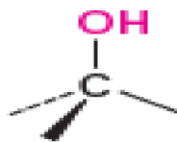


# Alcohols

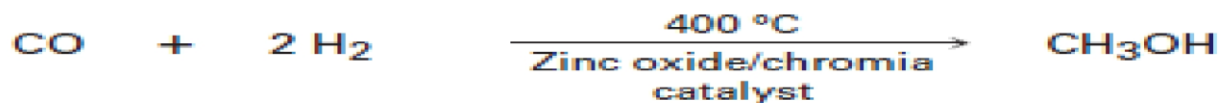
**Alcohols** can be thought of as organic derivatives of water in which one of the water's hydrogens is replaced by an organic group: H-O-H versus R-O-H. In practice, the group name *alcohol* is restricted to compounds that have their -OH group bonded to a saturated,  $sp^3$ -hybridized carbon atom.



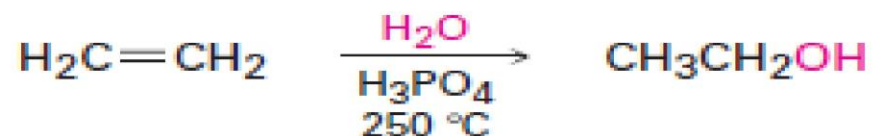
An alcohol

Alcohols occur widely in nature and have many industrial and pharmaceutical applications. Methanol, for instance, is one of the most important of all industrial chemicals.

Methanol is manufactured by catalytic reduction of carbon monoxide with hydrogen gas. Methanol is toxic to humans, causing blindness in small doses (15 mL) and death in larger amounts (100–250 mL). Industrially, it is used both as a solvent and as a starting material for production of formaldehyde ( $\text{CH}_2\text{O}$ ) and acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ).

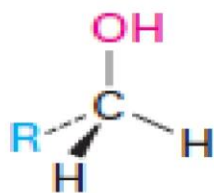


Ethanol was one of the first organic chemicals to be prepared and purified. Its production by fermentation of grains and sugars and its purification by distillation. Ethanol for industrial use as a solvent or chemical intermediate is largely obtained by acid-catalyzed hydration of ethylene at high temperature.

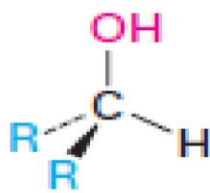


## Naming Alcohols

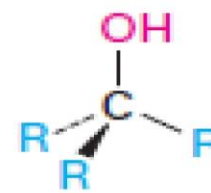
Alcohols are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ), or tertiary ( $3^\circ$ ), depending on the number of organic groups bonded to the hydroxyl-bearing carbon.



A primary ( $1^\circ$ ) alcohol



A secondary ( $2^\circ$ ) alcohol



A tertiary ( $3^\circ$ ) alcohol

Simple alcohols are named by the IUPAC system as derivatives of the parent alkane, using the suffix *-ol*.

### Rule 1

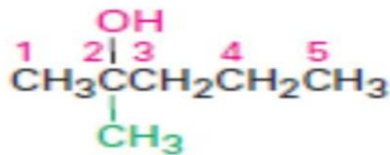
Select the longest carbon chain containing the hydroxyl group, and derive the parent name by replacing the *-e* ending of the corresponding alkane with *-ol*. The *-e* is deleted to prevent the occurrence of two adjacent vowels: propanol rather than propaneol, for example.

### Rule 2

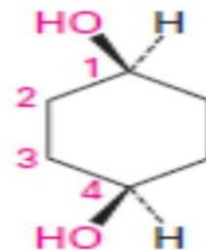
Number the alkane chain beginning at the end nearer the hydroxyl group.

### Rule 3

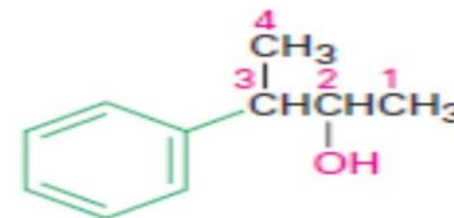
Number the substituents according to their position on the chain, and write the name, listing the substituents in alphabetical order and identifying the position to which the -OH is bonded. Note that in naming *cis*-1,4-cyclohexanediol, the final *-e* of cyclohexane is not deleted because the next letter, *d*, is not a vowel; that is, cyclohexanediol rather than cyclohexandiol. Also, as with alkenes, newer IUPAC naming recommendations place the locant immediately before the suffix rather than before the parent.



