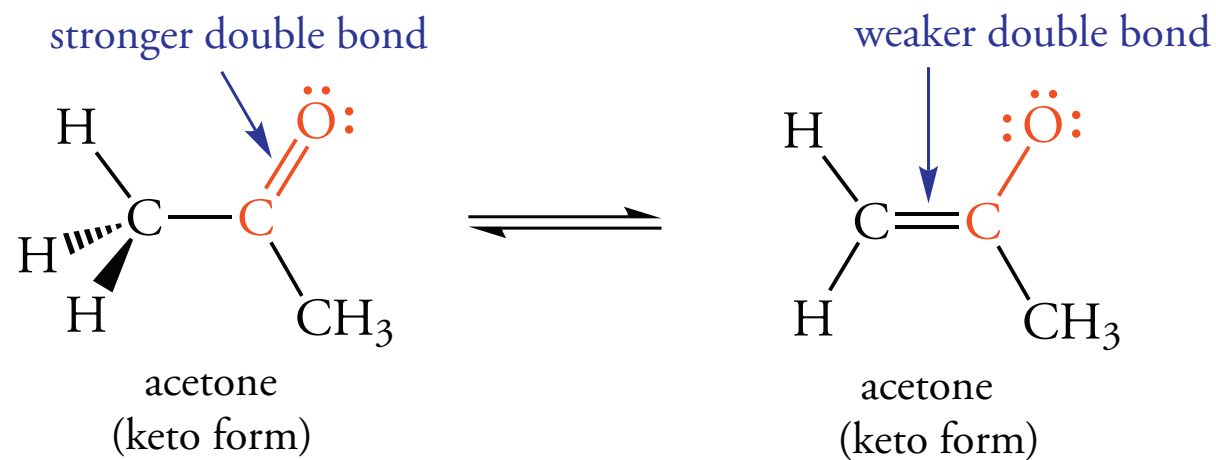
acidic  $\alpha$ -hydrogen atom



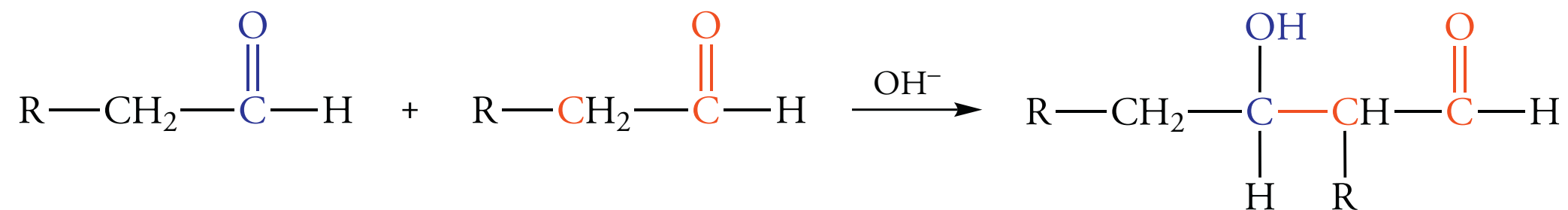




## Keto-Enol Equilibria

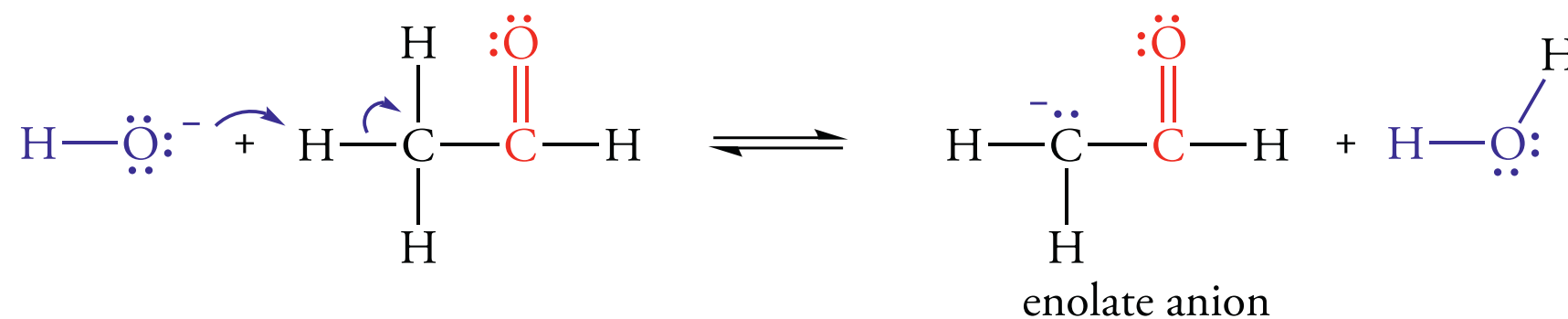


## 10.11 THE ALDOL CONDENSATION

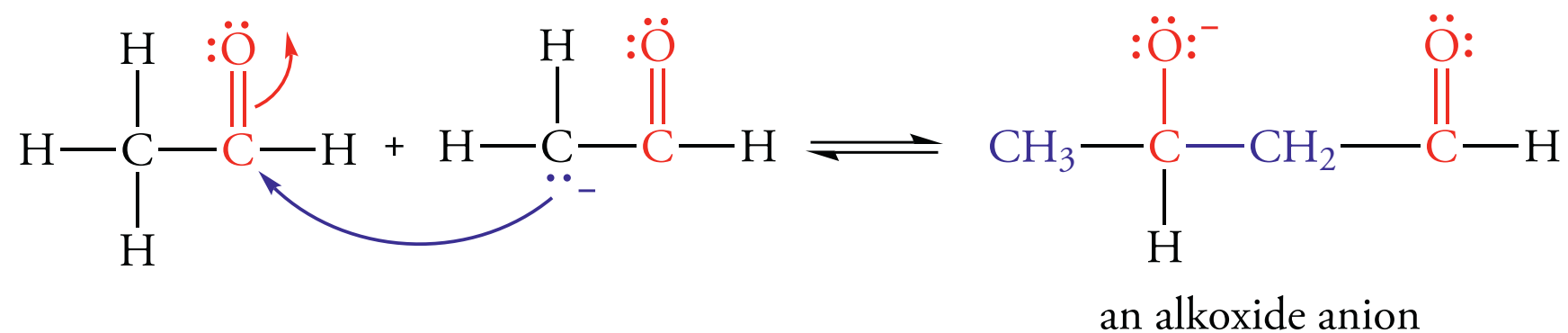


