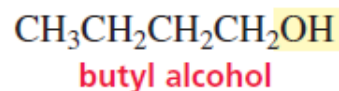
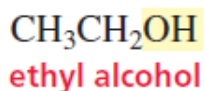
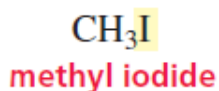
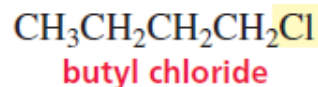
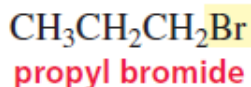
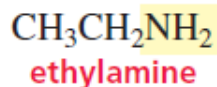
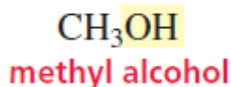


## Compounds containing a single bond to heteroatom:

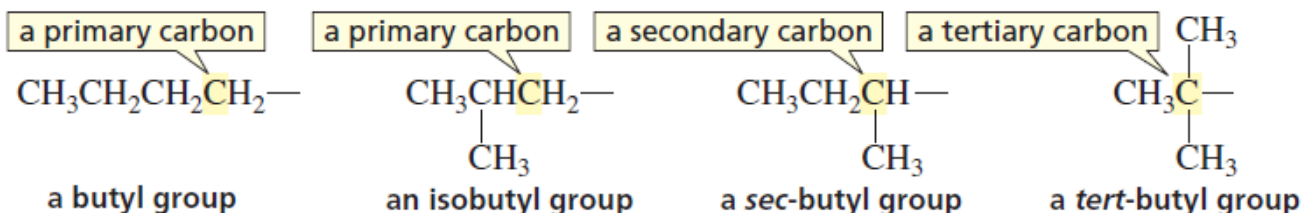
Several types of functional groups contain a carbon atom singly bonded to a heteroatom. Common examples include **alkyl halides (RX, X: F, Cl, Br, I)**, **alcohols (ROH)**, **ethers (ROR)**, and **amines (RNH<sub>2</sub>, R<sub>2</sub>NH, R<sub>3</sub>N, R<sub>4</sub>N<sup>+</sup>)**.

## Nomenclature of Alkyl Substituents

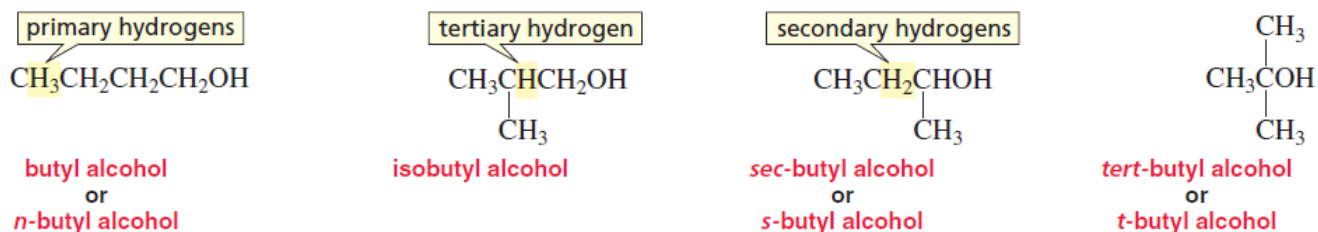
An alkyl group name followed by the name of the class of the compound (alcohol, amine, etc.) yields the common name of the compound. The following examples show how alkyl group names are used to build common names:



Notice that there is a space between the name of the alkyl group and the name of the class of compound, except in the case of amines.

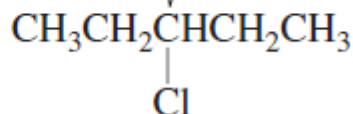
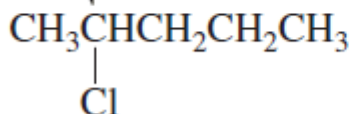


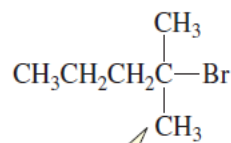
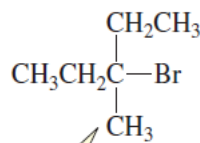
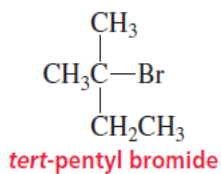
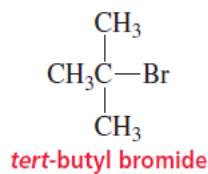
Like the carbons, the hydrogens in a molecule are also referred to as primary, secondary, and tertiary. Primary hydrogens are attached to primary carbons, secondary hydrogens to secondary carbons, and tertiary hydrogens to tertiary carbons.