**2-Methyl-2-pentanol**  
(New: **2-Methylpentan-2-ol**)

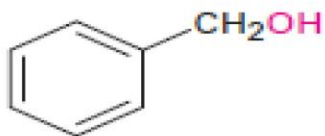


**cis-1,4-Cyclohexanediol**  
(New: **cis-Cyclohexane-1,4-diol**)

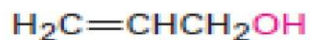


**3-Phenyl-2-butanol**  
(New: **3-Phenylbutan-2-ol**)

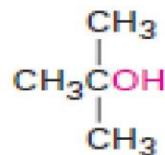
Some simple and widely occurring alcohols have common names that are accepted by IUPAC. For example:



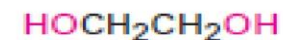
**Benzyl alcohol**  
(phenylmethanol)



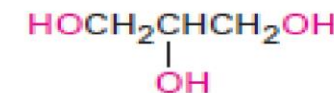
**Allyl alcohol**  
(2-propen-1-ol)



**tert-Butyl alcohol**  
(2-methyl-2-propanol)



**Ethylene glycol**  
(1,2-ethanediol)



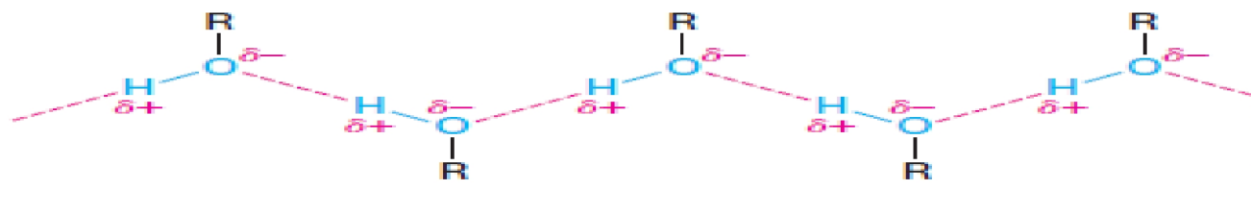
**Glycerol**  
(1,2,3-propanetriol)

## Properties of Alcohols

Alcohols have nearly the same geometry around the oxygen atom as water. The R-O-H bond angle has an approximately tetrahedral value ( $108.5^\circ$  in methanol, for instance), and the oxygen atom is  $sp^3$ -hybridized. Also like water, alcohols have higher boiling points than might be expected, because of hydrogen-bonding. A positively polarized -OH hydrogen atom from one molecule is attracted to a lone pair of electrons on the electronegative oxygen atom of another molecule, resulting in a

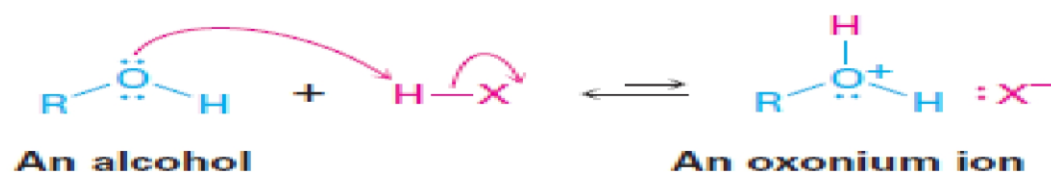


weak force that holds the molecules together (**Figure 17-1**). These intermolecular attractions must be overcome for a molecule to break free from the liquid and enter the vapor state, so the boiling temperature is raised. For example, 1-propanol (MW = 60), butane (MW = 58), and chloroethane (MW = 65) have similar molecular weights, yet 1-propanol boils at 97 °C, compared with 20.5 °C for the alkane and 12.5 °C for the chloroalkane.