The aldol condensation occurs in two steps.

1. One aldehyde molecule reacts with base ( $\text{OH}^-$ ) at its  $\alpha$  C—H bond to give a nucleophilic enolate anion.

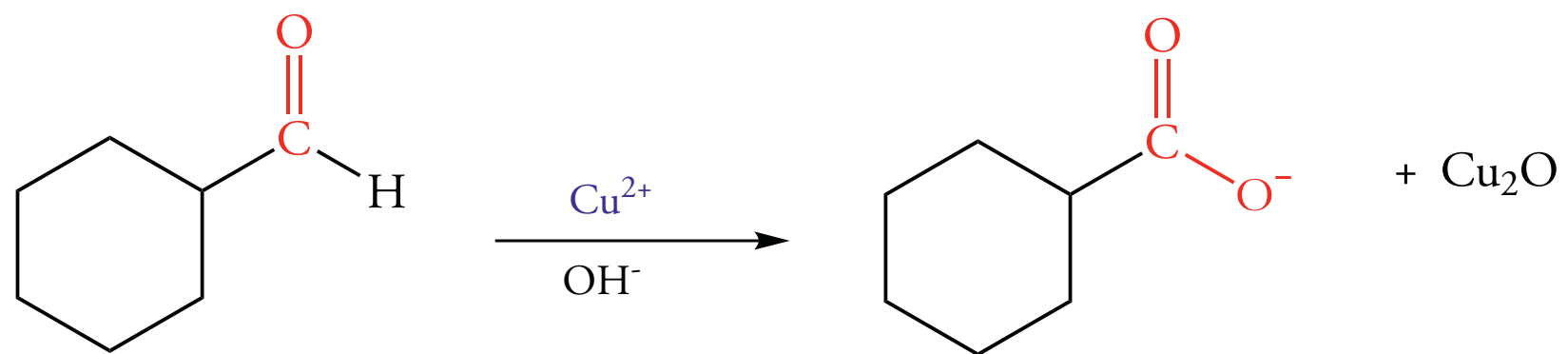
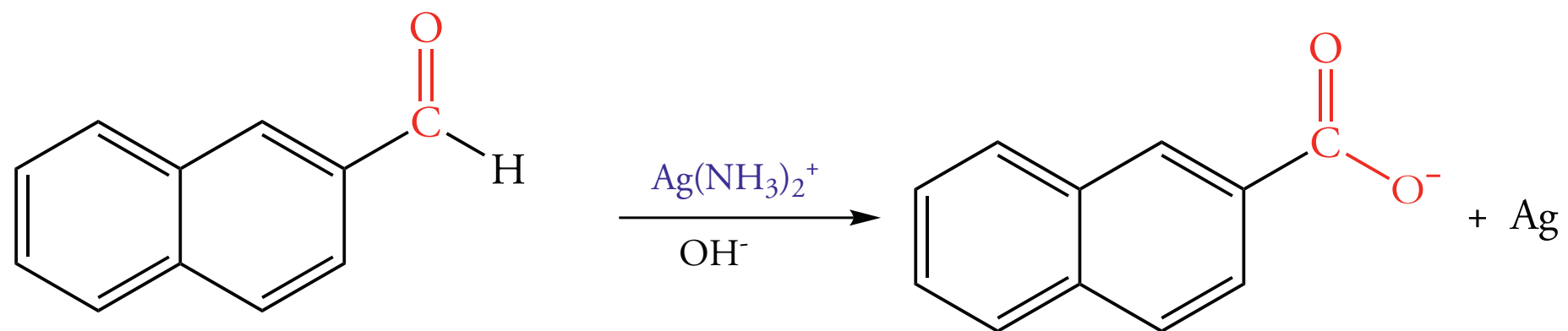