Because a chemical name must specify only one compound, the only time you will see the prefix “sec” is in sec-butyl. The name “sec-pentyl” cannot be used because pentane has two different secondary carbon atoms. Therefore, there are two different alkyl groups that result from removing a hydrogen from a secondary carbon of pentane. Because the name would specify two different compounds, it is not a correct name.

Both alkyl halides have five carbon atoms with a chloride attached to a secondary carbon, so both compounds would be named sec-pentyl chloride.





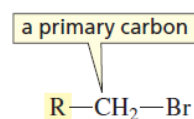
Both alkyl bromides have six carbon atoms with a bromine attached to a tertiary carbon, so both compounds would be named *tert*-hexyl bromide.

Incorrect

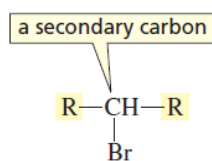
methyl	CH <sub>3</sub> —	<i>sec</i> -butyl	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}— \\   \\ \text{CH}_3 \end{array}$	neopentyl	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CCH}_2— \\   \\ \text{CH}_3 \end{array}$
ethyl	CH <sub>3</sub> CH <sub>2</sub> —			hexyl	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> —
propyl	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —	<i>tert</i> -butyl	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{C}— \\   \\ \text{CH}_3 \end{array}$	isohexyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2— \\   \\ \text{CH}_3 \end{array}$
isopropyl	$\begin{array}{c} \text{CH}_3\text{CH}— \\   \\ \text{CH}_3 \end{array}$				
butyl	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> —	pentyl	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> —		
isobutyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2— \\   \\ \text{CH}_3 \end{array}$	isopentyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2— \\   \\ \text{CH}_3 \end{array}$		

## Nomenclature of Alkyl Halides

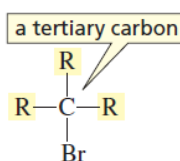
Alkyl halides are compounds in which a hydrogen of an alkane has been replaced by a halogen. Alkyl halides are classified as primary, secondary, or tertiary, depending on the carbon to which the halogen is attached.



a primary alkyl halide



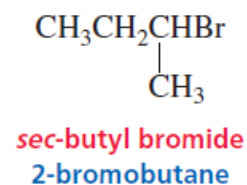
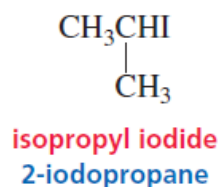
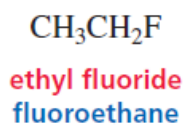
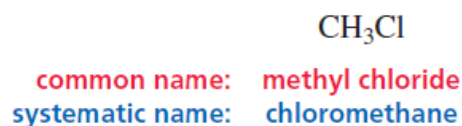
a secondary alkyl halide



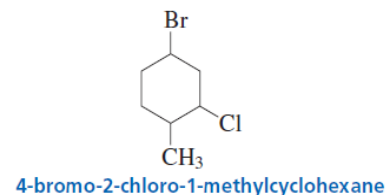
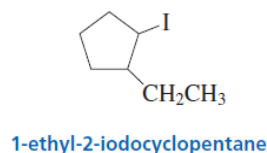
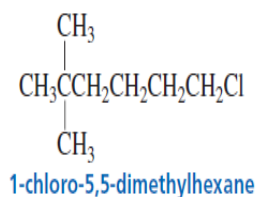
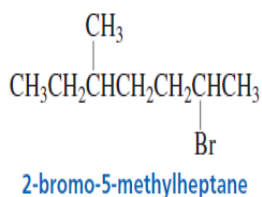
a tertiary alkyl halide

The number of alkyl groups attached to the carbon to which the halogen is bonded determines whether an alkyl halide is primary, secondary, or tertiary.

The common names of alkyl halides consist of the name of the alkyl group, followed by the name of the halogen with the “ine” ending of the halogen name replaced by “ide” (i.e., fluoride, chloride, bromide, iodide).

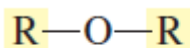


In the IUPAC system, alkyl halides are named as substituted alkanes. The substituent prefix names for the halogens end with “o” (i.e., “fluoro,” “chloro,” “bromo,” “iodo”). Therefore, alkyl halides are often called haloalkanes.