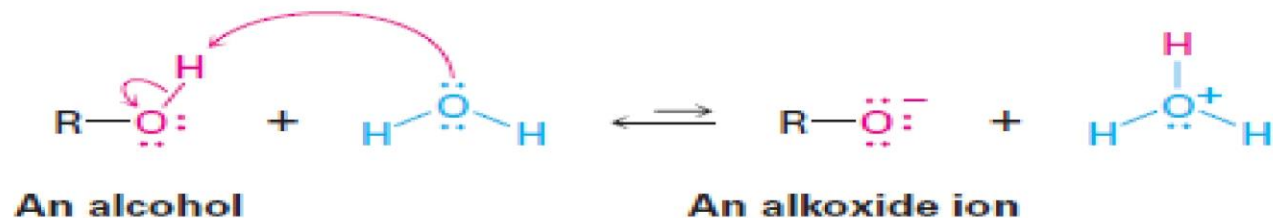


**Figure 17-1** Hydrogen bonding in alcohols. Attraction between a positively polarized -OH hydrogen and negatively polarized oxygen holds molecules together. The electrostatic potential map of methanol shows the positively polarized -OH hydrogen and the negatively polarized oxygen.

Another similarity with water is that alcohols and phenols are both weakly basic and weakly acidic. As weak bases, they are reversibly protonated by strong acids to yield oxonium ions,  $\text{ROH}_2^+$ .



As weak acids, they dissociate slightly in dilute aqueous solution by donating a proton to water, generating  $\text{H}_3\text{O}^+$  and an **alkoxide ion,  $\text{RO}^-$** .




The strength of any acid HA in water can be expressed by an acidity constant,  $K_a$ .

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \quad pK_a = -\log K_a$$

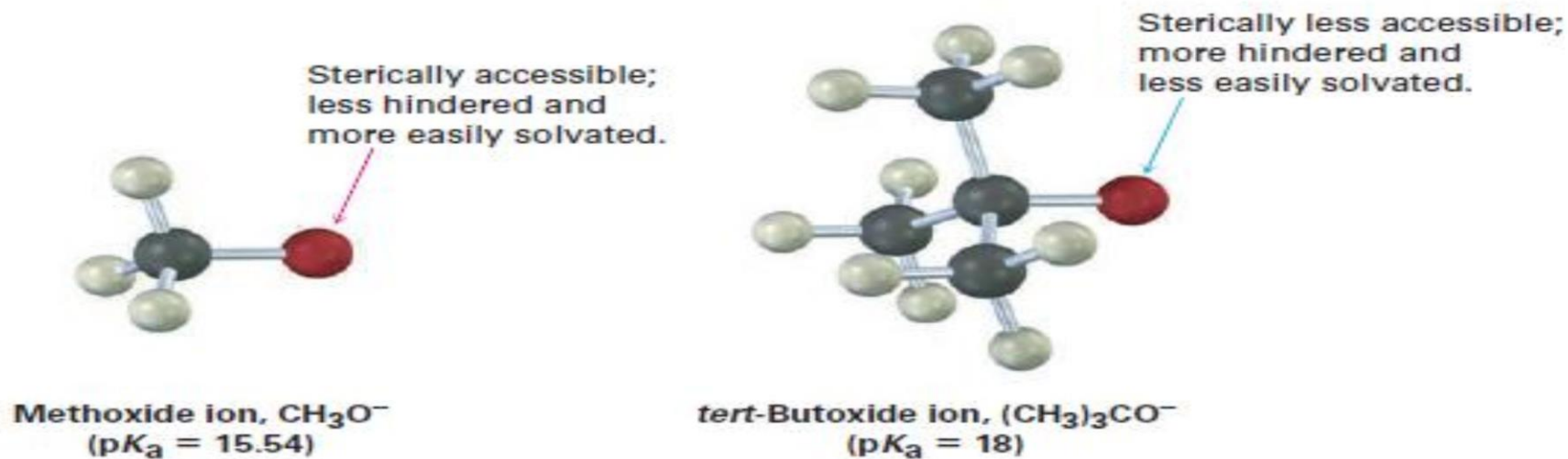
Compounds with a smaller  $K_a$  and larger  $pK_a$  are less acidic, whereas compounds with a larger  $K_a$  and smaller  $pK_a$  are more acidic. As shown in **Table 17-1**, simple alcohols like methanol and ethanol are about as acidic as water, but the more highly substituted *tert*-butyl alcohol is somewhat weaker. Substituent groups also have a significant effect: 2,2,2-trifluoroethanol is approximately 3700 times stronger than ethanol, for instance.