2. The nucleophilic enolate anion reacts with the carbonyl carbon atom of another aldehyde molecule. The alkoxide ion product is the conjugate base of an aldol.

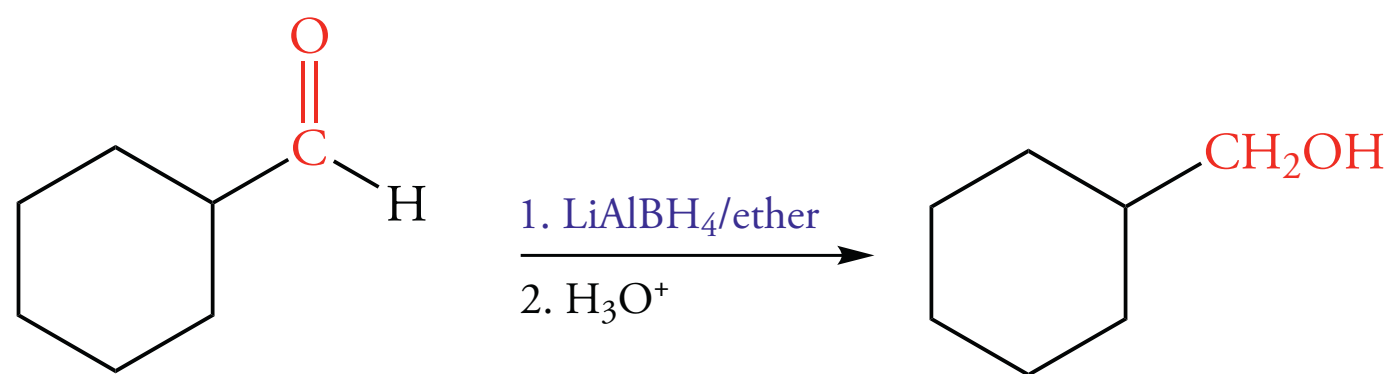
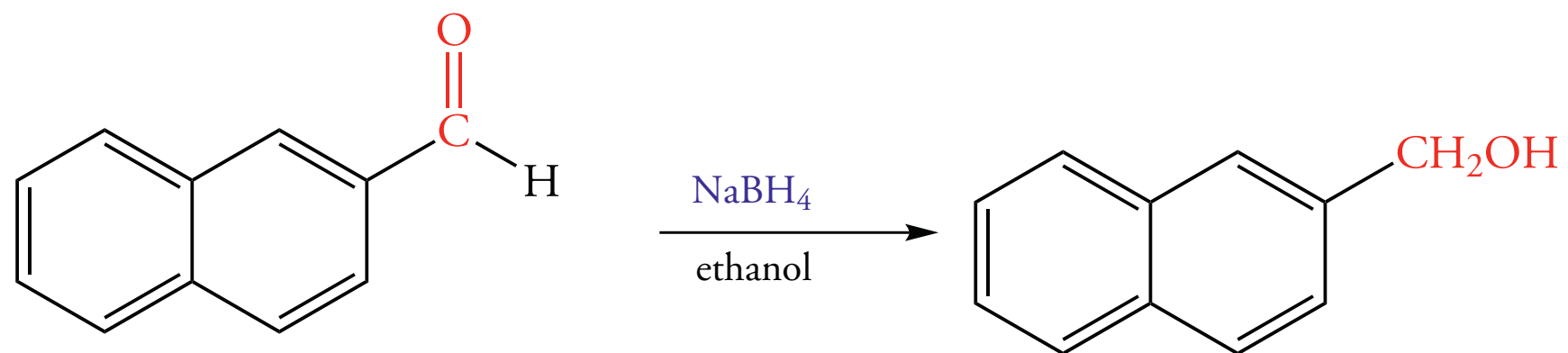