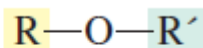


## Nomenclature of Ethers

**Ethers** are compounds in which an oxygen is bonded to two alkyl substituents. If the alkyl substituents are identical, the ether is a **symmetrical ether**. If the substituents are different, the ether is an **unsymmetrical ether**.

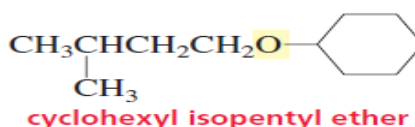
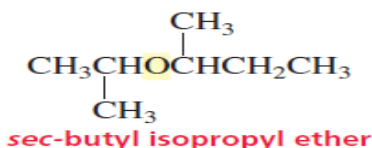
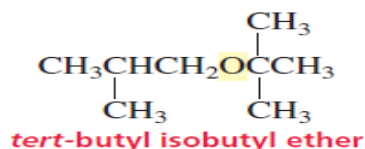
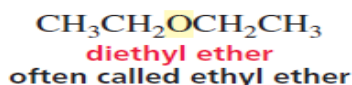


a symmetrical ether

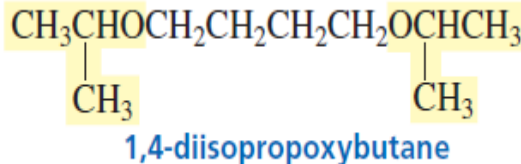
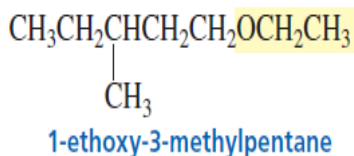
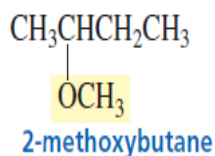


an unsymmetrical ether

The common name of an ether consists of the names of the two alkyl substituents (in alphabetical order), followed by the word “ether.” The smallest ethers are almost always named by their common names.

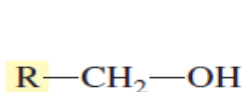


The IUPAC system names ether as an alkane with an RO substituent. The substituents are named by replacing the “yl” ending in the name of the alkyl substituent with “oxy.”

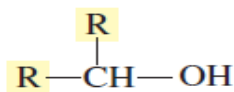


## Nomenclature of Alcohols

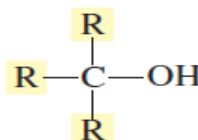
Alcohols are compounds in which a hydrogen of an alkane has been replaced by an OH group. **Alcohols** are classified as **primary**, **secondary**, or **tertiary**, depending on whether the OH group is bonded to a primary, secondary, or tertiary carbon—the same way alkyl halides are classified.



a primary alcohol

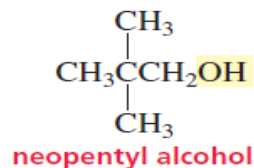
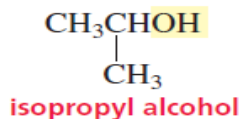
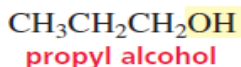
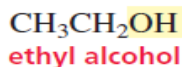


a secondary alcohol



a tertiary alcohol

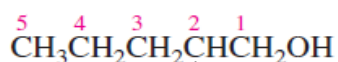
The common name of an alcohol consists of the name of the alkyl group to which the OH group is attached, followed by the word “alcohol.”



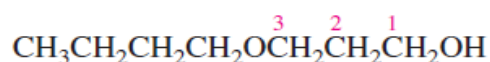
The IUPAC system uses a suffix to denote certain functional groups. The systematic name of an alcohol, for example, is obtained by replacing the “e” at the end of the name of the parent hydrocarbon with the suffix “ol.”