**TABLE 17-1** Acidity Constants of Some Alcohols and Phenols

Compound	$pK_a$	
$(CH_3)_3COH$	18	 <p>Weaker acid</p> <p>Stronger acid</p>
$CH_3CH_2OH$	16	
$H_2O$	15.74	
$CH_3OH$	15.54	
$CF_3CH_2OH$	12.43	
<i>p</i> -Aminophenol	10.46	
$CH_3SH$	10.3	
<i>p</i> -Methylphenol	10.17	
Phenol	9.89	
<i>p</i> -Chlorophenol	9.38	
<i>p</i> -Nitrophenol	7.15	

The effect of alkyl substitution on alcohol acidity is due primarily to solvation of the alkoxide ion formed on acid dissociation. The more readily the alkoxide ion is solvated by water, the more stable it is, the more its formation is energetically favored, and the greater the acidity of the parent alcohol. For example, the oxygen atom of an unhindered alkoxide ion, such as that from methanol, is sterically accessible and is easily solvated by water.

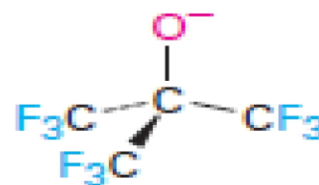
The oxygen atom of a hindered alkoxide ion, however, such as that from *tert*-butyl alcohol, is less easily solvated and is therefore less stable.



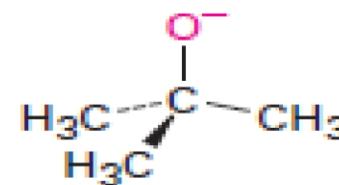
Inductive effects are also important in determining alcohol acidities. Electron-withdrawing halogen substituents, for instance, stabilize an alkoxide ion by spreading the charge over a larger volume, thus making the alcohol more acidic. Compare, for example, the acidities of ethanol ( $\text{p}K_a = 16$ ) and 2,2,2-trifluoroethanol ( $\text{p}K_a = 12.43$ ), or of *tert*-butyl alcohol ( $\text{p}K_a = 18$ ) and nonafluoro-*tert*-butyl alcohol ( $\text{p}K_a = 5.4$ ).



Electron-withdrawing groups stabilize the alkoxide ion and lower the  $pK_a$  of the alcohol.



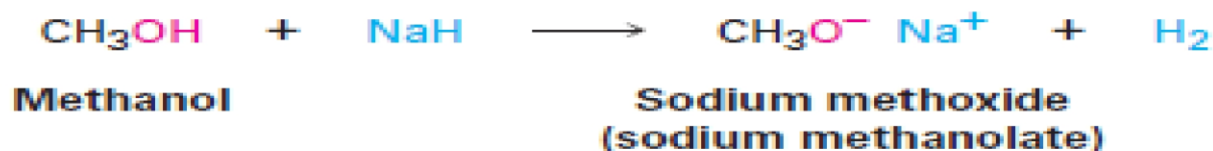
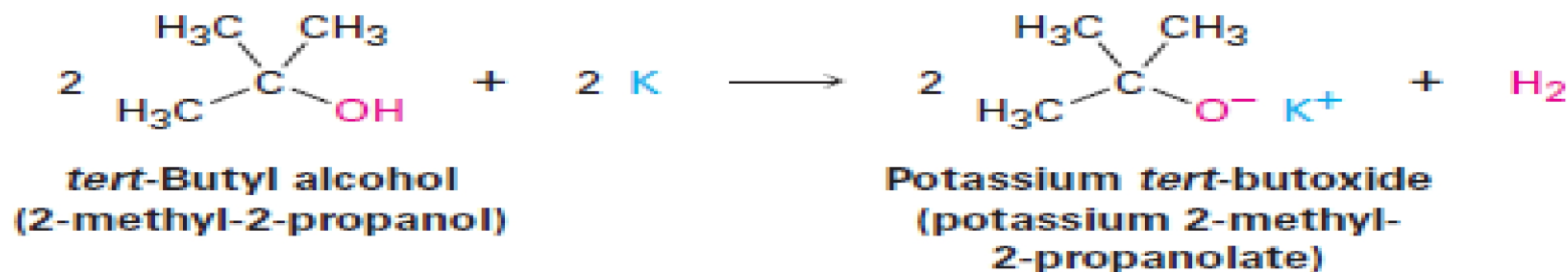
versus