## Summary of Reactions

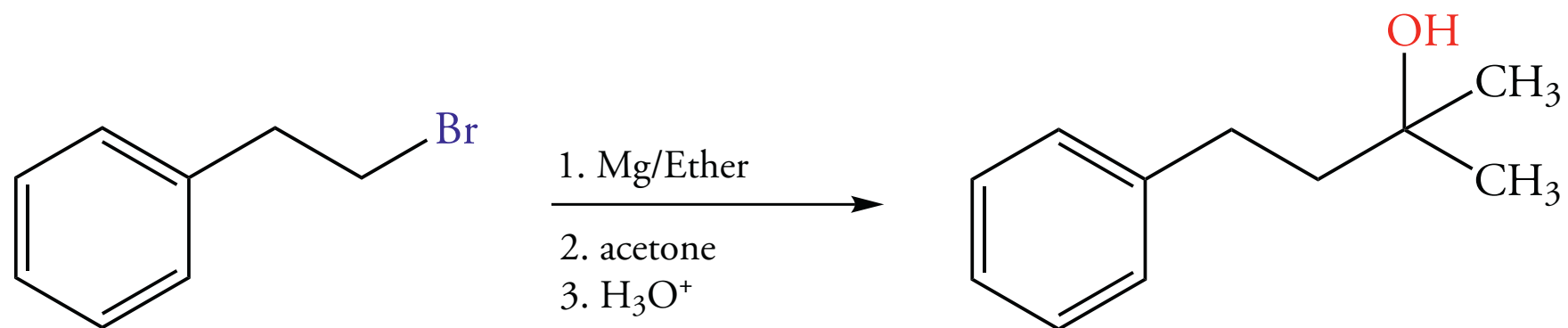
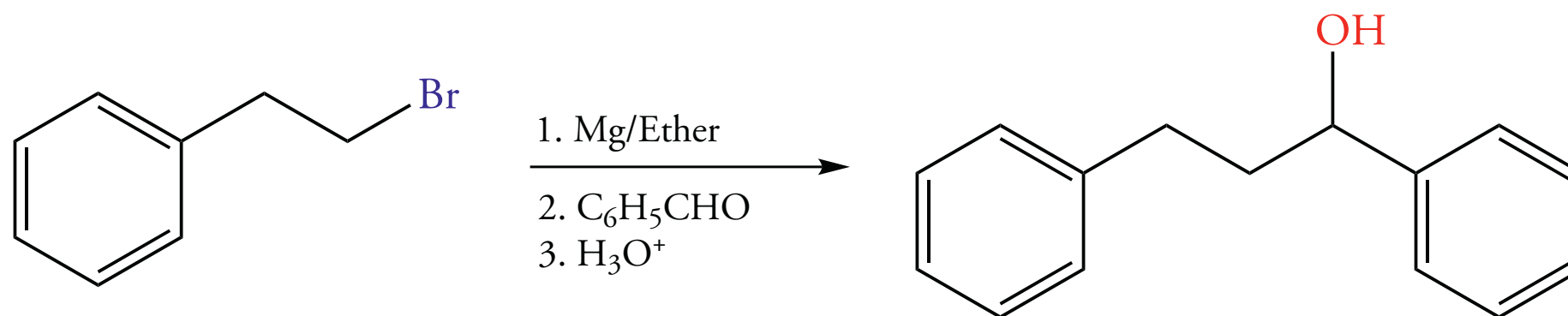
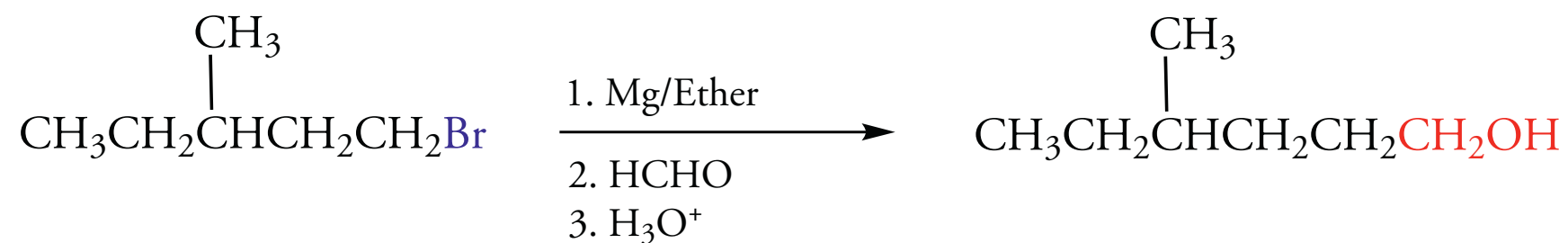
### 1. Oxidation of Aldehydes (Section 10.4)