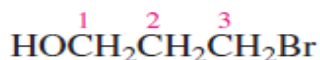
2-butanol  
or  
butan-2-ol



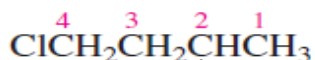
2-ethyl-1-pentanol  
or  
2-ethylpentan-1-ol



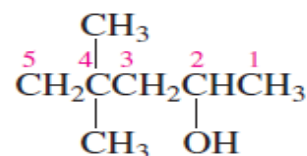
3-butoxy-1-propanol  
or  
3-butoxypropan-1-ol



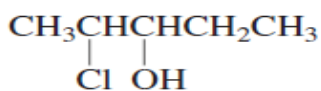
3-bromo-1-propanol



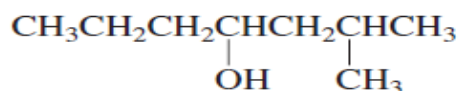
4-chloro-2-butanol



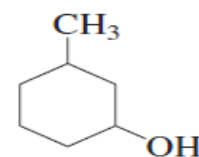
4,4-dimethyl-2-pentanol



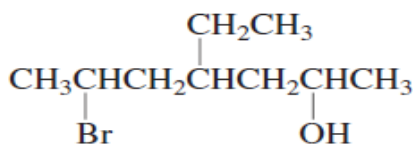
2-chloro-3-pentanol  
not  
4-chloro-3-pentanol



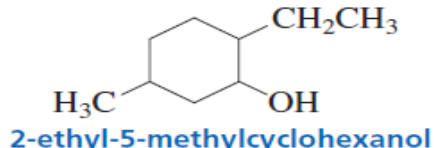
2-methyl-4-heptanol  
not  
6-methyl-4-heptanol



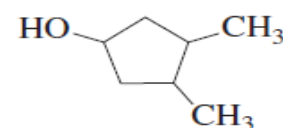
3-methylcyclohexanol  
not  
5-methylcyclohexanol



6-bromo-4-ethyl-2-heptanol



2-ethyl-5-methylcyclohexanol

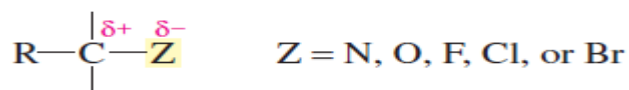


3,4-dimethylcyclopentanol

### Physical Properties of Alkyl Halides, Alcohols, Ethers, and Amines

The boiling points of the compounds in any homologous series increase as their molecular weights increase because of the increase in van der Waals forces.

The boiling points of these compounds, however, are also affected by the polar character of the bond (where Z denotes N, O, F, Cl, or Br) because nitrogen, oxygen, and the halogens are more electronegative than the carbon to which they are attached.



As the table shows, alcohols have much higher boiling points than amines, alkanes and ethers of comparable molecular weight because, in addition to van der Waals forces and the dipole - dipole interactions of the C-O bond, alcohols can form **hydrogen bonds**.

Nitrogen is not as electronegative as oxygen, however, which means that the hydrogen bonds between amine molecules are weaker than the hydrogen bonds between alcohol molecules.

Alkanes	Ethers	Alcohols	Amines
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> -42.1	CH <sub>3</sub> OCH <sub>3</sub> -23.7	CH <sub>3</sub> CH <sub>2</sub> OH 78	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> 16.6
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> -0.5	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>3</sub> 10.8	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH 97.4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> 47.8
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> 36.1	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub> 34.5	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH 117.3	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> 77.8

Both van der Waals forces and dipole–dipole interactions must be overcome in order for an alkyl halide to boil. As the halogen atom increases in size, the size of its electron cloud increases

### Comparative Boiling Points of Alkanes and Alkyl Halides (°C)

	Y				
	H	F	Cl	Br	I
CH <sub>3</sub> —Y	-161.7	-78.4	-24.2	3.6	42.4
CH <sub>3</sub> CH <sub>2</sub> —Y	-88.6	-37.7	12.3	38.4	72.3
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —Y	-42.1	-2.5	46.6	71.0	102.5
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> —Y	-0.5	32.5	78.4	101.6	130.5
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> —Y	36.1	62.8	107.8	129.6	157.0

### Solubility

The general rule that explains **solubility** on the basis of the polarity of molecules is that “like dissolves like.” In other words, polar compounds dissolve in polar solvents, and nonpolar compounds dissolve in nonpolar solvents.

The interaction between a solvent and a molecule or an ion dissolved in that solvent is called **solvation**.

Alcohols with fewer than four carbons are soluble in water, but alcohols with more than four carbons are insoluble in water.

Similarly, the oxygen atom of an ether can drag only about three carbons into solution in water. Diethyl ether an ether with four carbons is not soluble in water.

Low-molecular-weight amines are soluble in water because amines can form hydrogen bonds with water.