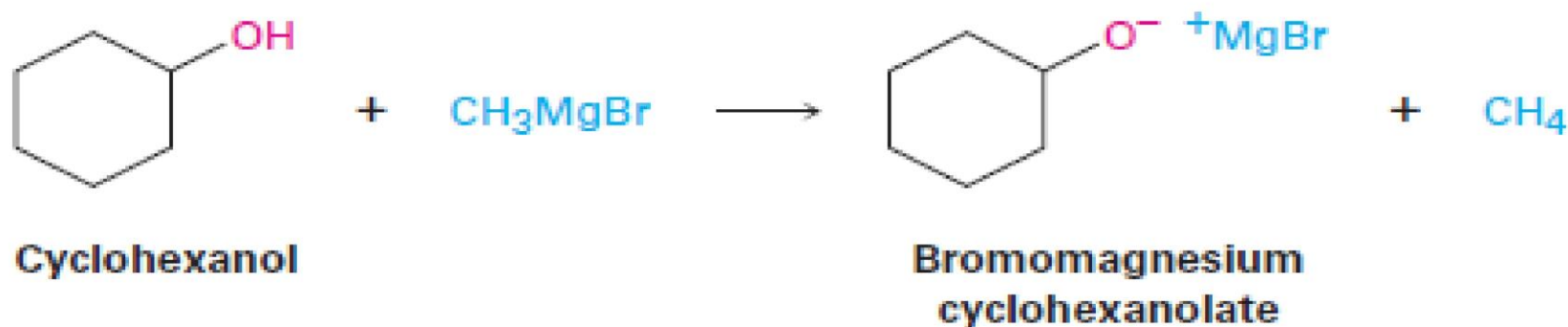
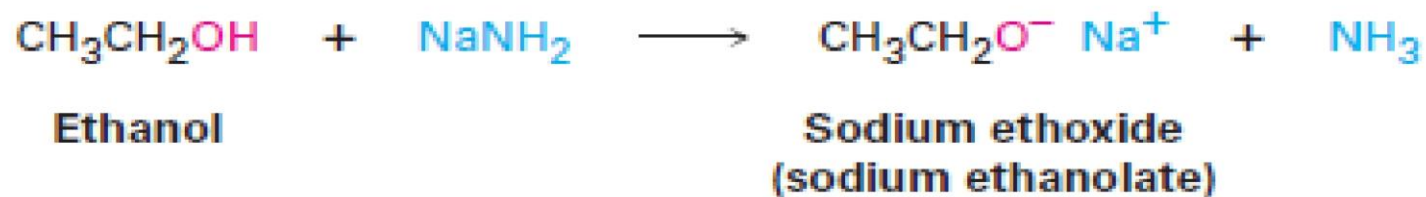


