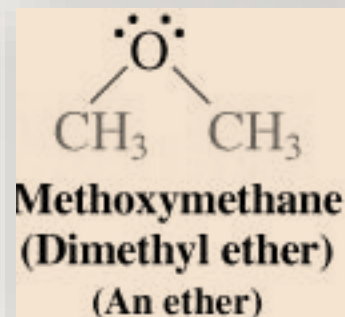
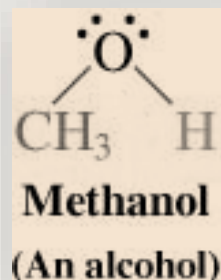
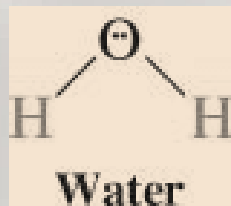


# **CHM-134 ORGANIC CHEMISTRY**

## **CHAPTER-7: ALCOHOLS, PHENOLS AND THIOLS**

Alcohols can be thought of as a derivative of water in which a hydrogen atom has been replaced by an alkyl group.

Replacement of the 2nd hydrogen on the water molecule leads to an ether.



## 7.1 NAMING THE ALCOHOLS

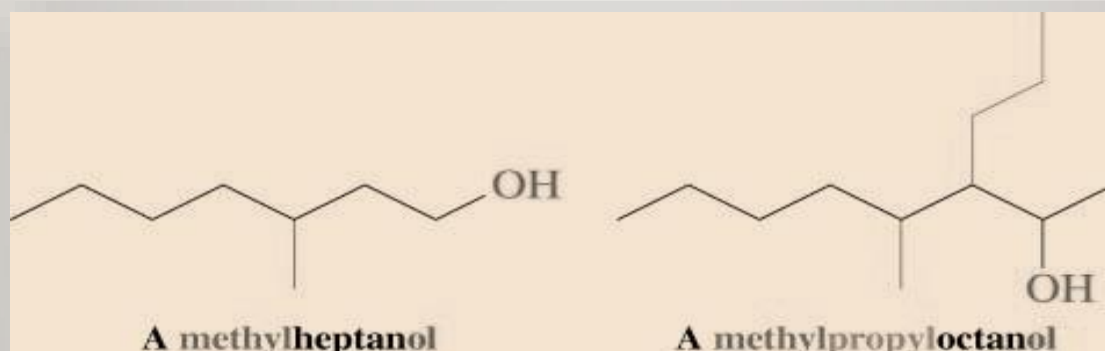
The systematic nomenclature of alcohols treats them as derivatives of alkanes.

The **-e** is dropped from the alkane name and is replaced by **-ol**.

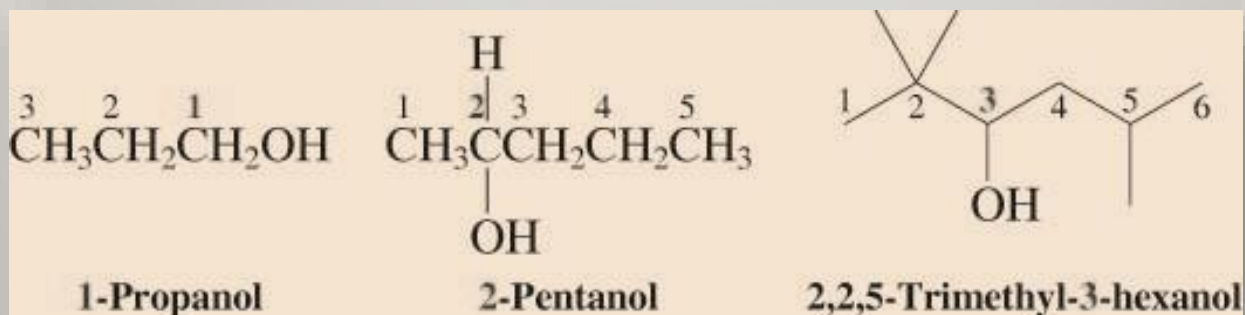
Alkane → Alkanol

In complicated, branched alkanes, the name of the alcohol is based on the longest chain containing the **-OH** group.

Other substituents are then named using the IUPAC rules for hydrocarbons.

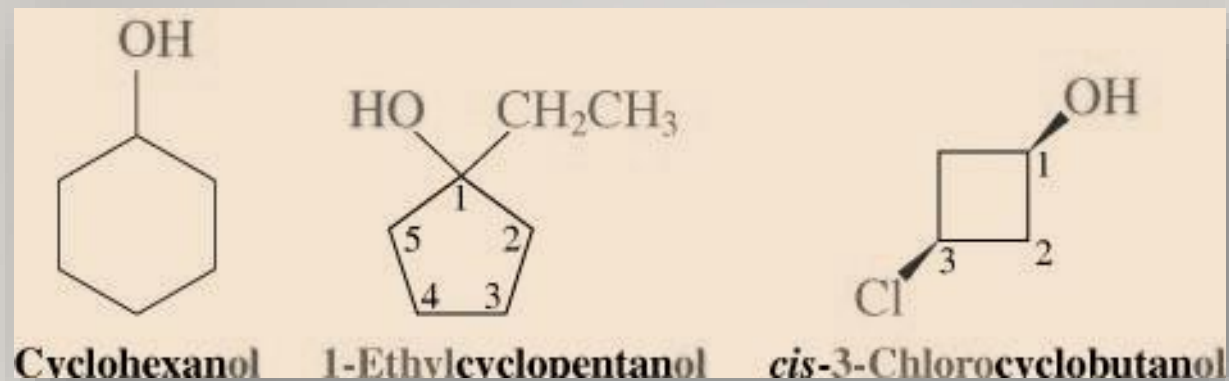


The number of the chain is from the end closest to the **OH** group.

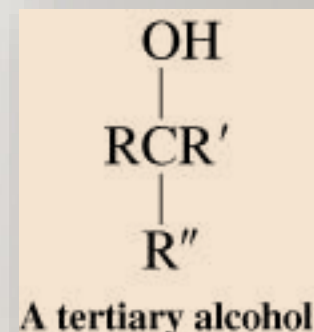
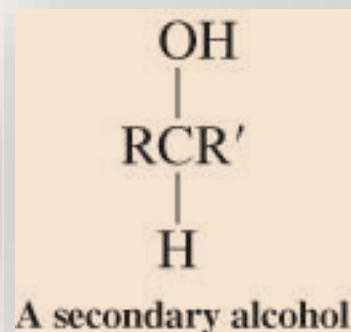
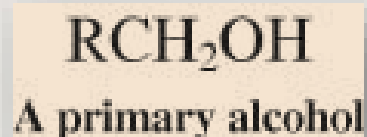


## 7.1 NAMING THE ALCOHOLS

Cyclic alcohols are called cycloalkanols and the carbon carrying the  $\text{-OH}$  group is the 1 carbon.



Alcohols can be classified as **primary**, **secondary** or tertiary:



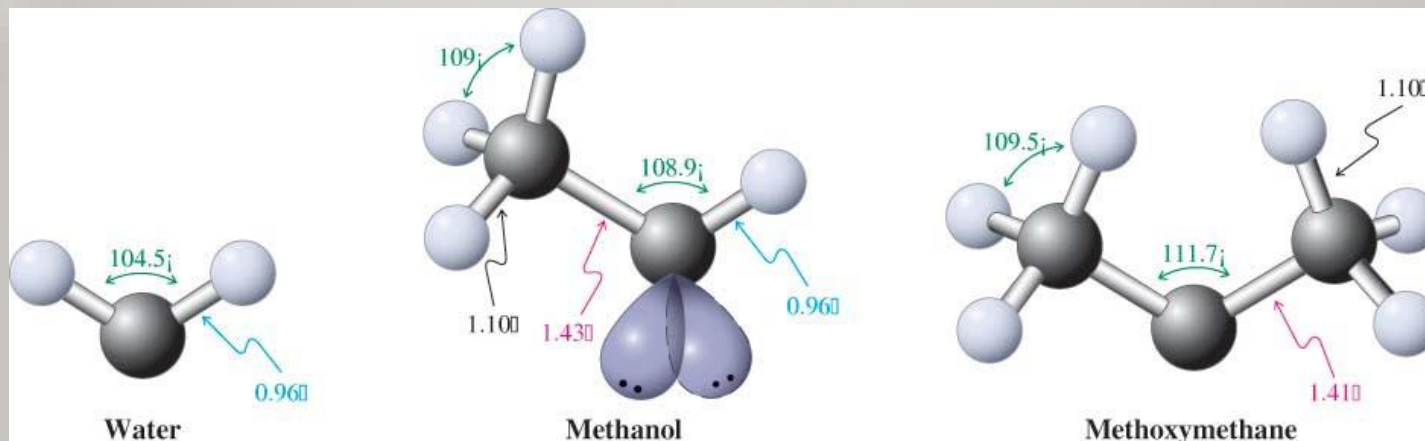
In common notation (non-IUPAC), the word alcohol directly follows the name of the alkane.