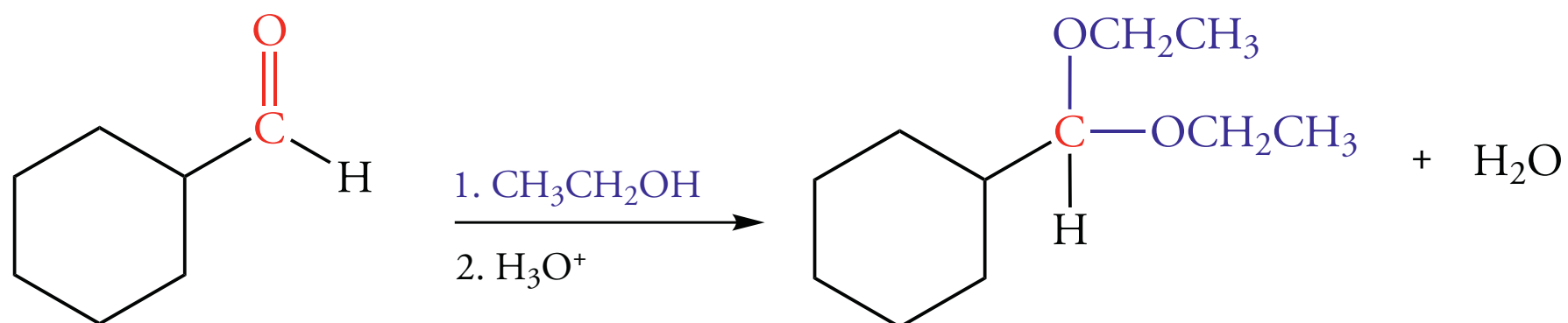
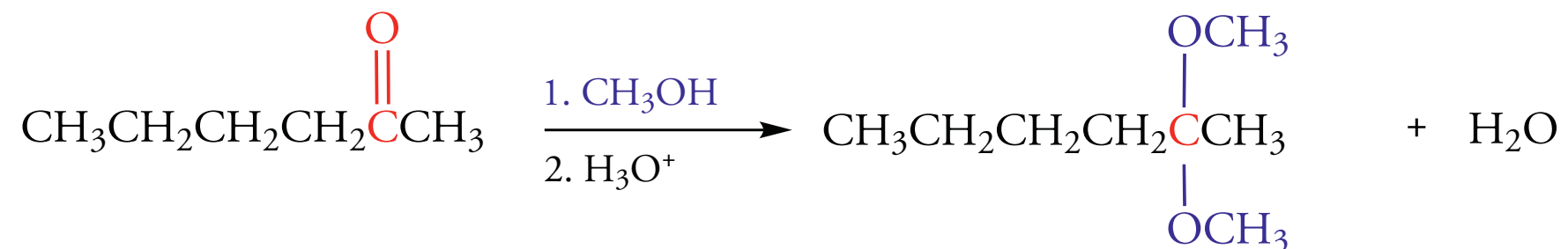
## 2. Reduction of Aldehydes and Ketones to Alcohols (Section 10.4)



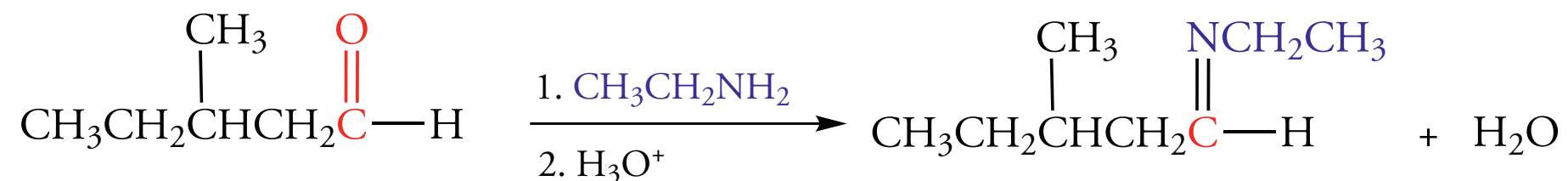
#### 4. Reduction of Aldehydes and Ketones to Methylene Groups (Section 10.4)



## 5. Formation of Acetals and Ketals (Section 10.8)



## 6. Addition of Nitrogen Compounds to Carbonyl Compounds (Section 10.9)



## 7. Aldol Condensation (Section 10.10)