$pK_a = 5.4$

$pK_a = 18$

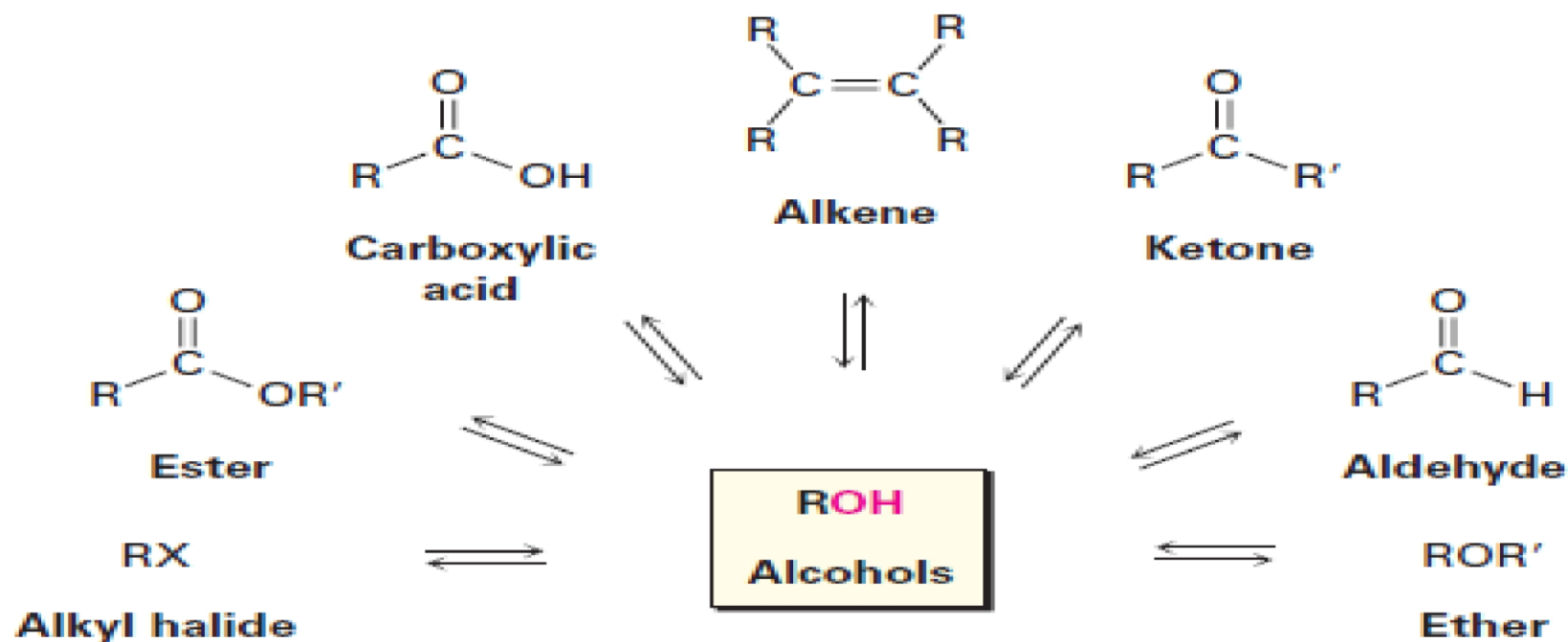
Because alcohols are weak acids, they don't react with weak bases, such as amines or bicarbonate ion, and they only react to a limited extent with metal hydroxides such as NaOH. Alcohols do, however, react with alkali metals and with strong bases such as sodium hydride (NaH), sodium amide (NaNH<sub>2</sub>), and Grignard reagents (RMgX). Alkoxides are themselves bases that are frequently used as reagents in organic chemistry. They are named systematically by adding the *-ate* suffix to the name of the alcohol. Methanol becomes methanolate, for instance.





