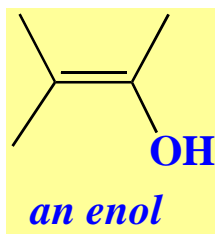


Section 1--Structure and Nomenclature

Alcohols

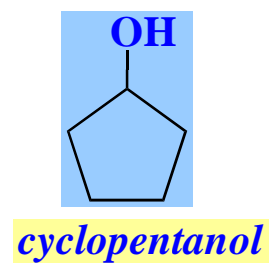
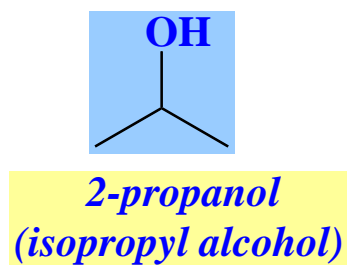
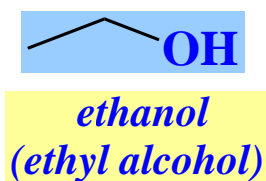
Alcohols have the *hydroxyl group* attached to a saturated carbon atom. When the hydroxyl is attached to an unsaturated carbon in an alkene, the name *enol* is used. Aromatic alcohols are called *phenols*.

R-OH
an alcohol



Ar-OH
a phenol

Examples of alcohols



Classification of Alcohols



primary, 1°



secondary, 2°



tertiary, 3°



2-methyl-2-propanol
(tert-butyl alcohol)

a 3° alcohol

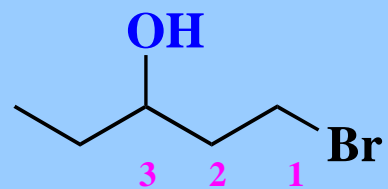
Nomenclature of Alcohols

- (1) Select the longest continuous chain containing the hydroxyl group as the **parent**.
- (2) Drop the "e" in the alkane name and add the suffix "**ol**."
- (3) Number from the end of the chain to give the hydroxyl group the lower number.
- (4) Use the standard numbering rules (locants) to indicate positions of substituents.

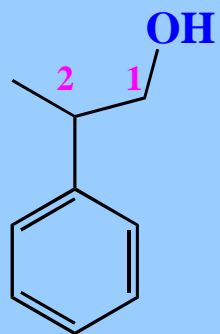
Examples



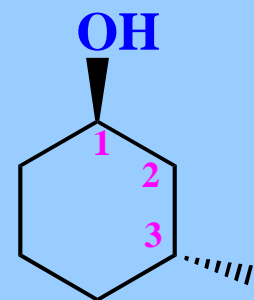
2-methyl-1-butanol



1-bromo-3-pentanol



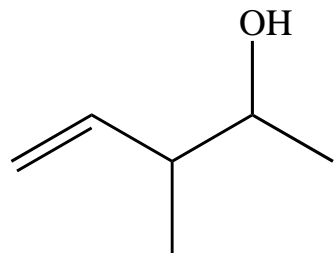
2-phenyl-1-propanol



trans-3-methylcyclohexanol

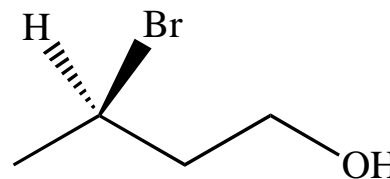
Quiz 11.01

Name the following alcohols.

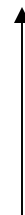


(ignore the stereocenters)

3-methyl-4-penten-2-ol



(S)-3-bromo-1-butanol



Incorrect; what is the right answer?

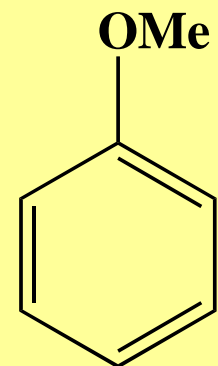
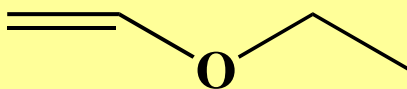
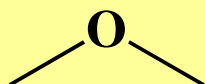
Ethers

Ethers have the general structure



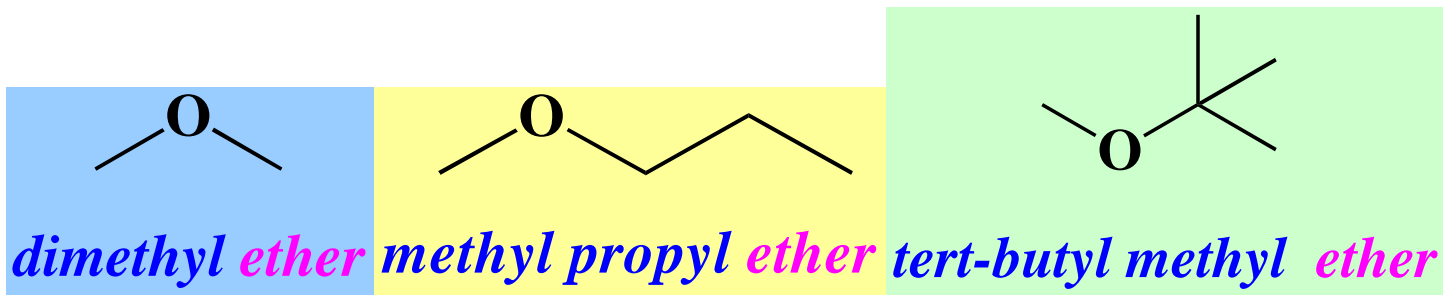
where R and R' may be alkyl, alkenyl, alkynyl, or aryl.