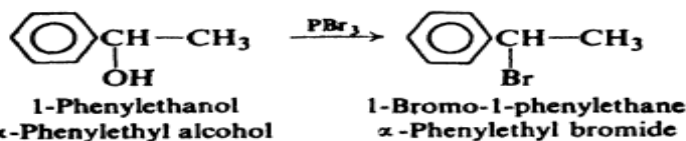
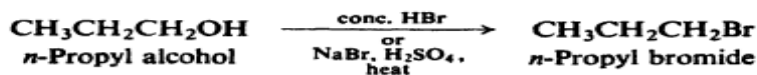
Alkyl halides have some polar character, but only the alkyl fluorides have an atom that can form a hydrogen bond with water. This means that alkyl fluorides are the most water soluble of the alkyl halides. The other alkyl halides are less soluble in water than ethers or alcohols with the same number of carbons.

## Preparations

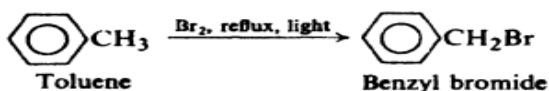
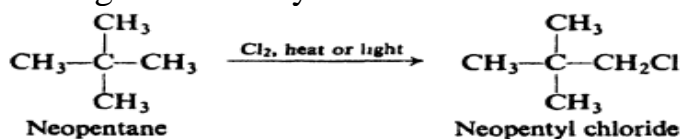
In the laboratory alkyl halides are most often prepared by the methods outlined below.

1: From alcohols:

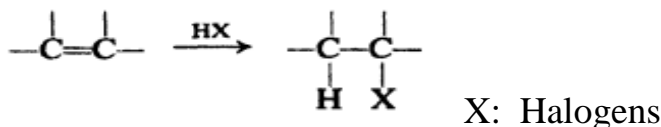
*Examples:*



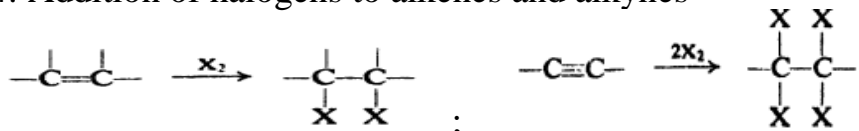
2: Halogenation of hydrocarbons:



3: Addition of hydrogen halides to alkenes.



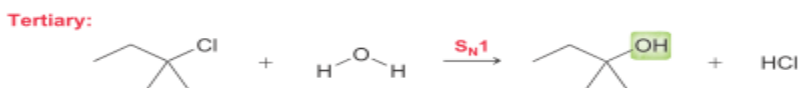
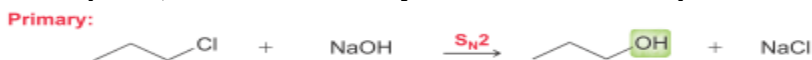
4: Addition of halogens to alkenes and alkynes



## Preparation of Alcohols:

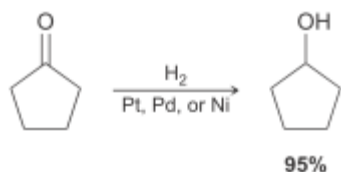
### 1. Substitution reaction

Alcohols can be prepared by substitution reactions in which a leaving group is replaced by a hydroxyl group. A primary substrate will require S<sub>N</sub>2 conditions (a strong nucleophile), while a tertiary substrate will require S<sub>N</sub>1 conditions (a weak nucleophile).