- Methyl alcohol
- Isopropyl alcohol
- Tert-Butyl alcohol

## 7.2 STRUCTURAL AND PHYSICAL PROPERTIES OF ALCOHOLS

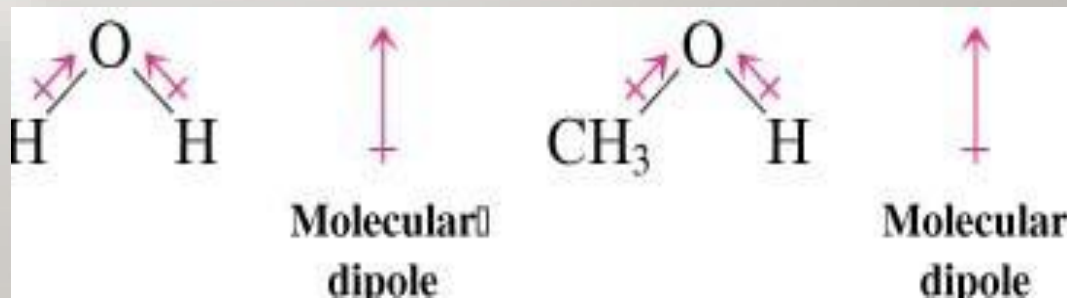
The structure of alcohols resembles that of water.

In the structures of water, methanol, and methoxymethane, the oxygen atoms are all  $sp^3$  hybridized and their bond angles are all nearly tetrahedral.



- ✓ The O-H bond is shorter than the C-H bonds.
- ✓ The bond strength of the O-H bond is greater than that of the C-H bonds.

Due to the electronegativity difference between oxygen and hydrogen, the O-H bond is polar.



## 7.2 STRUCTURAL AND PHYSICAL PROPERTIES OF ALCOHOLS

Hydrogen bonding raises the boiling points and water solubilities of alcohols.

- ❑ Alcohols have unusually high boiling points compared to the corresponding alkanes and haloalkanes.
- ❑ Hydrogen bonding between alcohol molecules is much stronger than the London forces and dipole-dipole interactions in alkanes and haloalkanes, although much weaker than O-H covalent bonds.
  - $\text{O} \cdots \text{H}-\text{O} \quad \Delta H^\circ \sim 5-6 \text{ kcal mol}^{-1}$
  - Covalent O-H  $\Delta H^\circ = 104 \text{ kcal mol}^{-1}$ .
- ❖ The extensive network of H-bonds between neighboring alcohol molecules makes it difficult for a molecule to leave the surface of the liquid.
- ❖ An alcohol molecule makes slightly less than 2 hydrogen bonds to other alcohol molecules on the average. A water molecule, on the other hand, forms hydrogen bonds to slightly less than 4 other water molecules. Water has an abnormally high boiling point for a molecule of its size due to this hydrogen bonding.
- ❖ Many alcohols are appreciably soluble in water whereas their parent alkanes are not.
- ❖ Alkanes and most alkyl chains are said to be hydrophobic (water-hating).
- ❖ In order to dissolve, alkanes must interrupt the strong hydrogen bonding between water molecules which is then replaced by weaker dipole-induced dipole forces ( $\Delta H > 0$ ).

## 7.2 STRUCTURAL AND PHYSICAL PROPERTIES OF ALCOHOLS

- ❖ In addition, long hydrocarbon chains force water molecules to form a cage-like (or clathrate) structure about the non-polar chain which greatly reduces the entropy of the water molecules involved ( $\Delta S < 0$ ). The  $-\text{OH}$  groups of alcohols (as well as groups like  $-\text{COOH}$  and  $-\text{NH}_2$ ) are said to be hydrophilic (water-loving) and enhance solubility.
- ❖ The longer the alkyl chain of an alcohol, the lower its solubility in water (it looks more and more like an alkane). Alcohols are popular protic solvents for  $\text{S}_\text{N}2$  reactions.

**TABLE 8-1**

**Physical Properties of Alcohols and Selected Analogous Haloalkanes and Alkanes**

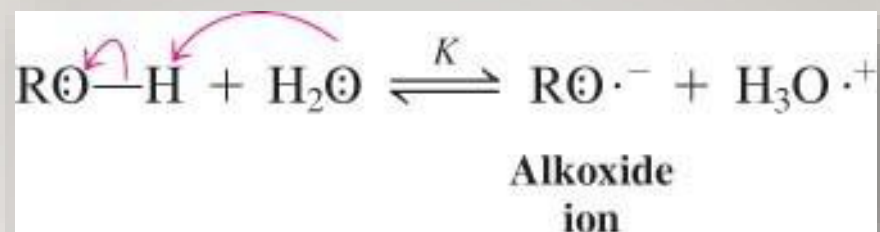
Compound	IUPAC name	Common name	Melting point ( $^{\circ}\text{C}$ )	Boiling point ( $^{\circ}\text{C}$ )	Solubility in $\text{H}_2\text{O}$ at $23^{\circ}\text{C}$
$\text{CH}_3\text{OH}$	Methanol	Methyl alcohol	$-97.8$	$65.0$	Infinite
$\text{CH}_3\text{Cl}$	Chloromethane	Methyl chloride	$-97.7$	$-24.2$	$0.74 \text{ g}/100 \text{ mL}$
$\text{CH}_4$	Methane		$-182.5$	$-161.7$	$3.5 \text{ mL (gas)}/100 \text{ mL}$
$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol	Ethyl alcohol	$-114.7$	$78.5$	Infinite
$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane	Ethyl chloride	$-136.4$	$12.3$	$0.447 \text{ g}/100 \text{ mL}$
$\text{CH}_3\text{CH}_3$	Ethane		$-183.3$	$-88.6$	$4.7 \text{ mL (gas)}/100 \text{ mL}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1-Propanol	Propyl alcohol	$-126.5$	$97.4$	Infinite
$\text{CH}_3\text{CH}_2\text{CH}_3$	Propane		$-187.7$	$-42.1$	$6.5 \text{ mL (gas)}/100 \text{ mL}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	1-Butanol	Butyl alcohol	$-89.5$	$117.3$	$8.0 \text{ g}/100 \text{ mL}$
$\text{CH}_3(\text{CH}_2)_4\text{OH}$	1-Pentanol	Pentyl alcohol	$-79$	$138$	$2.2 \text{ g}/100 \text{ mL}$



## 7.3 ALCOHOLS AS ACIDS AND BASES

The acidity of alcohols resembles that of water.

The acidity constant for an alcohol can be defined as:



$$K_a = K[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{RO}^-]}{[\text{ROH}]} \text{ mol L}^{-1}, \text{ and } \text{p}K_a = -\log K_a$$

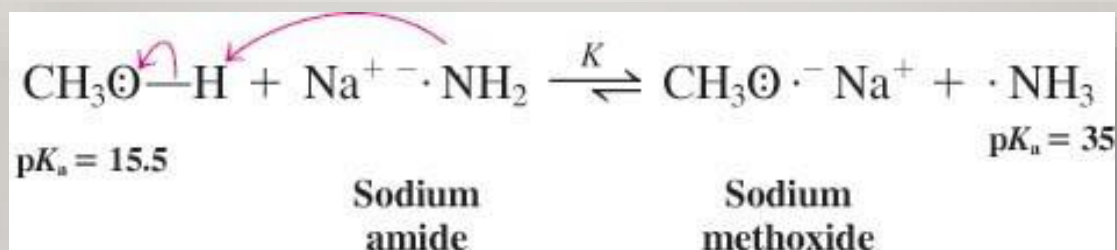
TABLE 8-2

$\text{p}K_a$  Values of Alcohols and Related Compounds in Water

Compound	$\text{p}K_a$	Compound	$\text{p}K_a$
$\text{H}_2\text{O}$	15.7	$\text{ClCH}_2\text{CH}_2\text{OH}$	14.3
$\text{CH}_3\text{OH}$	15.5	$\text{CF}_3\text{CH}_2\text{OH}$	12.4
$\text{CH}_3\text{CH}_2\text{OH}$	15.9	$\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$	14.6
$(\text{CH}_3)_2\text{CHOH}$	17.1	$\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	15.4
$(\text{CH}_3)_3\text{COH}$	18		

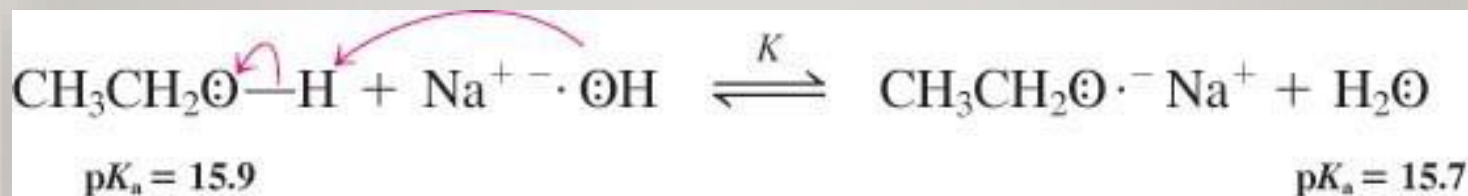
## 7.3 ALCOHOLS AS ACIDS AND BASES

- ✓ Alcohols are acidic compared to alkanes and haloalkanes because the electronegative oxygen atom is able to stabilize the negative charge of the alkoxide ion.
- ✓ To drive the alcohol/alkoxide equilibrium towards the conjugate base, a base stronger than alkoxide must be used to remove the proton:



The equilibrium constant for this reaction is about  $10^{19.5}$ .