Examples



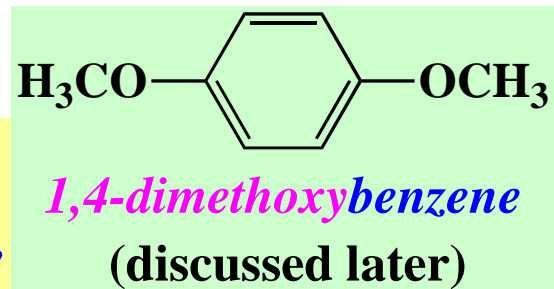
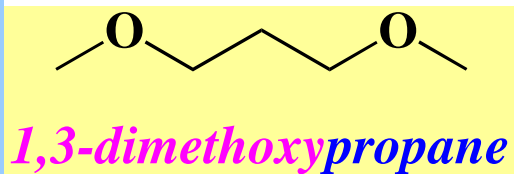
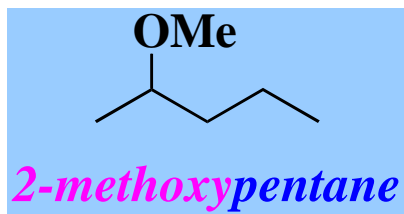
Nomenclature--Common Names

Simple ethers are named by giving the name of the alkyl groups in alphabetical order and adding "ether."



Nomenclature--IUPAC Names

Ethers may be named as **alkoxy**alkanes, **alkoxy**alkenes and **alkoxy**arenes.

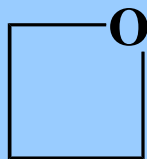


Some Cyclic Ethers

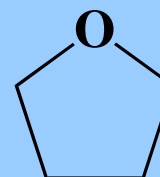
Common names are used with the simpler cyclic ethers. **Systematic names** use the prefix "**oxa**" with the cycloalkane name to indicate the replacement of a carbon with an oxygen atom.



oxirane
("ethylene oxide")
oxacyclopropane



oxetane
oxacyclobutane



tetrahydrofuran
oxacyclopentane

Section 2--Physical Properties of Alcohols and Ethers

Physical Properties of Alcohols

Alcohols contain both **hydrophobic** ("water-hating") and **hydrophilic** ("water-loving") structural parts, also called nonpolar and polar parts.

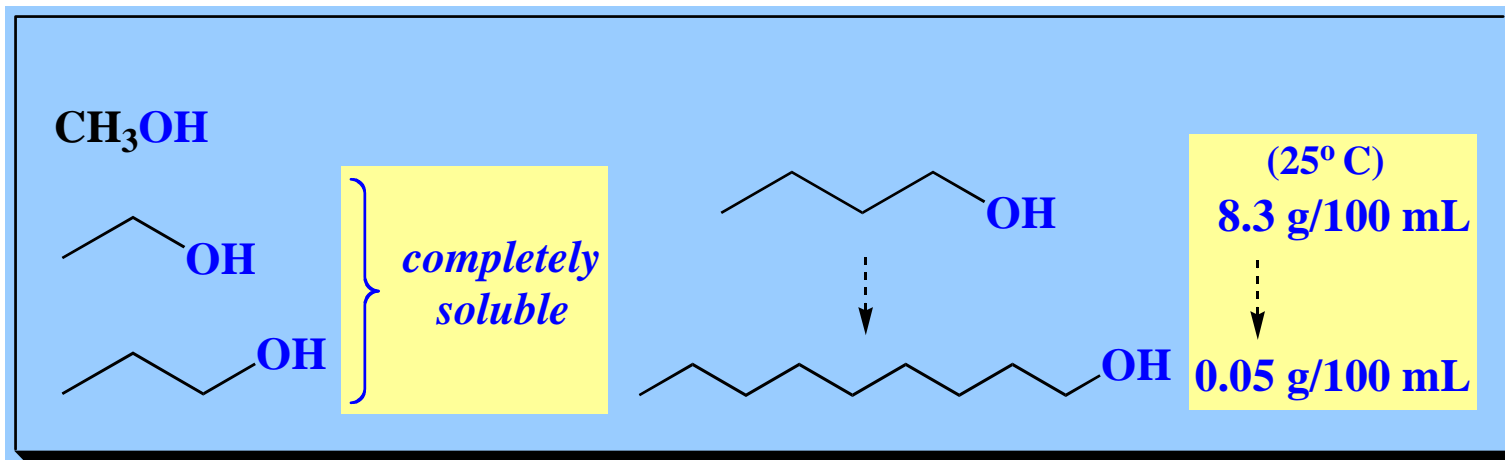


Melting Points and Boiling Points

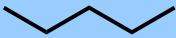

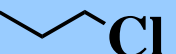

The melting and boiling points increase with the size of the R group for straight-chain alcohols. The branched alcohols form a separate sub-group with homologous properties.

Solubility in Water

The smallest size alcohols (up to C₃) are completely soluble in water. Alcohols up to C₈ have limited solubilities.