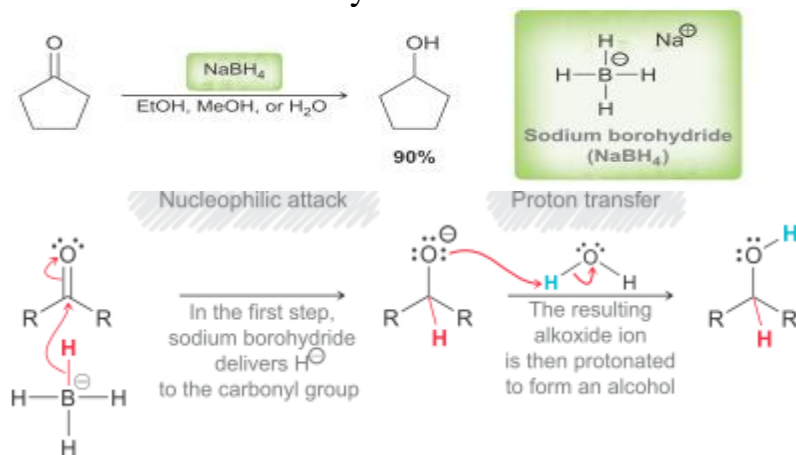


### 2. Reduction

1. Reduction using H<sub>2</sub> /catalyst

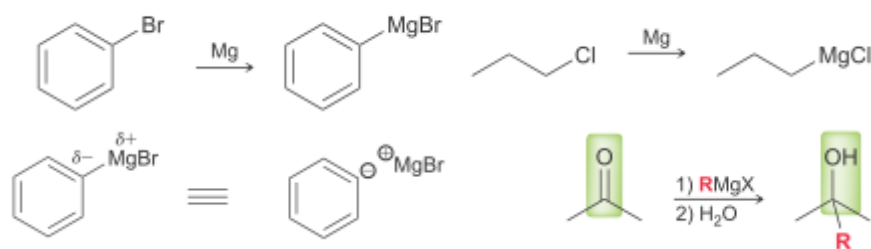


2- Sodium borohydride ( $\text{NaBH}_4$ ) is another common reducing agent that can be used to reduce ketones or aldehydes.



### 3. Grignard Reagents

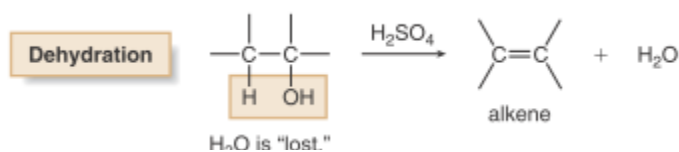
A Grignard reagent is formed by the reaction between an alkyl halide and magnesium.



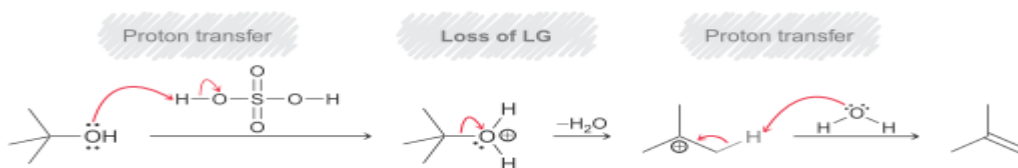
### Reaction of alcohols

#### 1. Dehydration:

When an alcohol is treated with a strong acid such as  $\text{H}_2\text{SO}_4$ , the elements of water are lost and an alkene is formed as product. Loss of  $\text{H}_2\text{O}$  from a starting material is called dehydration. Dehydration takes place by breaking bonds on two adjacent atoms—the  $\text{C}-\text{OH}$  bond and an adjacent  $\text{C}-\text{H}$  bond.



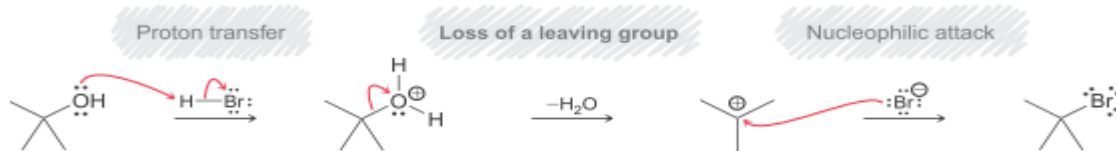
This transformation follows an  $\text{E1}$  mechanism:



#### 2. Substitution reaction:

$\text{S}_{\text{N}}1$  Reactions with Alcohols:

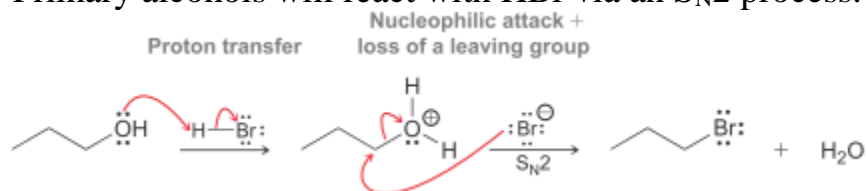
Tertiary alcohols will undergo a substitution reaction when treated with a hydrogen halide.



### $S_N2$ Reactions with Alcohols

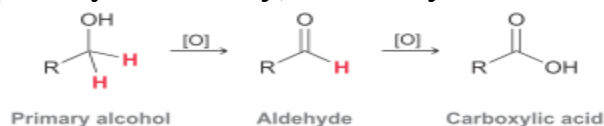
Primary and secondary alcohols will undergo substitution reactions with a variety of reagents, all of which proceed via an  $S_N2$  process.