Alkoxides in less than stoichiometric equilibrium concentrations can be generated by adding a metal hydroxide to an alcohol:



At equimolar starting concentrations, about  $\frac{1}{2}$  of the alcohol is converted to alkoxide. If the alcohol is the solvent, all of the base is in the alkoxide form (Le Chatelier's principle).



## 7.3 ALCOHOLS AS ACIDS AND BASES

Steric disruption and inductive effects control the acidity of alcohols.

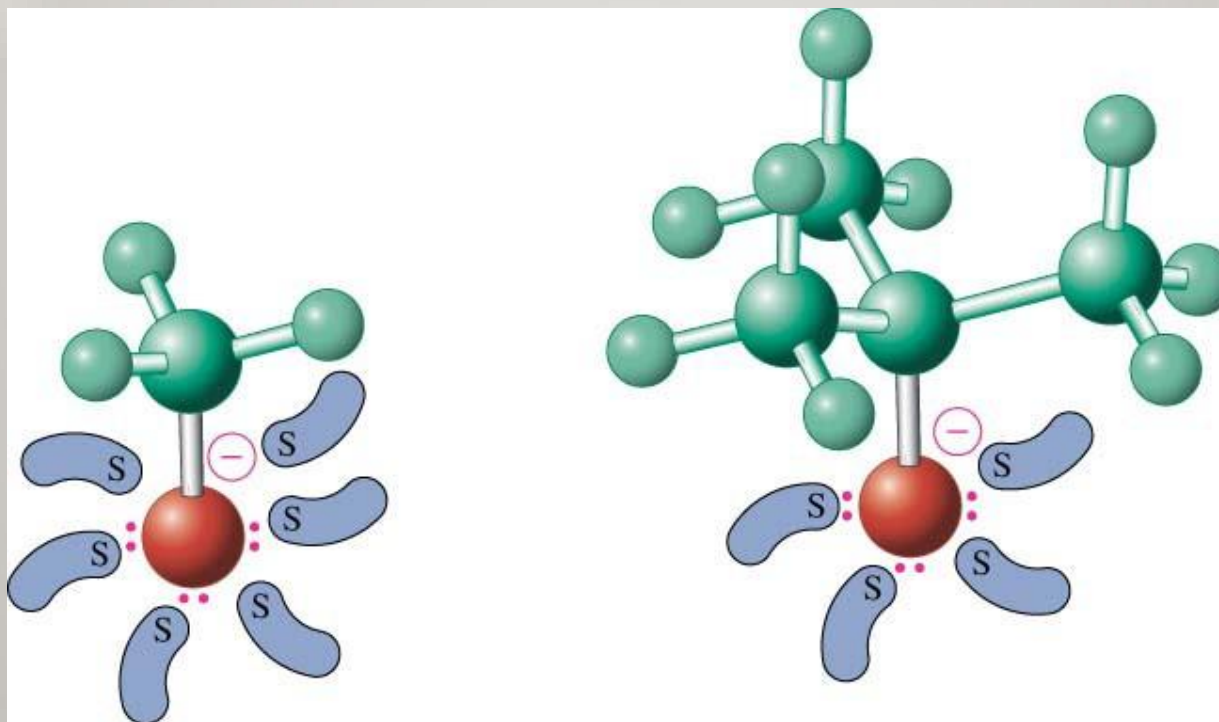
*The acidity of an alcohol varies (relative  $pK_a$  in solution):*

**Strongest acid**

$\text{CH}_3\text{OH} < \text{primary} < \text{secondary} < \text{tertiary}$

**Weakest acid**

This ordering is due to solvation and hydrogen bonding in the more sterically hindered alcohols.



## 7.3 ALCOHOLS AS ACIDS AND BASES

- ❑ The presence of halogens in the alcohol increases the acidity of the alcohol due to an inductive effect.
- ❑ The electronegative halogen atom polarizes the X-C bond producing a partial positive charge on the carbon atom. This charge is further transmitted through the C-O  $\sigma$ -bond to the oxygen atom which is then better able to stabilize the negative charge on the alkoxide oxygen.
- ❑ Inductive effects increase with the number of electronegative groups and decreases with the distance from the oxygen.

The lone electron pairs on oxygen make alcohols basic.

Alcohols may be weakly basic as well as being acidic. Molecules that can be both acidic and basic are called **amphoteric**.

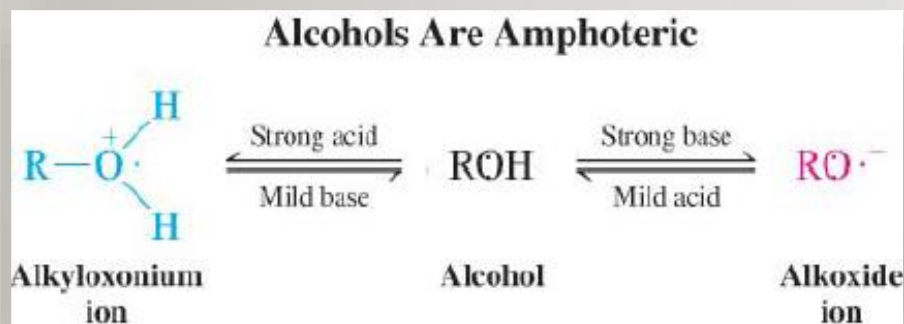


TABLE 8-3	
<i>pK<sub>a</sub></i> Values of Four Protonated Alcohols	
Compound	<i>pK<sub>a</sub></i>
CH <sub>3</sub> <sup>+</sup> OH <sub>2</sub>	-2.2
CH <sub>3</sub> CH <sub>2</sub> <sup>+</sup> OH <sub>2</sub>	-2.4
(CH <sub>3</sub> ) <sub>2</sub> CH <sup>+</sup> OH <sub>2</sub>	-3.2
(CH <sub>3</sub> ) <sub>3</sub> C <sup>+</sup> OH <sub>2</sub>	-3.8

Very strong acids are required to protonate alcohols.

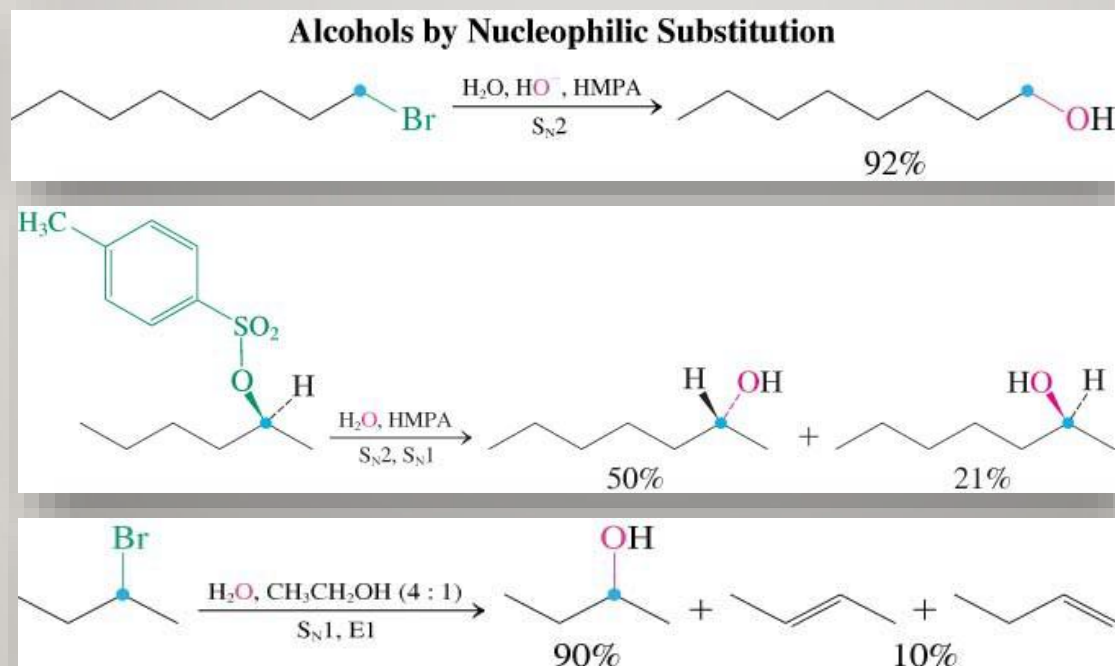
# 7.4 SYNTHESIS OF ALCOHOLS BY NUCLEOPHILIC SUBSTITUTION

If the required halides are available, the corresponding alcohols can be prepared by  $S_N2$  and  $S_N1$  processes using hydroxide and water respectively as nucleophiles.

These methods have some drawbacks:

- ❑ Bimolecular elimination is possible in hindered systems
- ❑ Tertiary halides form carbocations which may undergo E1 reactions.

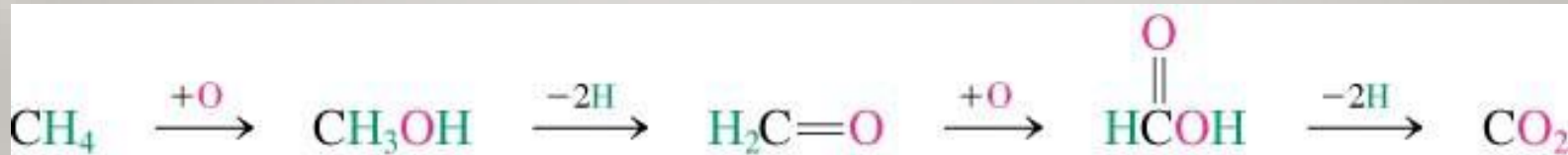
The use of polar, aprotic solvents alleviates some of these problems.