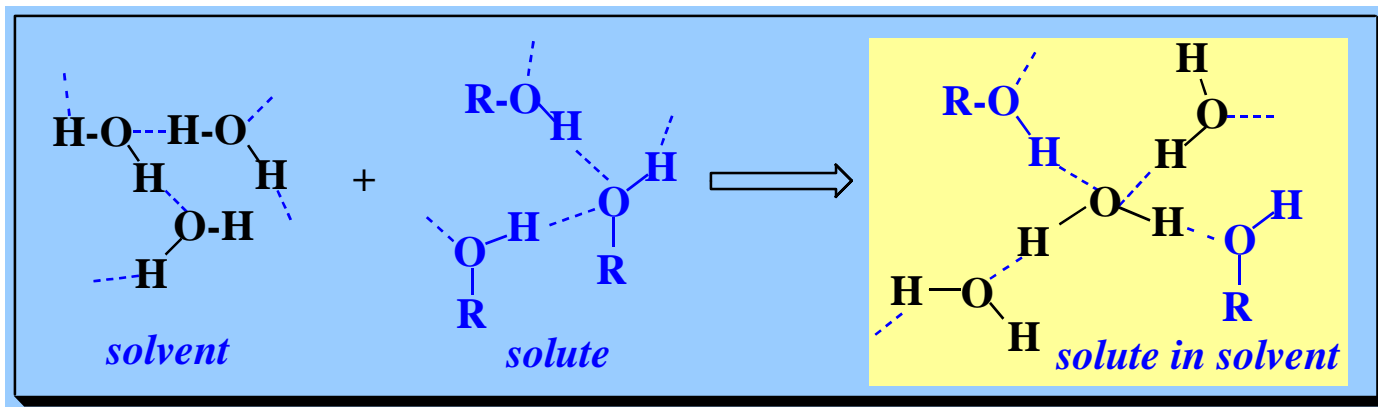


Comparison of physical properties

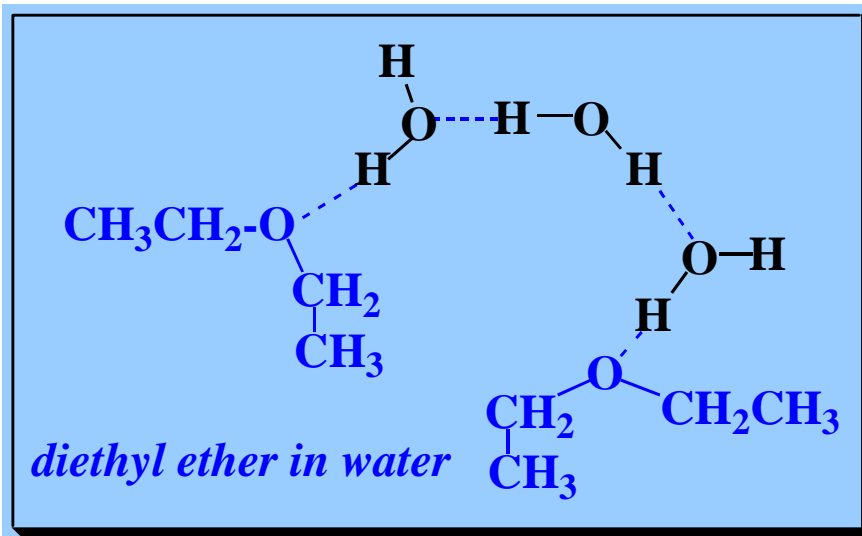
compound	name	m, D	BP (°C)
	pentane	0	36
	diethyl ether	1.18	35
	propyl chloride	2.10	47
	butyl alcohol	1.63	118 ←

Hydrogen Bonding in Water

When **alcohols** dissolve in water, there is strong association between solute and solvent through hydrogen bonding.



Hydrogen Bonding in Water (Ethers)



Ethers also form **hydrogen bonds** when they dissolve in water. Ethers and alcohols of similar size have similar solubilities in water. But since ethers in the pure liquid state are incapable of H-bonding, they have lower boiling points than alcohols.



7.5 g/100mL BP 35° C



8.0g/100mL BP 118° C

Quiz Chapter 11 Section 2

Which statement below is not true about alcohols and ethers that are constitutional isomers?

They have similar solubilities in water.

Both are soluble in concentrated sulfuric acid.

They have similar boiling points.

Neither will decolorize a solution of Br_2 in CCl_4 .

Section 5--Reactions of Alcohols

Section 6--Alcohols as Acids

Reactions of Alcohols

There are two general classes of reactions of alcohols:

(1) $\text{R}-\text{O}-\text{H}$ C-O bond breaking

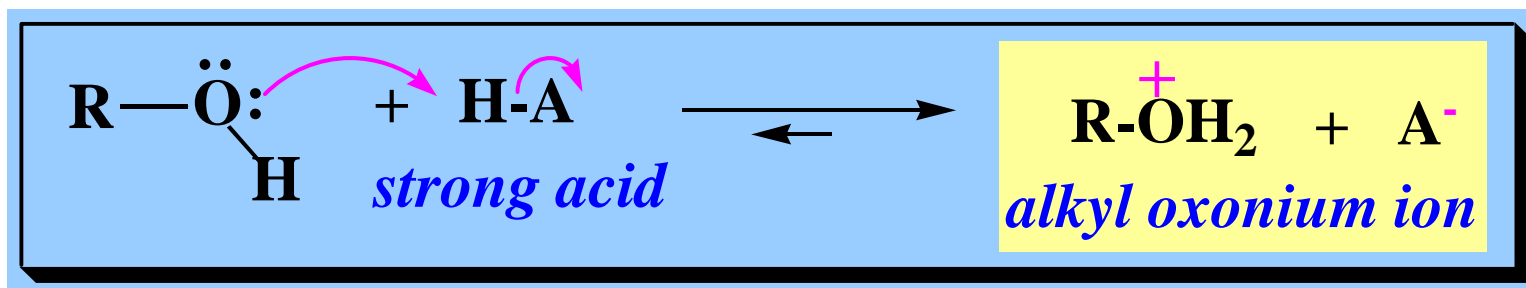
In (1) the **hydroxyl group**, or another oxygen function, is the **leaving group**.

(2) $\text{R}-\text{O}-\text{H}$ O-H bond breaking

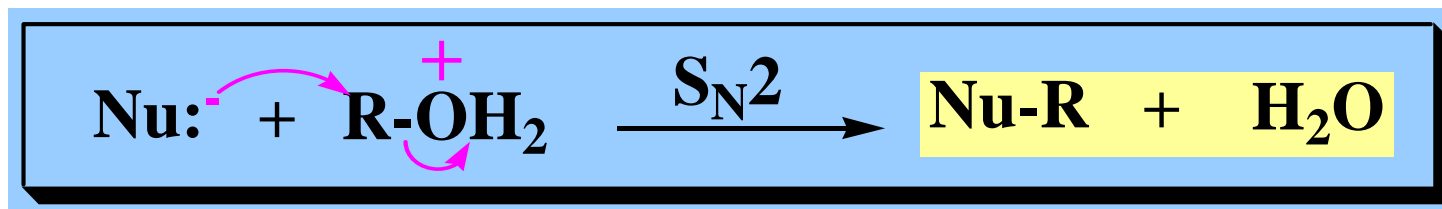
In (2) the alcohol acts as an **acid**.

Alcohols as Bases/Nucleophiles

alcohols react with strong acids:

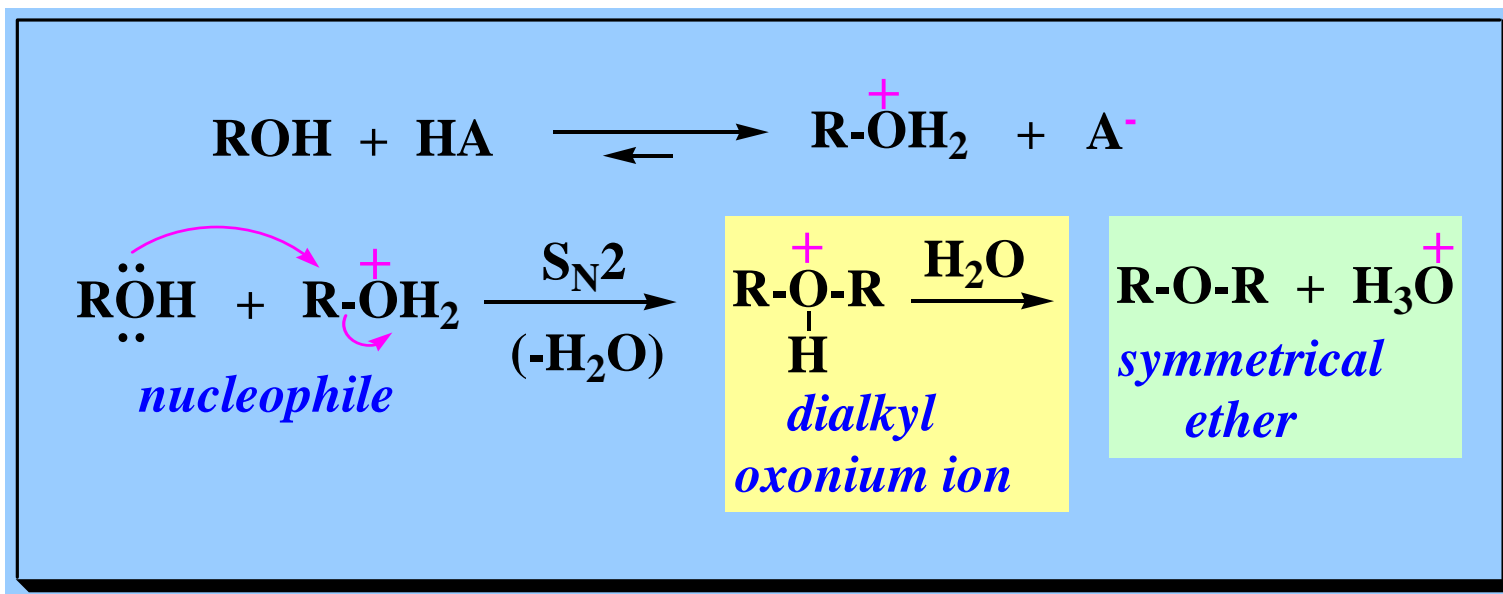


The protonated alcohol function is a much better leaving group than the hydroxyl group. Nucleophiles react with the alkyl oxonium ion in $\text{S}_{\text{N}}2$ reactions:



Alcohols as Bases/Nucleophiles

Symmetrical ethers are produced from alcohols in the presence of strong acids:



Alcohols as Acids

With the exception of methanol ($\text{pK}_a = 15.5$), alcohols are slightly less acidic than water ($\text{pK}_a = 15.7$).