1: Primary alcohols will react with HBr via an  $S_N2$  process.



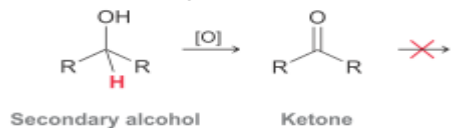
### 3. Oxidation

The outcome of an oxidation process depends on whether the starting alcohol is primary, secondary, or tertiary. Let's first consider the oxidation of a primary alcohol.

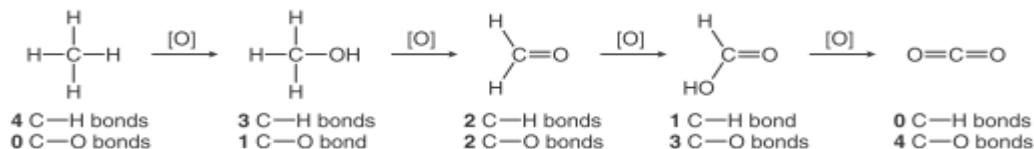


Notice that a primary alcohol has two protons at the  $\alpha$  position (the carbon atom bearing the Hydroxyl group). As a result, primary alcohols can be oxidized twice. The first oxidation produces an aldehyde, and then oxidation of the aldehyde produces a carboxylic acid.

Secondary alcohols only have one proton at the  $\alpha$  position so they can only be oxidized once, forming a ketone.



Tertiary alcohols do not have any protons at the  $\alpha$  position, and as a result, they generally do not undergo oxidation:

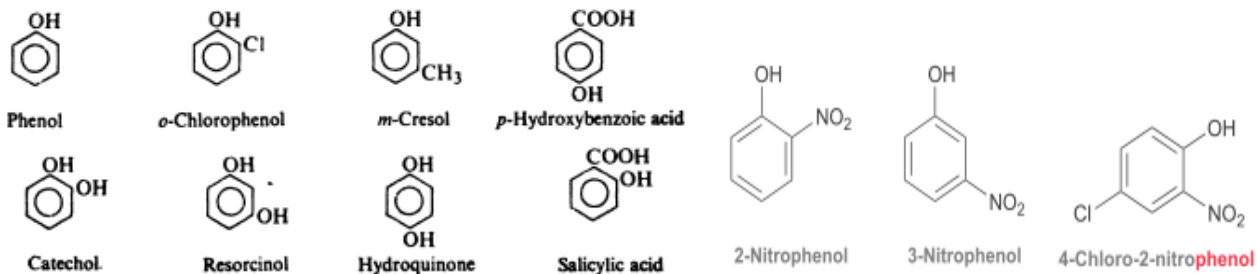


### Phenols

#### Structure and nomenclature

Phenols are compounds of the general formula  $ArOH$ , where  $Ar$  is phenyl, substituted phenyl, or one of the other aryl groups. Phenols differ from alcohols in having the  $OH$  group attached directly to an aromatic ring. Phenols are generally named as derivatives of the simplest member of the family, phenol. The methyl phenols are given the special name of cresols. Occasionally phenols are named as hydroxyl compounds.