# 7.4 SYNTHESIS OF ALCOHOLS BY OXIDATION-REDUCTION

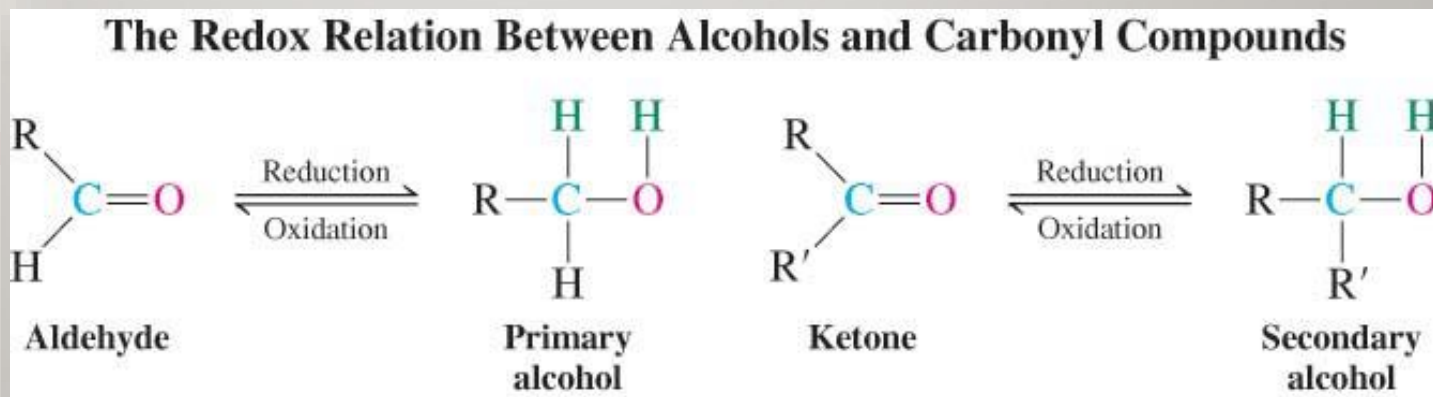
- ❖ Oxidation and reduction have special meanings in organic chemistry.
- ❖ A process that adds electronegative atoms such as halogen or oxygen to a molecule constitutes an oxidation.
- ❖ A process that removes hydrogen from a molecule also constitutes an oxidation.
- ❖ The reversal of either of these two steps constitutes a reduction.

## Step-by-Step Oxidation of CH<sub>4</sub> to CO<sub>2</sub>:



Aldehydes and primary alcohols, ketones and secondary alcohols can be interconverted using reduction and oxidation reactions involving 2 atoms of hydrogen:

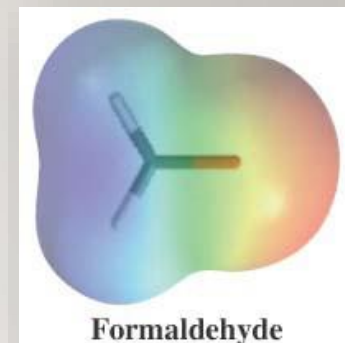
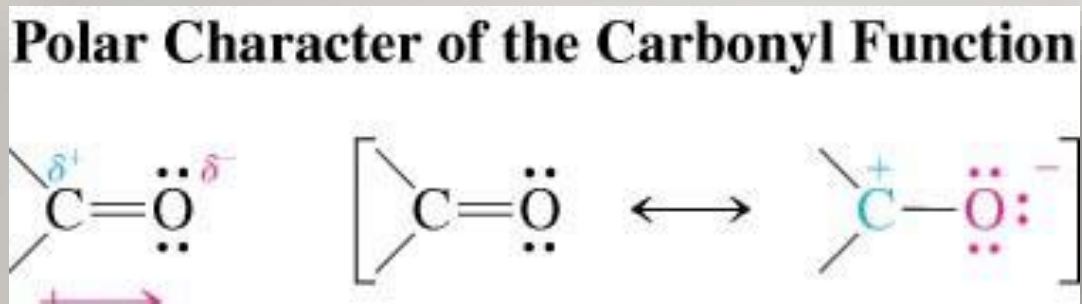
Reduction of carbonyl compounds is carried out using hydride reagents.



## 7.4 SYNTHESIS OF ALCOHOLS BY OXIDATION-REDUCTION

Alcohols can form by hydride reduction of the carbonyl group

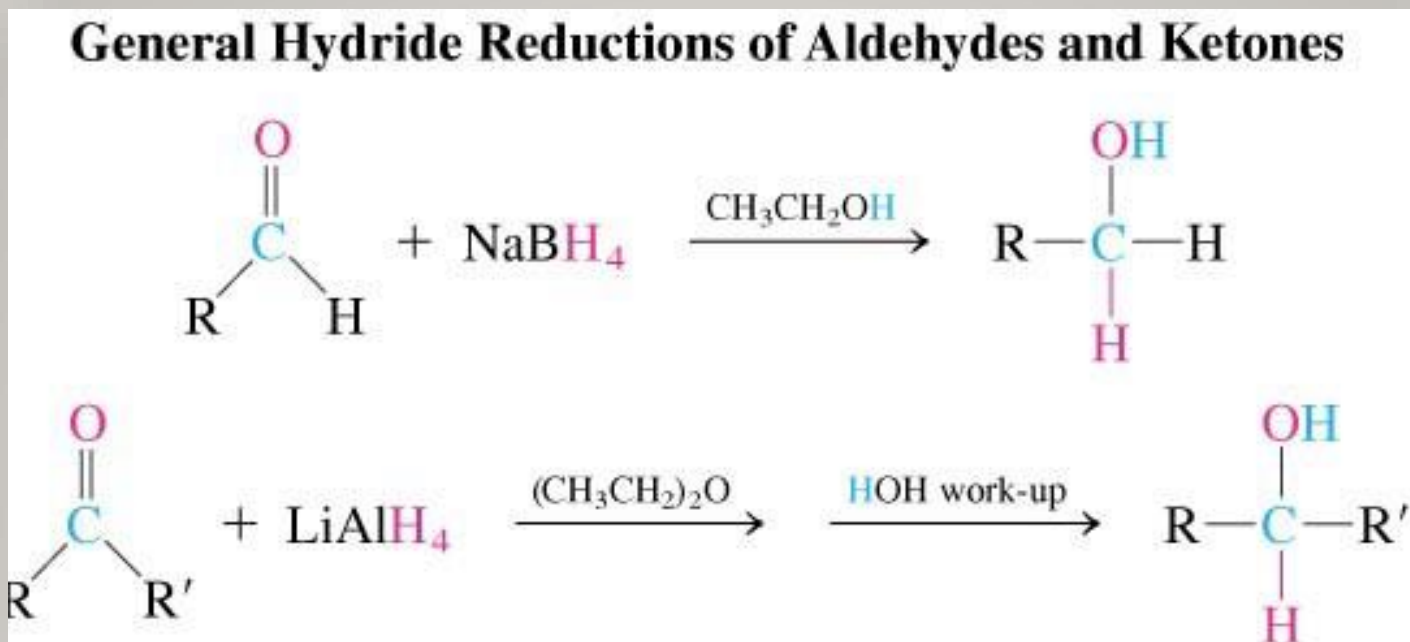
The carbonyl functional group is polarized due to the high electronegativity of the carbonyl oxygen atom:



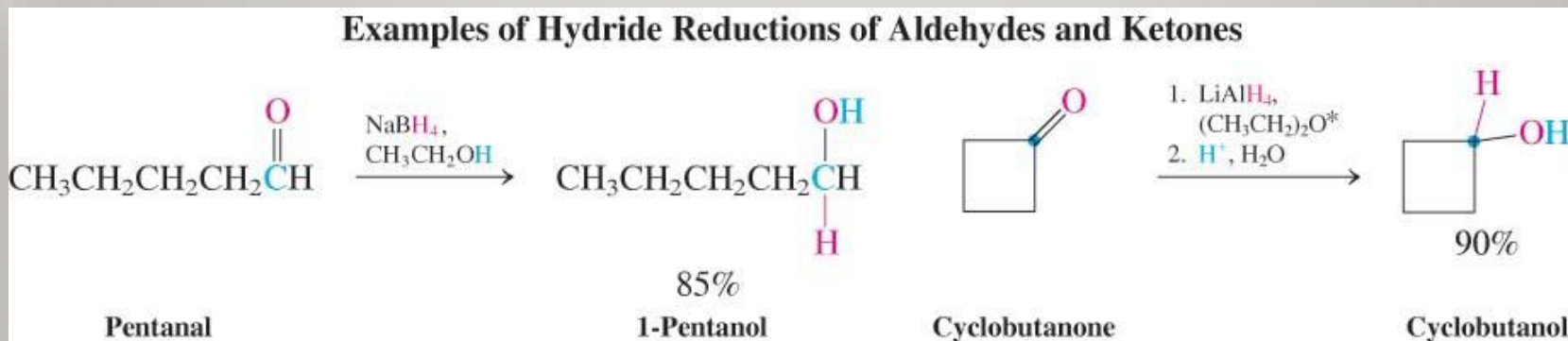
The carbonyl carbon can be attacked by a nucleophilic hydride ion,  $\text{H}^-$ , furnished by a hydride reagent.