	$\text{CH}_3\text{O-H}$	H-O-H	$\text{CH}_3\text{CH}_2\text{O-H}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CO-H} \\ \\ \text{CH}_3 \end{array}$
pK_a	15.5	15.7	15.9	18.0

Sterically hindered alcohols (such as tert-butyl alcohol) are less acidic because solvation of the anion is hindered which destabilizes the anion.

Section 7--Conversions of Alcohols to Alkyl Halides

**Section 8--Alkyl Halides from the Reaction of
Alcohols with Hydrogen Halides**

Conversion of Alcohols into Alkyl Halides

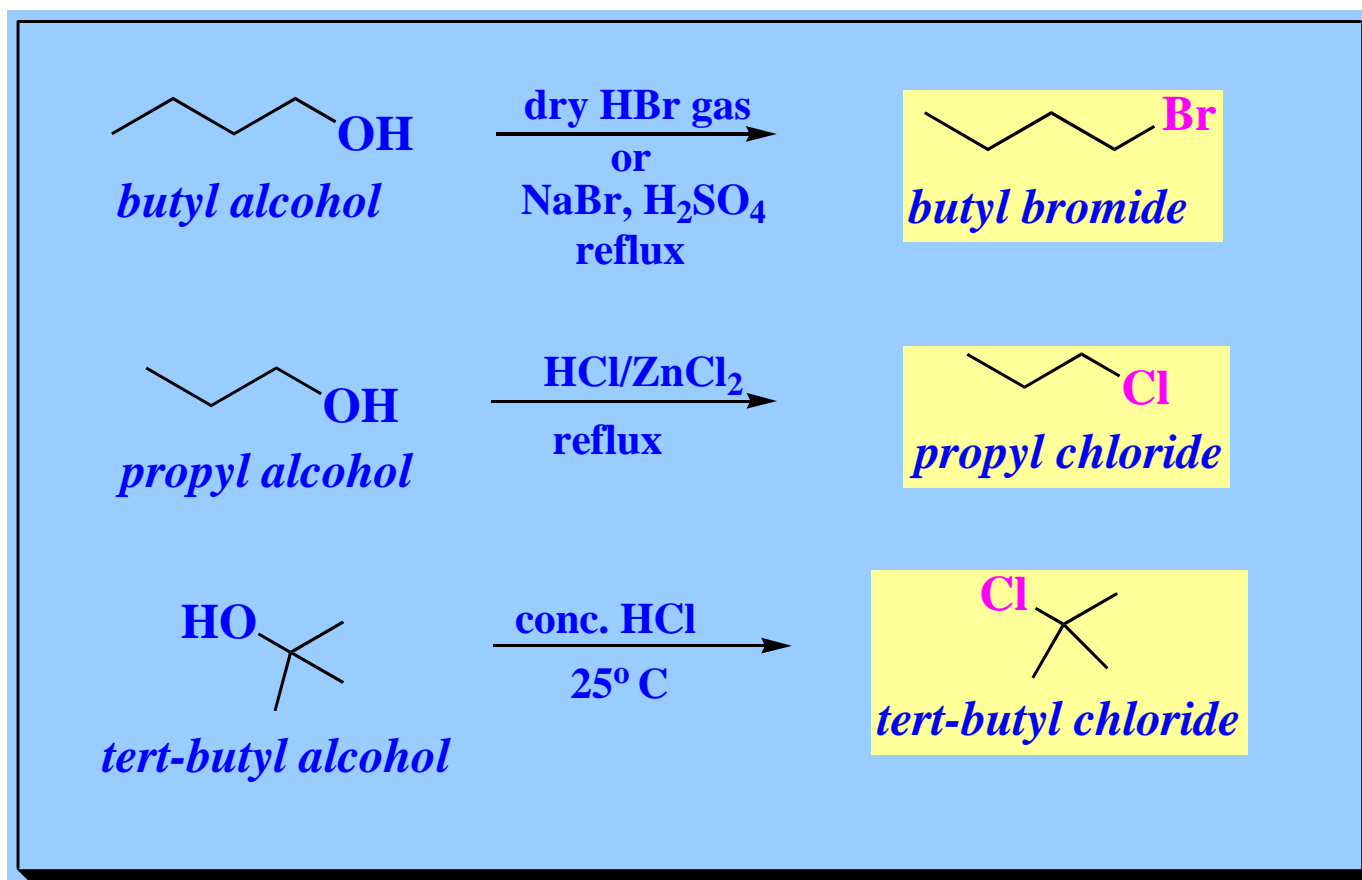
A common synthetic transformation is the conversion of an alcohol into an alkyl halide:



There are numerous reagents for this conversion including **hydrogen halides (HX)**, **phosphorous halides (PX₃)** and **thionyl chloride (SOCl₂)**.