## Preparation of Alcohols: A Review

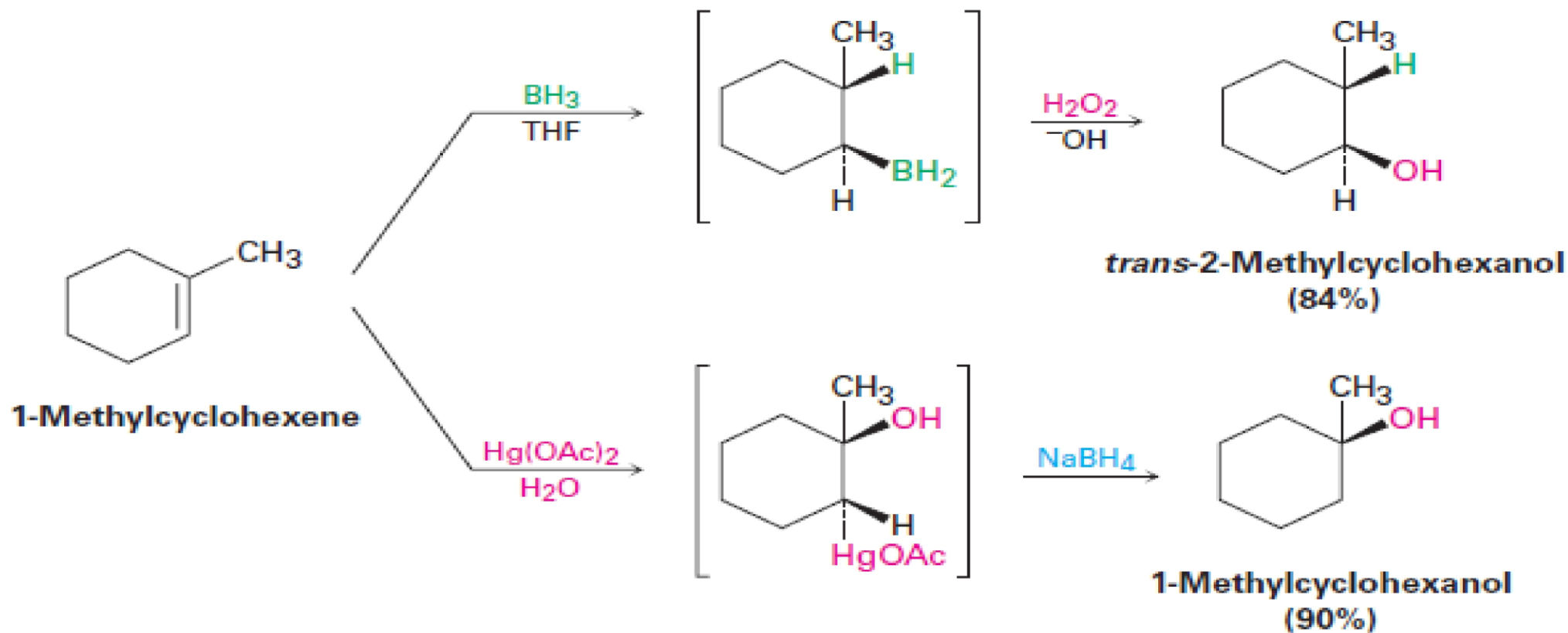
Alcohols occupy a central position in organic chemistry. They can be prepared from many other kinds of compounds (alkenes, alkyl halides, ketones, esters, and aldehydes, among others), and they can be transformed into an equally wide assortment of compounds (**Figure 17-3**).



**Figure 17-3** The central position of alcohols in organic chemistry. Alcohols can be prepared from, and converted into, many other kinds of compounds.