Sodium borohydride,  $\text{NaBH}_4$ , and lithium aluminum hydride,  $\text{LiAlH}_4$ , are commonly used for hydride reductions because their solubilities are higher in common organic solvents than  $\text{LiH}$  and  $\text{NaH}$ .

## 7.4 SYNTHESIS OF ALCOHOLS BY OXIDATION-REDUCTION



These reductions are achieved by the addition of a  $\text{H}^-$  ion to the electropositive carbon and a proton to the electronegative oxygen.



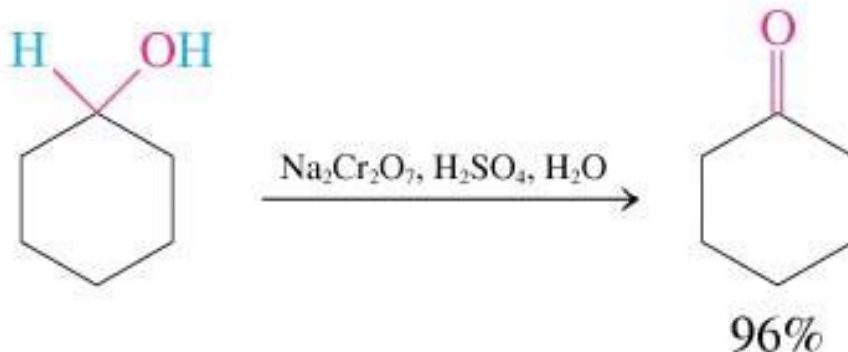


## 7.4 SYNTHESIS OF ALCOHOLS BY OXIDATION-REDUCTION

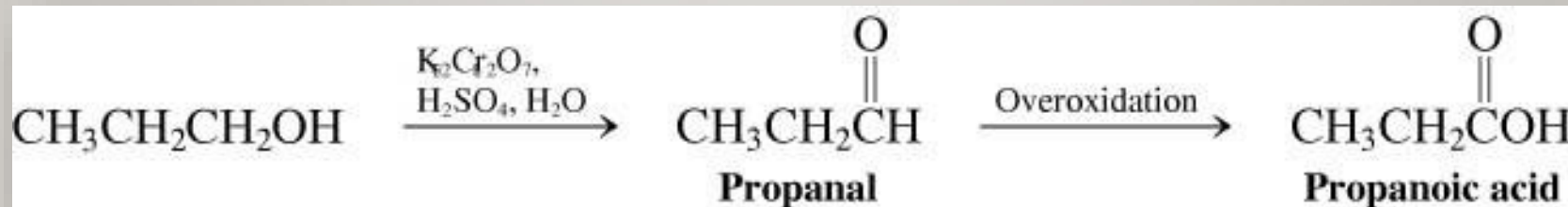
Alcohol synthesis by reduction can be reversed: chromium reagents.

Alcohols can be oxidized back to aldehydes and ketones using chromium (VI) compounds. During this process, the yellow-orange Cr(VI) species is reduced to a deep green Cr(III) species.  $K_2Cr_2O_7$  or  $Na_2Cr_2O_7$ , or  $CrO_3$  are commonly used Cr(VI) reagents. Secondary alcohols can be oxidized to ketones in aqueous solution:

### Oxidation of a Secondary Alcohol to a Ketone with Aqueous Cr(VI)

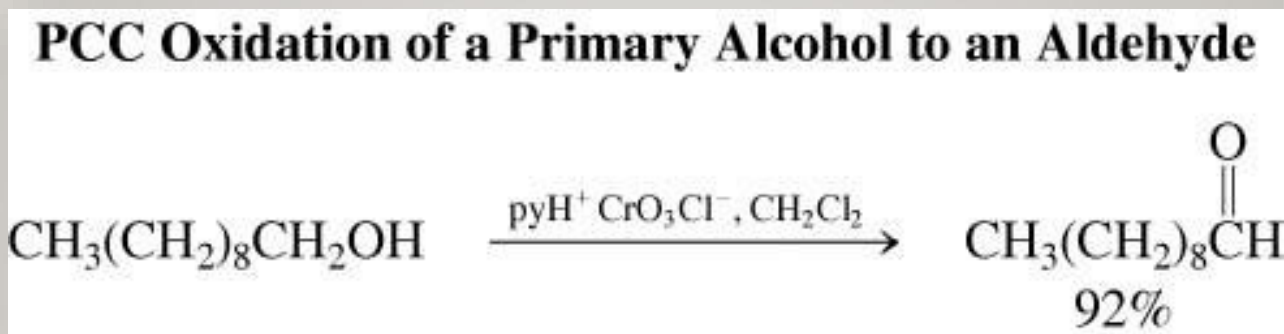


Primary alcohols tend to over oxidize to carboxylic acids when oxidized in aqueous solution:



## 7.4 SYNTHESIS OF ALCOHOLS BY OXIDATION-REDUCTION

Overoxidation of primary alcohols is not a problem in the absence of water. The oxidizing agent, pyridinium chlorochromate can be used in dichloromethane to successfully oxidize these alcohols:



- ❖ PCC oxidation is also used with secondary alcohols instead of the aqueous chromate method to minimize side reactions and improve yields.
- ❖ Tertiary alcohols cannot be oxidized by chromium reagents since the alcoholic carbon atom carries no hydrogen atoms and cannot readily form a double bond with the oxygen.

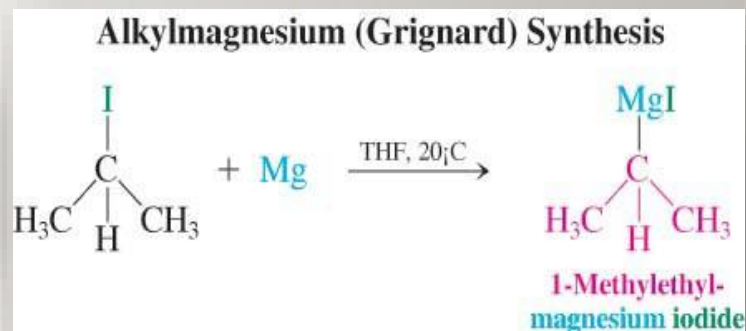
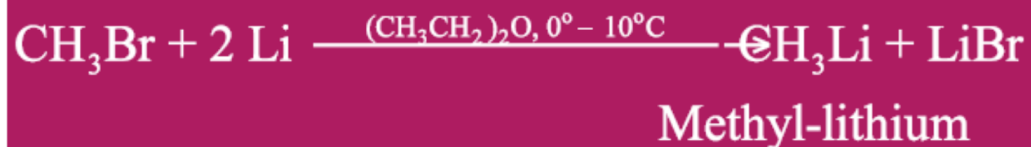
## 7.5 ORGANOMETALLIC REAGENTS IN THE SYNTHESIS OF ALCOHOLS

- ❖ If the carbonyl carbon of an aldehyde or ketone could be attacked by a nucleophilic carbon atom,  $R^-$ , instead of a hydride ion, both an alcohol and a new Carbon-Carbon bond would be formed.
- ❖ The class of compounds called organometallic reagents are strong bases and good nucleophiles and are useful in this kind of synthesis.

Alkyl lithium and alkyl magnesium reagents are prepared from haloalkanes

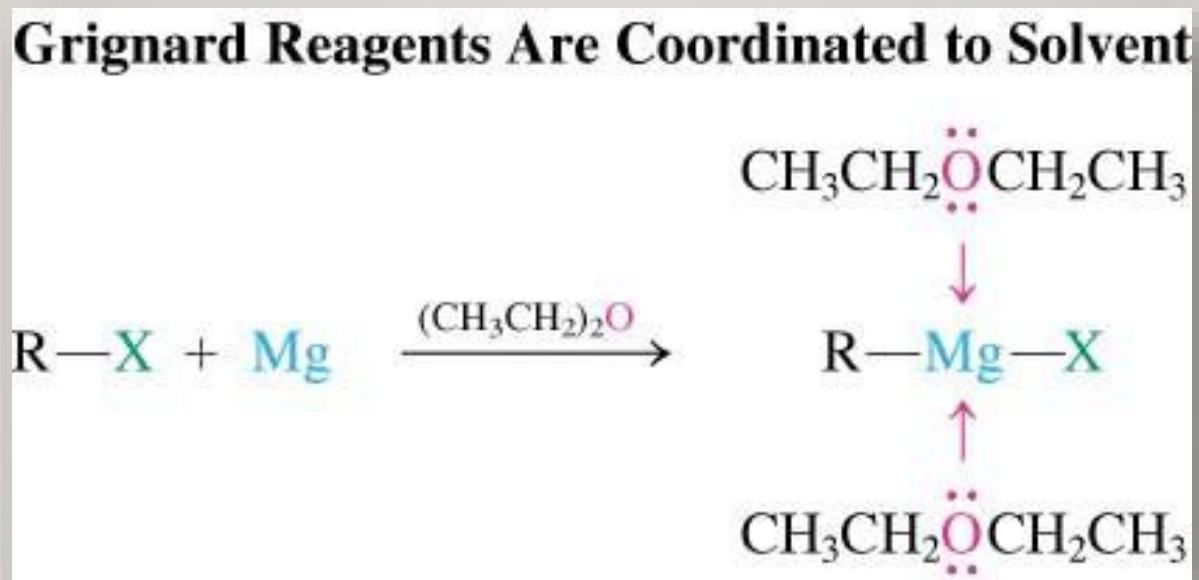
Alkyl lithium and alkyl magnesium compounds can be prepared by reaction of alkyl halides with lithium or magnesium in ethoxyethane (diethylether) or oxacyclopentane (THF).

The order of reactivity of the haloalkane is  $Cl < Br < I$



## 7.5 ORGANOMETALLIC REAGENTS IN THE SYNTHESIS OF ALCOHOLS

- Grignard reagents,  $\text{RMgX}$ , can be formed from primary, secondary, and tertiary haloalkane, as well as from haloalkenes and halobenzenes.
- Grignard reagents are very sensitive to moisture and air and are formed in solution and used immediately.
- The metal atoms in a Grignard reagent are electron-deficient and become coordinated to two solvent molecules:



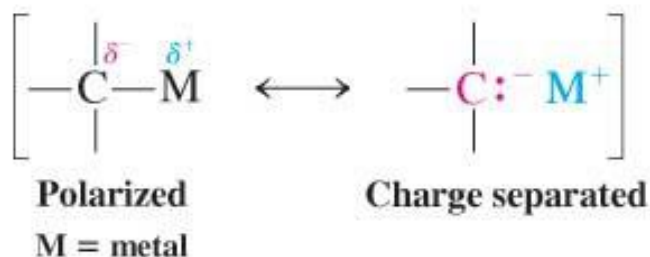
## 7.5 ORGANOMETALLIC REAGENTS IN THE SYNTHESIS OF ALCOHOLS

- The alkylmetal bond is strongly polar.

The carbon-lithium bond in  $\text{CH}_3\text{Li}$  has about 40% ionic character, and the carbon-magnesium bond in  $\text{CH}_3\text{MgCl}$  has about 35% ionic character.

The metal atom is strongly electropositive and is at the positive end of the dipole.

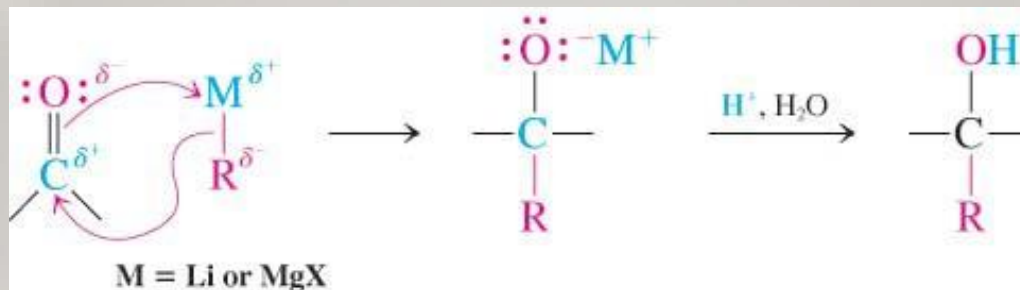
### Carbon-Metal Bond in Alkyl lithium and Alkylmagnesium Compounds



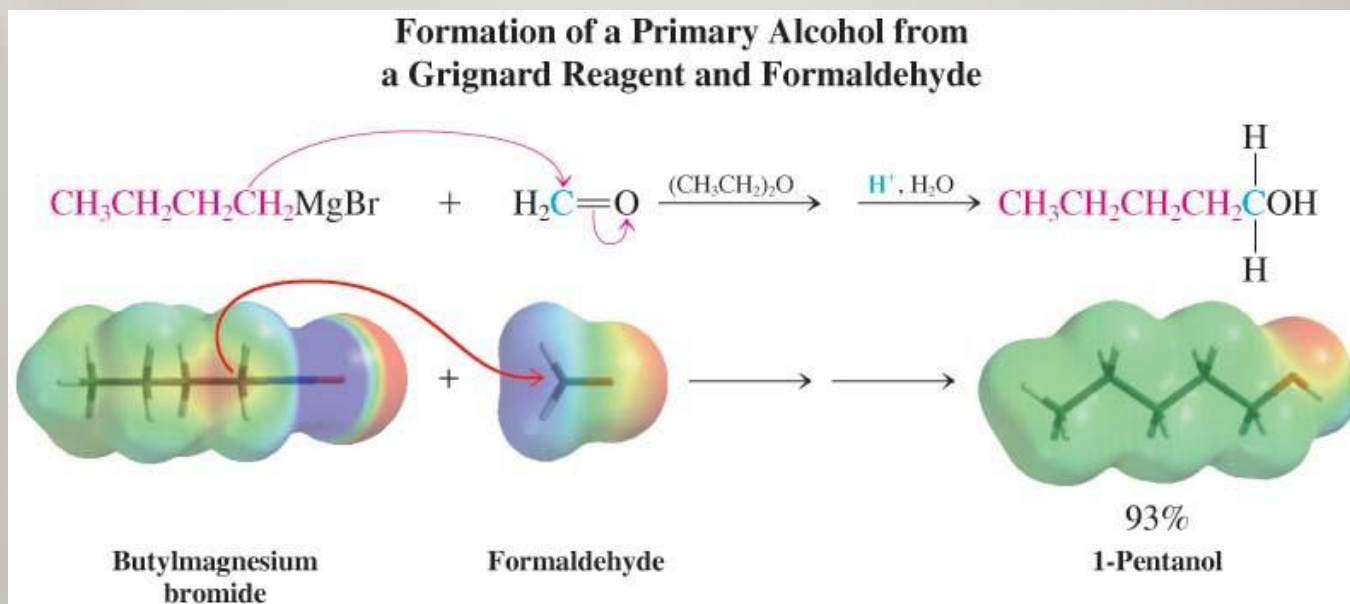
The formation of a Grignard reagent is an example of reverse polarization. In the haloalkane, the carbon atom attached to the halogen was electrophilic. In the Grignard reagent, the carbon atom has become nucleophilic.

## 7.5 ORGANOMETALLIC REAGENTS IN THE SYNTHESIS OF ALCOHOLS

One of the most useful reactions of organometallic reagents is the reaction with aldehydes and ketones to produce an alcohol containing a new C-C bond.



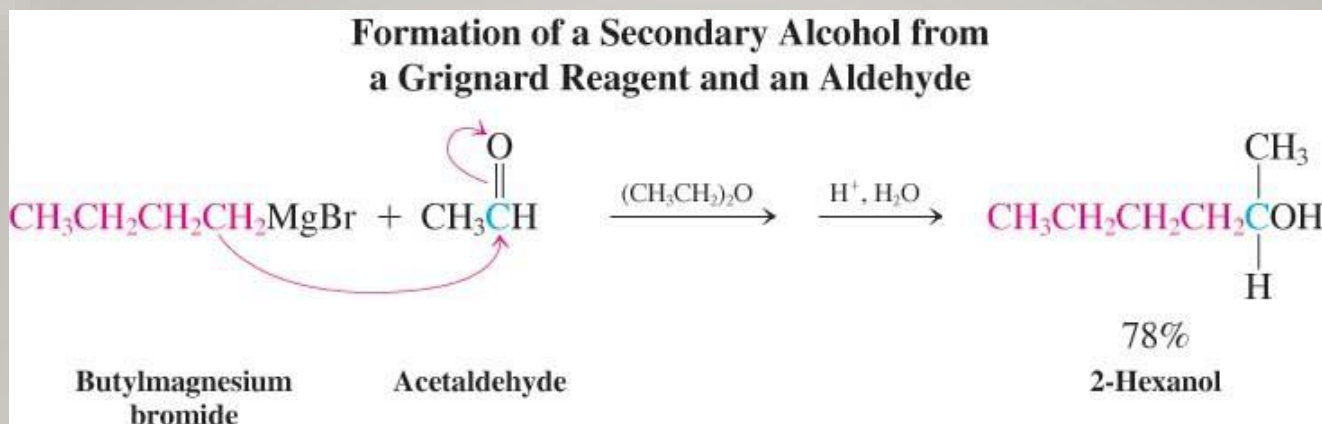
Reaction with formaldehyde produces a primary alcohol.



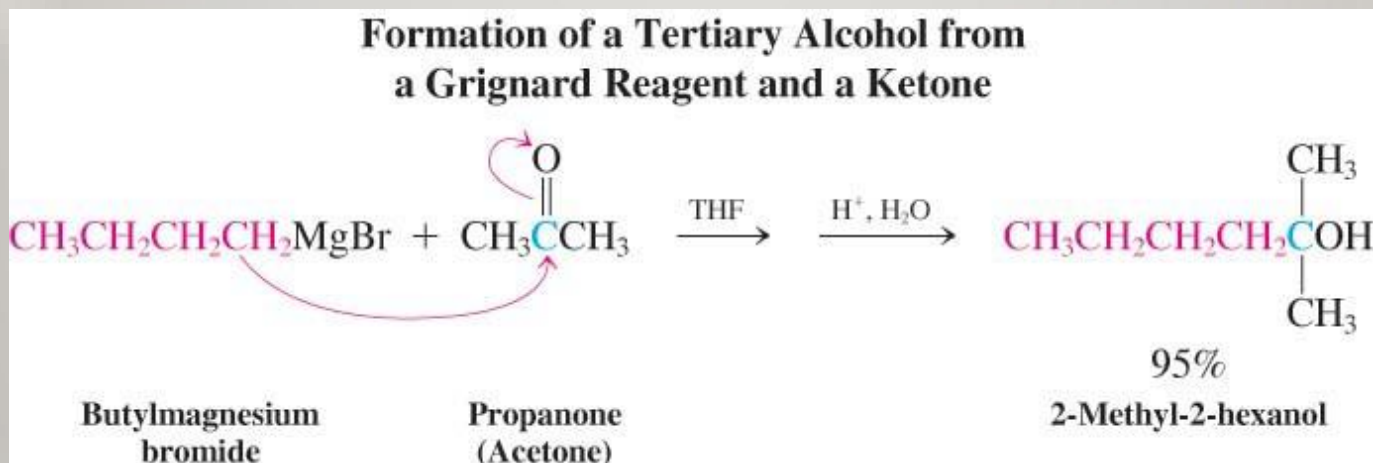


## 7.5 ORGANOMETALLIC REAGENTS IN THE SYNTHESIS OF ALCOHOLS

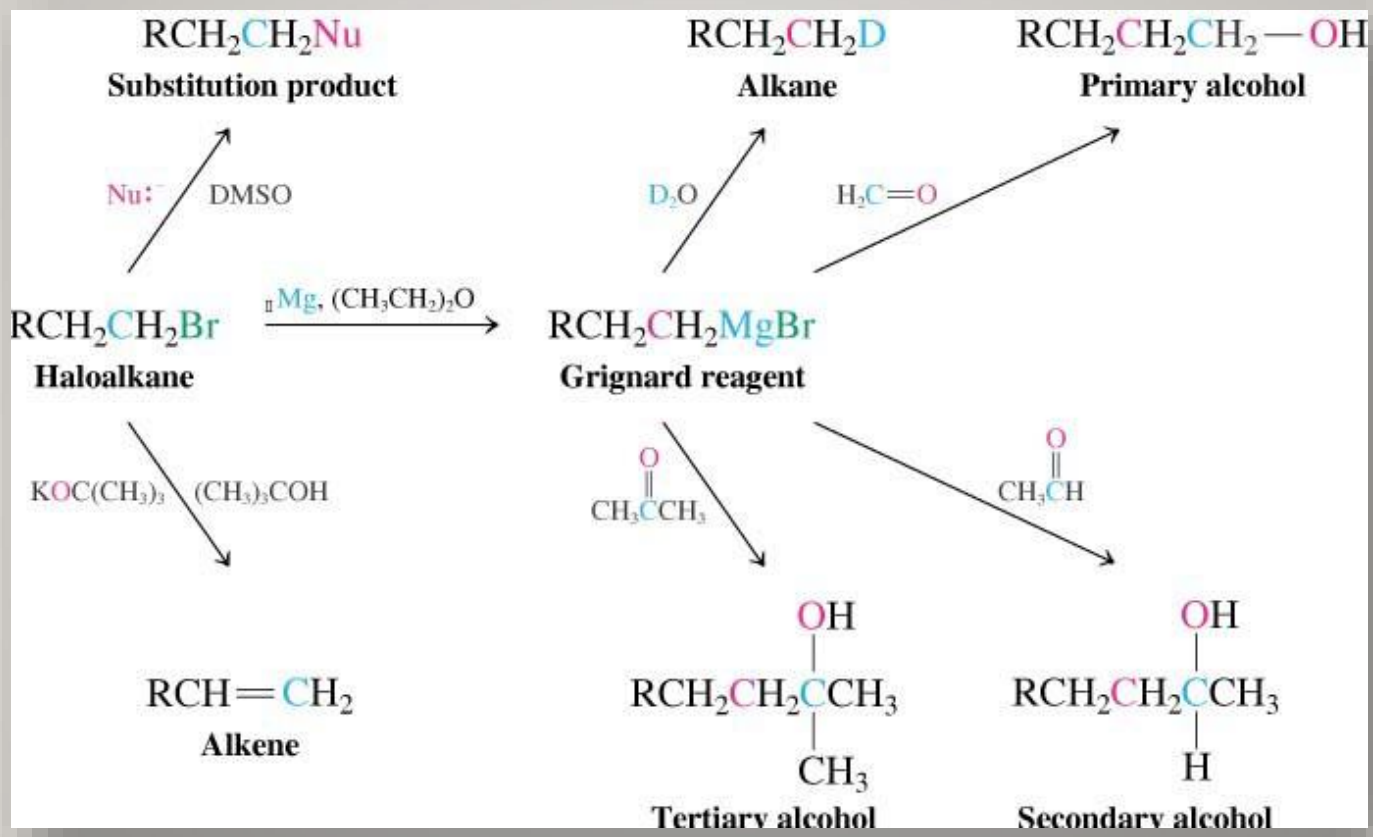
Aldehydes other than formaldehyde form secondary alcohols.



Ketones react to form tertiary alcohols.



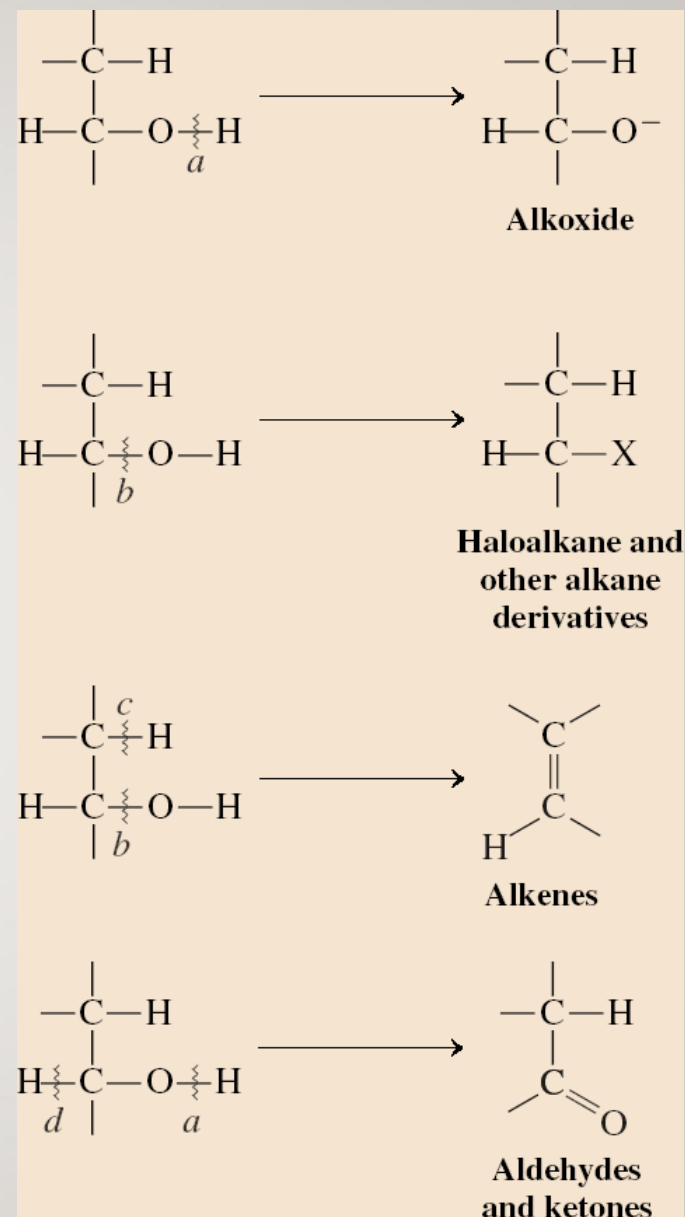
OVERVIEW:



## 7.6 REACTIONS OF ALCOHOLS

A variety of reaction modes are available to alcohols.