Hydrogen Halide Reagents

The conditions needed for preparing alkyl halides with HX reagents depends on the structure of the R group and HX. HBr (stronger acid) is more reactive than HCl.

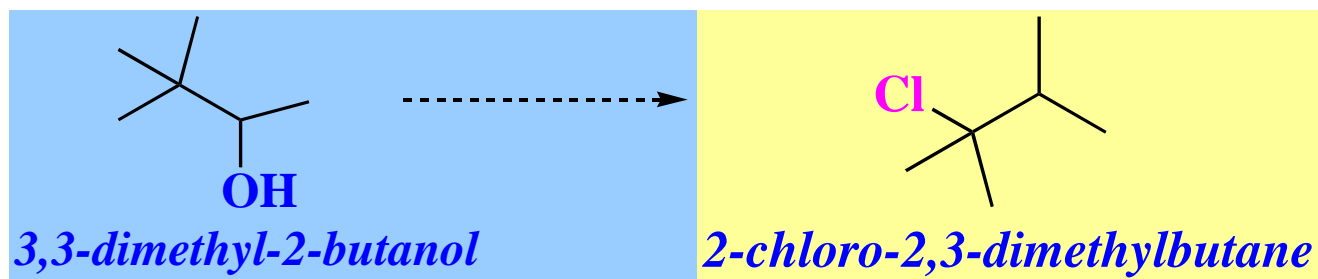


Some Observations

(A) Catalysis by Acid

Addition of acids stronger than HX (such as H₂SO₄) speeds up the reaction.

(B) Beware of rearrangements when you produce carbocation intermediates



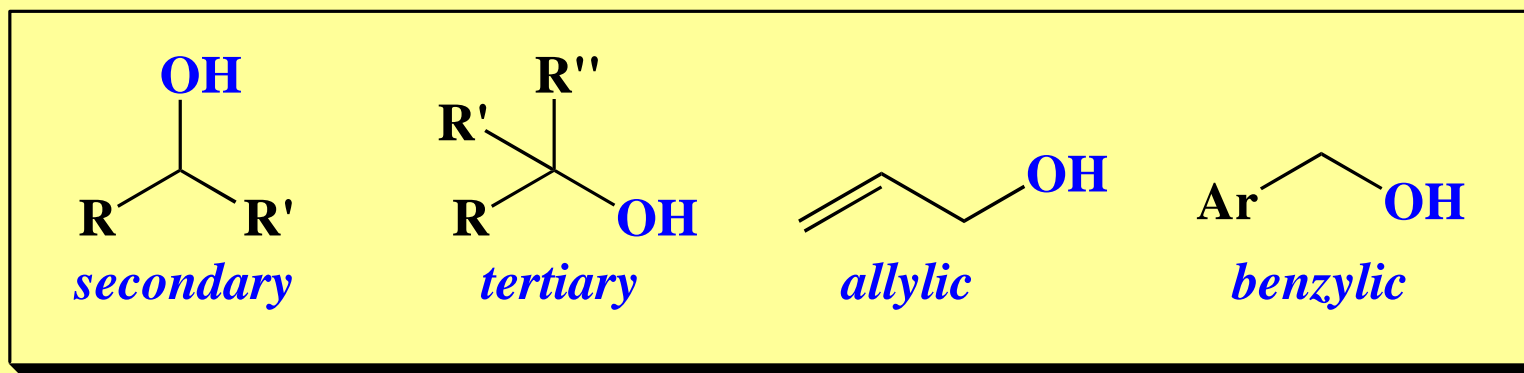
(C) Reactivity Order of ROH

The reactivity order of ROH towards a single HX reagent is $3^\circ > 2^\circ > 1^\circ < \text{CH}_3\text{OH}$. The reactivity decreases from tertiary through primary, but then increases again with methyl alcohol.

Proposed Mechanism for the Reaction of Alcohols with HX Reagents

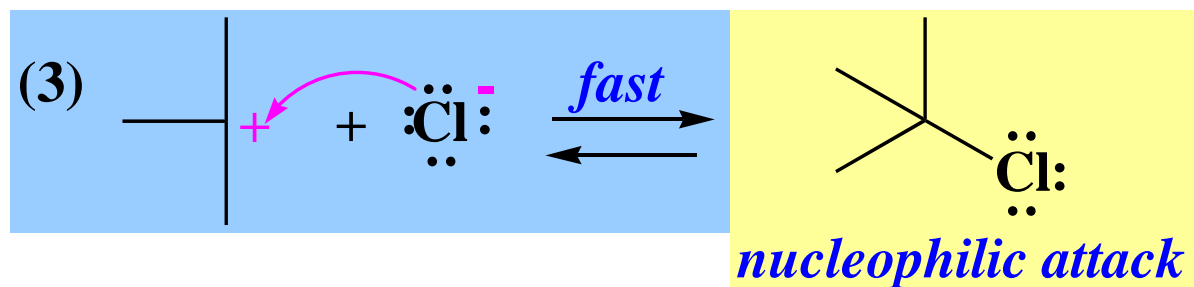
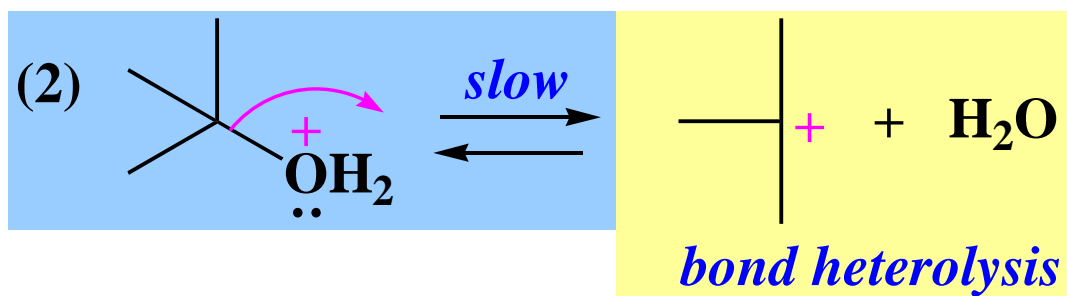
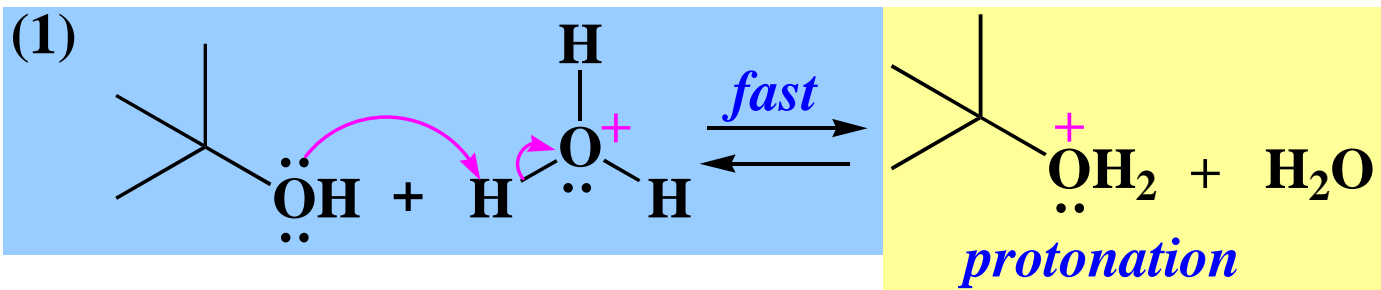
S_N1 Mechanism: Carbocation Intermediates:

A carbocation intermediate seems to form with **secondary, tertiary, allylic and benzylic alcohols** in the presence of HX reagents. An S_N1 mechanism is proposed where the role of acid is to protonate the hydroxyl group facilitating bond heterolysis in the RDS.



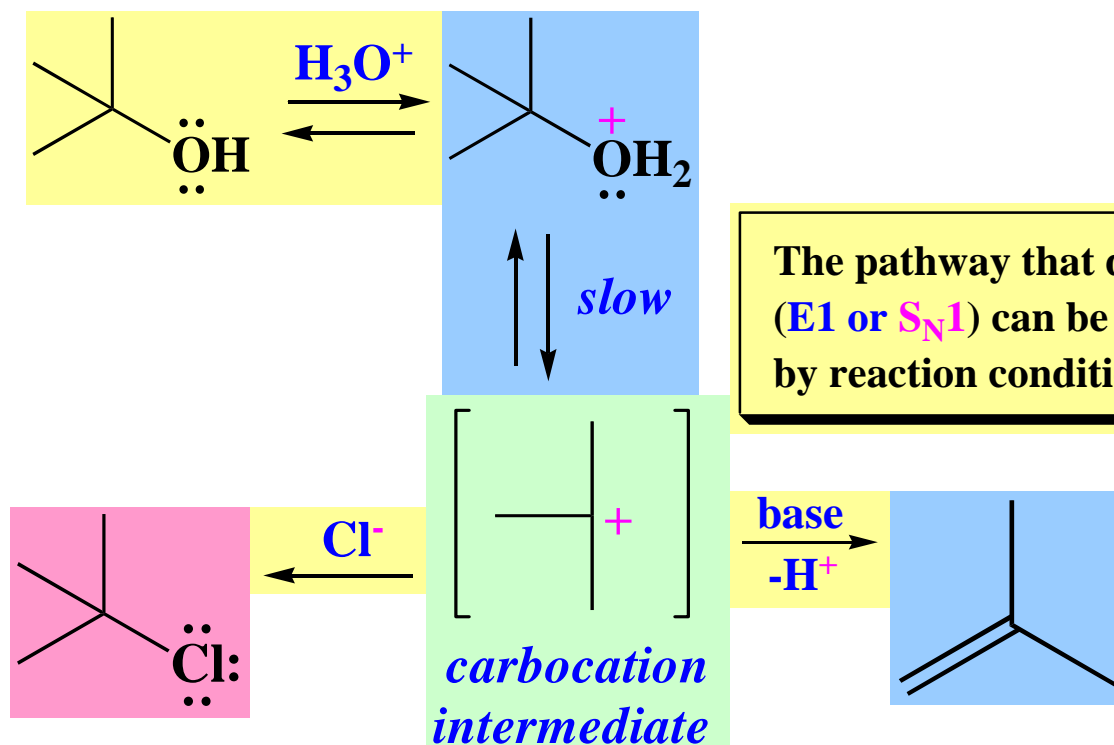
The Reaction of *tert*-Butyl Alcohol and concentrated HCl

S_N1 Mechanism:



Competition between Dehydration and Nucleophilic Substitution

The first two steps in this mechanism that produce the carbocation intermediate are identical to the acid-catalyzed dehydration of alcohols.