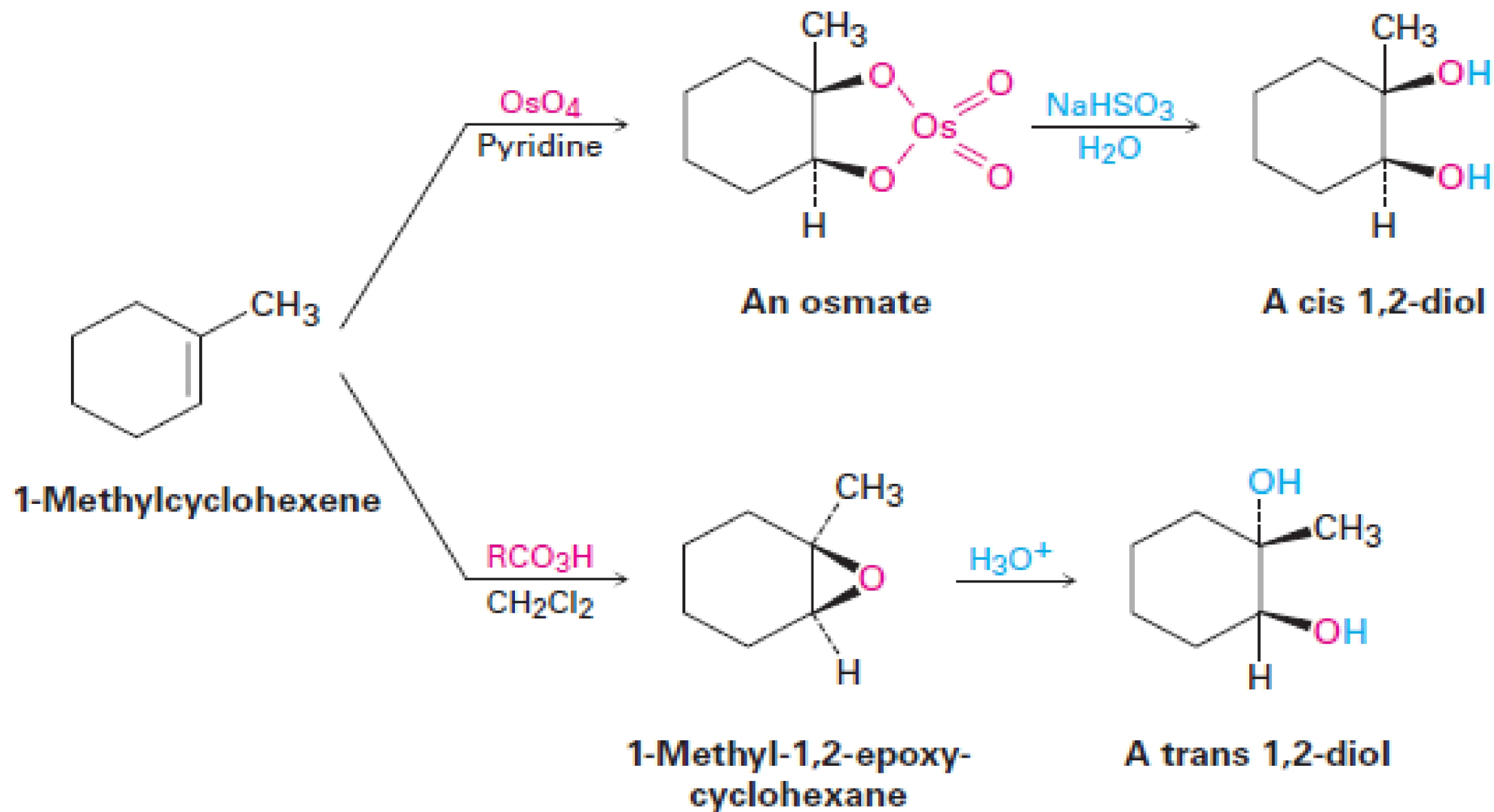
We've already seen several methods of alcohol synthesis:

- Alcohols can be prepared by hydration of alkenes. Because the direct hydration of alkenes with aqueous acid is generally a poor reaction in the laboratory, two indirect methods are commonly used. Hydroboration–oxidation yields the syn, non-Markovnikov hydration product, whereas oxymercuration–demercuration yields the Markovnikov hydration product.



1,2-Diols can be prepared either by direct hydroxylation of an alkene with  $\text{OsO}_4$  followed by reduction with  $\text{NaHSO}_3$  or by acid-catalyzed hydrolysis of an epoxide. The  $\text{OsO}_4$  reaction occurs with syn stereochemistry to give a cis diol, and epoxide opening occurs with anti-stereochemistry to give a trans diol.





## Alcohols from Carbonyl Compounds: Reduction

The most general method for preparing alcohols, both in the laboratory and in living organisms, is by the reduction of a carbonyl compound. Just as reduction of an alkene adds hydrogen to a C=C bond to give an alkane, reduction of a carbonyl compound adds hydrogen to a C=O bond to give an alcohol. Any kind of carbonyl compound can be reduced, including aldehydes, ketones, carboxylic acids, and esters.



## Reduction of Aldehydes and Ketones

Aldehydes are easily reduced to give primary alcohols, and ketones are reduced to give secondary alcohols.



Dozens of reagents are used in the laboratory to reduce aldehydes and ketones, depending on the circumstances, but sodium borohydride,  $NaBH_4$ , is usually chosen because of its safety and ease of handling. Sodium borohydride is a white, crystalline solid that can be weighed in the open atmosphere and used in either water or alcohol solution.