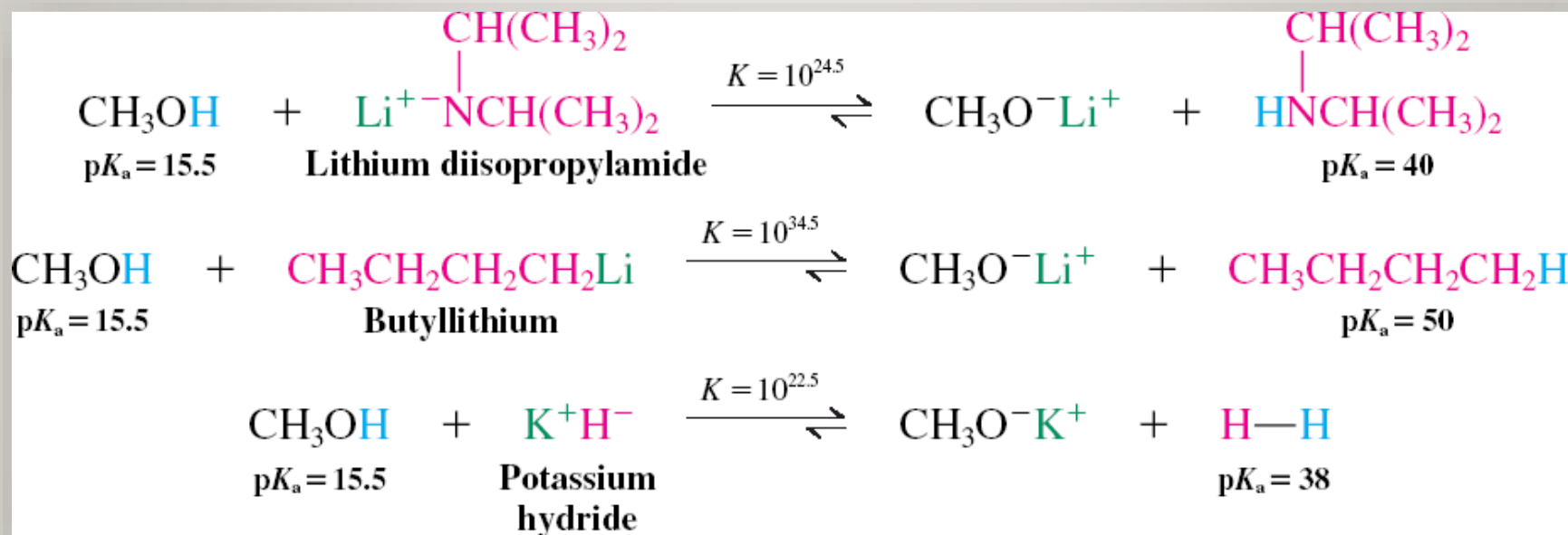
**Figure 9-1** Four typical reaction modes of alcohols. In each mode, one or more of the four bonds marked *a–d* are cleaved (wavy line denotes bond cleavage): (*a*) deprotonation by base; (*b*) protonation by acid followed by uni- or bimolecular substitution; (*b, c*) elimination; and (*a, d*) oxidation.



## 7.6 REACTIONS OF ALCOHOLS

Strong bases are needed to deprotonate alcohols completely.

- Base strength must be stronger than that of the alkoxide.



## 7.6 REACTIONS OF ALCOHOLS

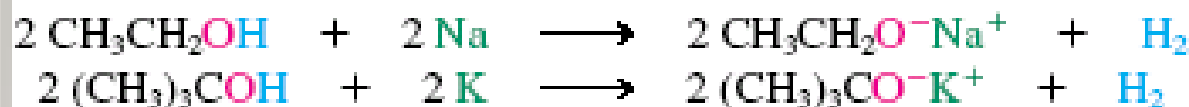
Alkali metals also deprotonate alcohols, but by reduction of  $\text{H}^+$ .

Vigorous:



Less Vigorous:

### Alkoxides from Alcohols and Alkali Metals



Relative reactivities:

### Relative Reactivity of ROH with Alkali Metals



Uses for alkoxides: Hindered alkoxides

E2 reactions with haloalkanes to form alkenes.

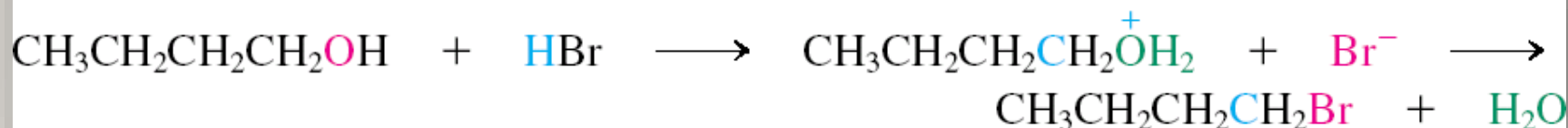
Less hindered alkoxides

$\text{S}_{\text{N}}2$  reactions with haloalkanes to form ethers.

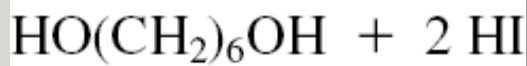
## 7.6 REACTIONS OF ALCOHOLS

Primary bromoalkanes and iodoalkanes can be prepared by the reaction with HBr and HI. Chloroalkanes cannot be prepared by this method because Cl<sup>-</sup> is too poor a nucleophile.

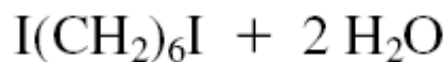
### Primary Bromoalkane Synthesis from an Alcohol



### Iodoalkane Synthesis



1,6-Hexanediol



85%

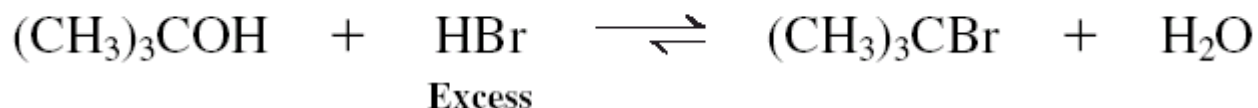
1,6-Diiodo-  
hexane



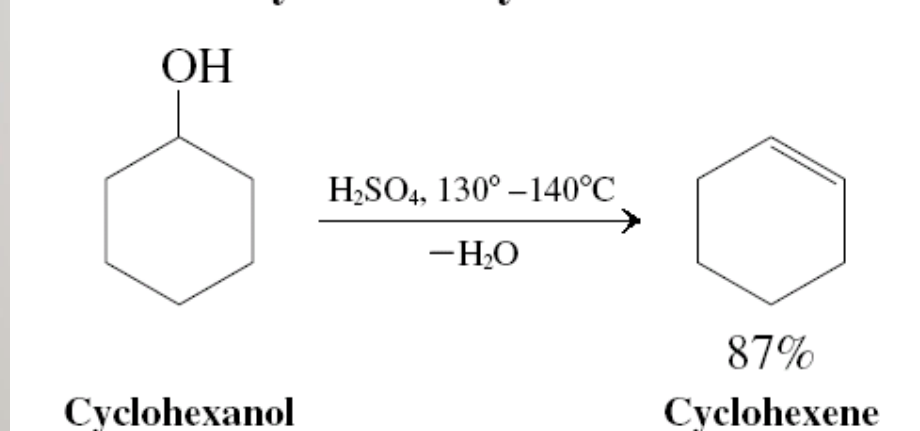
## 7.6 REACTIONS OF ALCOHOLS

- ❑ Primary alkyloxonium ions undergo only  $\text{S}_{\text{N}}2$  reactions with acid. Their carbocation transition state energies are too high to allow  $\text{S}_{\text{N}}1$  and  $\text{E}1$  reactions under ordinary laboratory conditions.
- ❑ Secondary and tertiary alkyloxonium ions lose water when treated with acid to form a carbocation.

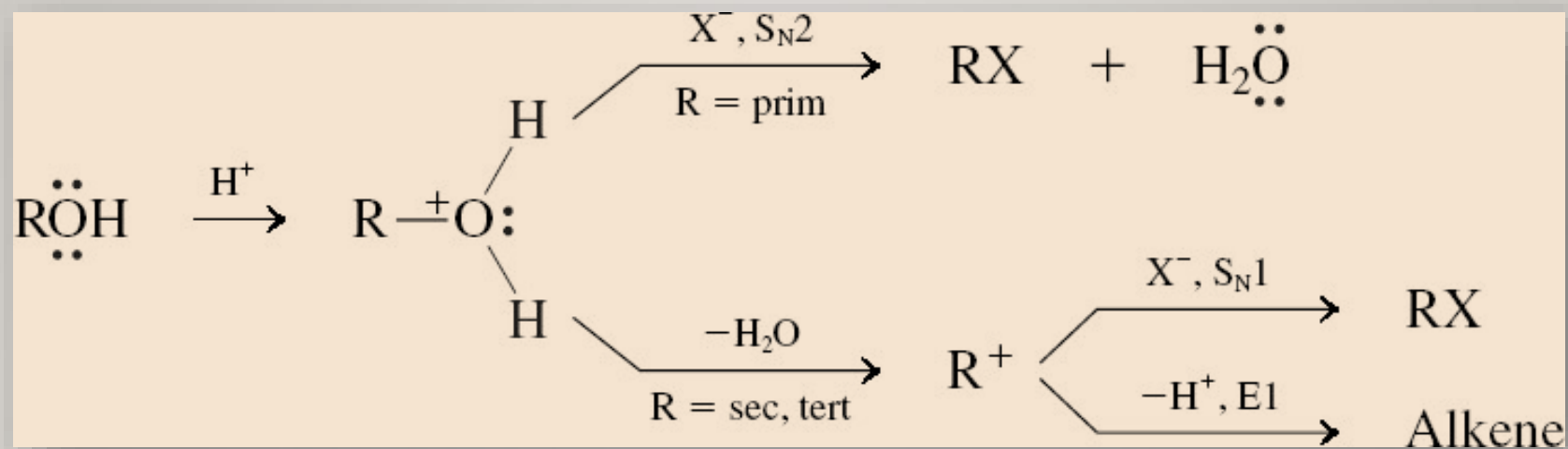
### Conversion of 2-Methyl-2-propanol into 2-Bromo-2-methylpropane



### Alcohol Dehydration by the $\text{E}1$ Mechanism



# OVERVIEW



## 7.6 REACTIONS OF ALCOHOLS

Haloalkanes can be made from alcohols through inorganic esters.

- ❑ As an alternative to the acid-catalyzed conversions of alcohols into haloalkanes, a number of inorganic reagents can convert the alcoholic hydroxyl group into a good leaving group under milder conditions.
- ❑ The reaction of  $\text{PBr}_3$  with a secondary alcohol yields a bromoalkane and phosphorous acid (all three bromine atoms can be utilized).