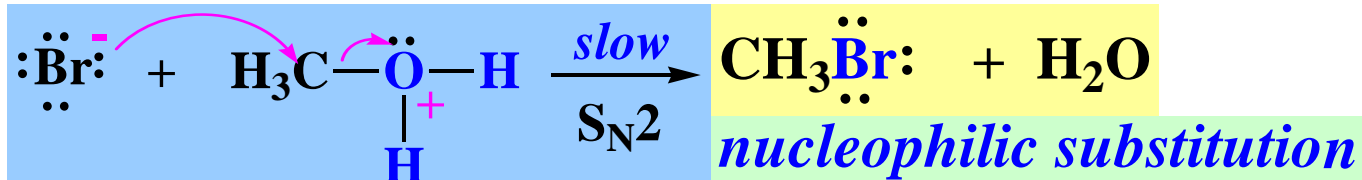
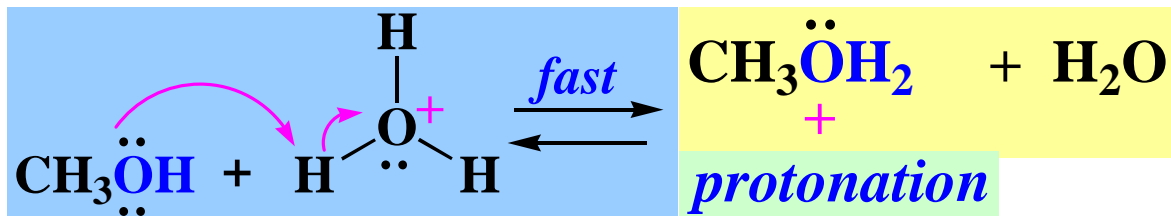
In the reaction with HCl , chloride ion is present, which is a good nucleophile that efficiently reacts with the carbocation intermediate.

In the dehydration reaction (E1), concentrated sulfuric acid is used. The only nucleophiles in the reaction are H_2O and HSO_4^- . Attack by water is reversible, while HSO_4^- is a poor nucleophile.

Mechanism for the Reaction of Methyl and 1° Alcohols with HX Reagents

An S_N2 Mechanism:

The reaction of Methanol and concentrated HBr

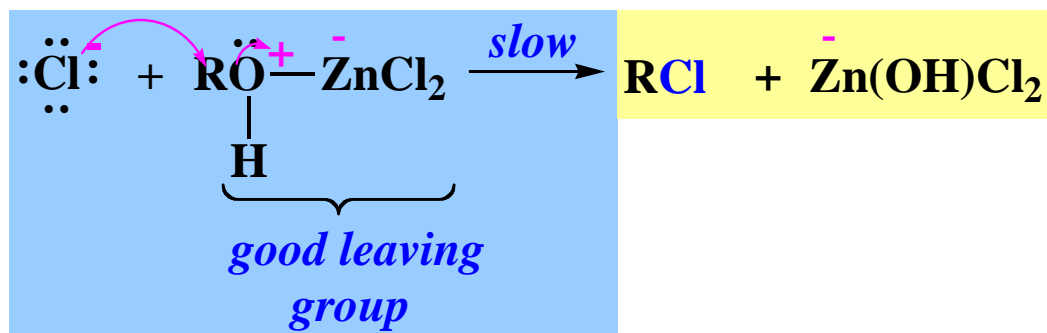
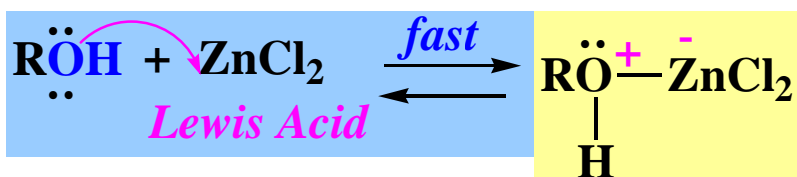


Fast and reversible protonation of the hydroxyl group produces a better leaving group for the S_N2 reaction with bromide ion.

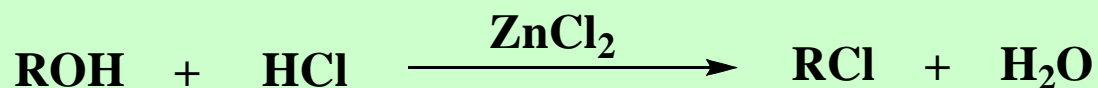
The S_N1 mechanism is **energetically unfavorable** because of the high energy methyl carbocation intermediate. The S_N2 reaction proceeds well with methyl and primary systems because of favorable steric factors.

Electrophilic Assistance with Zinc Chloride

The addition of zinc chloride (ZnCl_2) greatly accelerates the reaction of primary and secondary alcohols with HCl . The zinc chloride (a Lewis acid) catalyzes the reaction by coordinating to the oxygen and enhancing the rate of the key bond heterolysis step, as shown below.



overall



Quiz Chapter 11 Section 8

Provide the products of the following reactions.