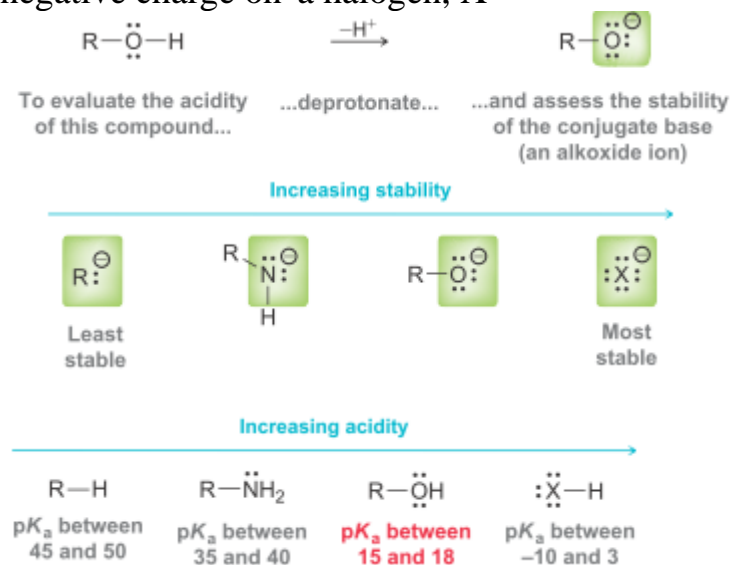
## Physical properties

The simplest phenols are liquids or low-melting solids; because of hydrogen bonding, they have quite high boiling points. Phenol itself is somewhat soluble in water (9 g per 100 g of water), presumably because of hydrogen bonding with the water; most other phenols are essentially insoluble in water. From a comparison of the physical properties of the isomeric nitro phenols we notice that *o*-nitro phenol is the only one of the three that is readily steam-distillable, its melting point is (45°) has a much lower melting point and much lower solubility in water (0.2gm/100ml) than its isomers (*m*- nitro phenol: m.p:96°), Solubility:(1.4gm/100ml) and (*p*-nitro phenol: m.p:114°) ,Solubility: (1.7gm/100ml); How can these differences be accounted for?

## Acidity of Alcohols and Phenols

### Acidity of the Hydroxyl Functional Group:

The acidity of a compound can be qualitatively evaluated by analyzing the stability of its conjugate base: The conjugate base of an alcohol is called an alkoxide ion, and it exhibits a negative charge on an oxygen atom. A negative charge on an oxygen atom is more stable than a negative charge on a carbon or nitrogen atom but less stable than a negative charge on a halogen, X

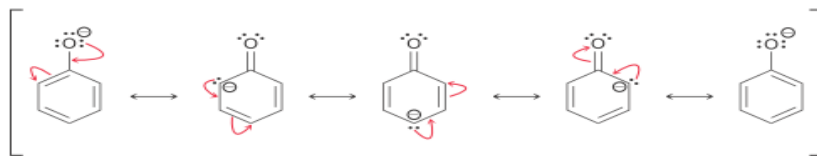


## Factors Affecting the Acidity of Alcohols and Phenols

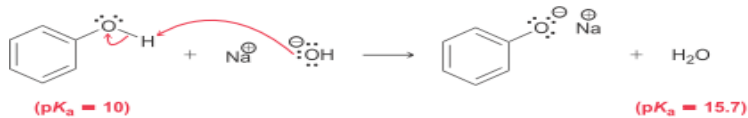
There are three factors for comparing the acidity:

1: **resonance** : Compare the pK<sub>a</sub> values of cyclohexanol and phenol:

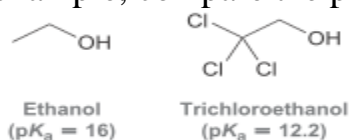
When phenol is deprotonated, the conjugate base is stabilized by resonance.



As a result, phenol does not need to be deprotonated with a very strong base like sodium hydride. Instead, it can be deprotonated by hydroxide.



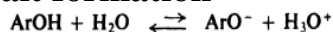
**2. Induction.** Another factor in comparing the acidity of alcohols is induction. As an example, compare the pK<sub>a</sub> values of ethanol and trichloroethanol.



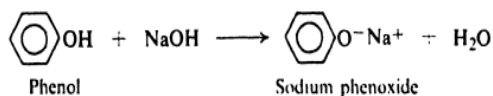
Trichloro ethanol is more acidic than ethanol, because the conjugate base of trichloro ethanol is stabilized by the electron-withdrawing effects of the nearby chlorine atoms.

## Reactions

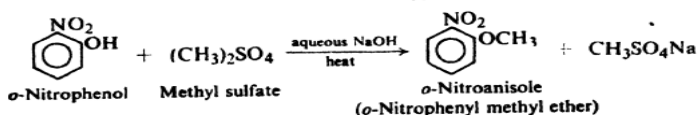
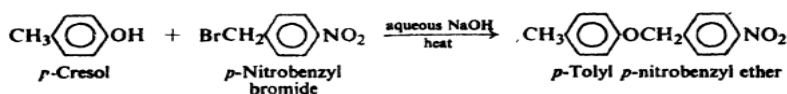
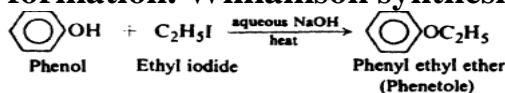
### 1: Acidity. Salt formation



Example:



### 2: Ether formation. Williamson synthesis:



### 3: Ester formation:

