

# **BOOKS**

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,
- 4) Organic Chemistry: A Brief Course, R. C. Atkins, F.A. Carey

## 5. ALCOHOLS

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#### 5.4.5 Oxidation of Alcohols

General formula of alcohols is  $C_nH_{2n+1}OH$  or  $C_nH_{2n+2}O$  and alcohols contain the hydroxyl group (-OH), bonded to a carbon atom of an alkyl or substituted alkyl group. The functional group of an alcohol is the hydroxyl group, -OH. Alcohols are some of the most important molecules in organic chemistry

### Classification of alcohols

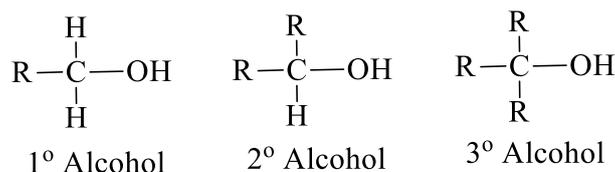
*a. According to the number of OH in the structure:*

If there is one-OH, is monoalcohol,

If there is two-OH, is dialcohol,  
 If there is three -OH, is trialcohol,  
 If there is more than one -OH, is polyalcohol.

*b. According to carbon atom is attached to OH group:*

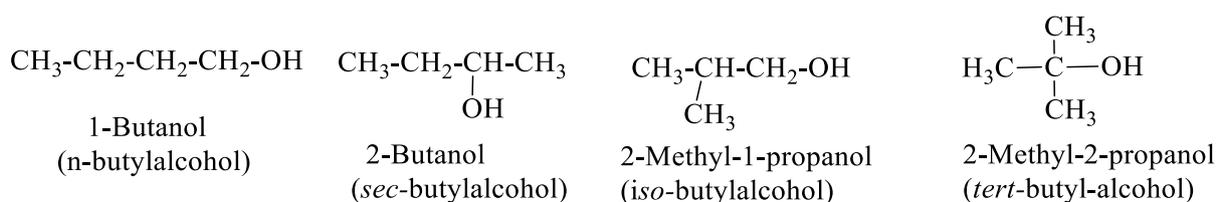
Alcohols are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) or tertiary ( $3^\circ$ ), which refers to the carbon bearing the hydroxyl group.



## 5.1 Nomenclature of Alcohols

The naming rules of alcohols are given below:

1. Start with the parent chain and replace the hydrocarbon -e ending with -ol.
2. Number the hydrocarbon chain. The carbon containing the -OH group should have the lowest number.
3. Number the position of the -OH group.
4. Number and name other side chains or function groups using IUPAC rules.



## 5.2 Physical Properties of Alcohols

The functional group of an alcohol is the hydroxyl group, -OH. This group has two reactive covalent bonds, the C-O bond and the O-H bond. The electronegativity of oxygen is greater than that of carbon and hydrogen. Therefore alcohols are polar compounds and there are dipole-dipole interactions between alcohol molecules. Alcohols, like water, can form *hydrogen bonds*. Alcohols have much higher boiling points than similar (same molecular mass) hydrocarbons (alkanes, alkenes, alkynes), haloalkane, ether or ketones. The

boiling point of monoalcohol increases as the carbon number increases. In the case of branched alcohols, b.p. is lower than that straight-chain analogues. If alcohols have same carbon atoms, as number of -OH group increases, b.p of the molecule increases.

<u>Molecule</u>	<u>Name</u>	<u>Boiling Point</u>
$\text{H}_3\text{C}-\text{CH}_2-\text{OH}$	Ethanol	b.p:78 °C
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	Butanol	b.p : 117.7 °C
$\begin{array}{c} \text{CH}_3 \\   \\ \text{H}_3\text{C}-\text{C}-\text{OH} \\   \\ \text{CH}_3 \end{array}$	2-Methy-2-propanol	b.p : 82.5 °C
$\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\   \quad   \\ \text{OH} \quad \text{OH} \end{array}$	Ethane-1,2-diol	b.p:198 °C
$\begin{array}{c} \text{H}_2\text{C}-\text{CH}-\text{CH}_2 \\   \quad   \quad   \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Propane-1,2,3-triol	b.p:290 °C degradable

Alcohols can hydrogen bond to water and have similar solubility in water, but alcohols, have properties between the extremes of hydrocarbons and water. When the hydrocarbon chain is short, the alcohol is soluble in water. As the hydrocarbon chain becomes longer, the alcohol becomes less soluble in water. Diols and triols have higher b.p's and they are also more water soluble compounds. Alcohols have acidities similar to water.

### 5.3 Synthesis of Alcohols

Alcohols can be prepared by the hydration of alkenes, from Grignard reagents, or by the reduction of aldehydes, ketones, and esters.

#### 5.3.1 Alcohols from Alkenes

##### 5.3.1.1 Hydration of Alkenes

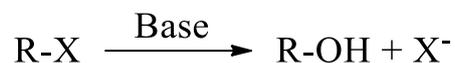
Acid catalysed addition of  $\text{H}_2\text{O}$ . See "Alkenes" Section for details

### 5.3.1.2 Oxidation of Alkenes

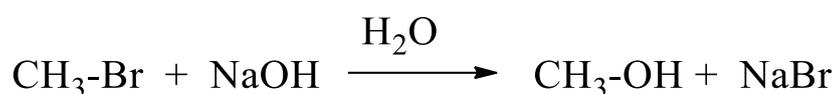
Reagents:  $\text{KMnO}_4/\text{OH}^-$  or  $\text{OsO}_4$ . See "Alkenes" section for details

### 5.3.2 Alcohols from Alkyl halides

Hydrolysis of alkyl-halides give alcohols.



This is a nucleophilic substitution reaction and  $\text{NaOH}$ ,  $\text{KOH}$  or  $\text{H}_2\text{O}$  can be used as a base.

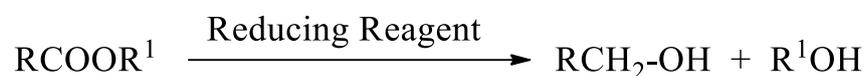


### 5.3.3 Reduction of Carbonyl Compounds

Carbonyl compounds, esters, aldehydes and ketones are reduced to alcohols with various reagents such as sodium borohydride,  $\text{NaBH}_4$ , lithium aluminium hydride,  $\text{LiAlH}_4$ , or  $\text{H}_2$ / catalysts (e.g.,  $\text{Pd}$ ,  $\text{Pt}$ ,  $\text{Ni}$ ). Lithium aluminium hydride is a very strong reducing agent that reduces many functional groups in addition to aldehydes and ketones. Sodium borohydride is a much weaker reducing agent that basically will reduce only aldehydes and ketones to alcohols.

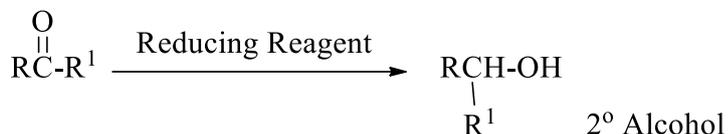
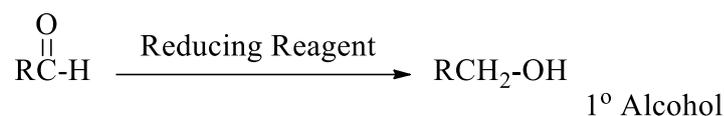
#### 5.3.3.1 Alcohol from Esters

Esters are reduced with lithium aluminium hydride. In these reactions, two alcohols are formed.



Reducing reagent :  $\text{Na}$ /ethanol or  $\text{LiAlH}_4$

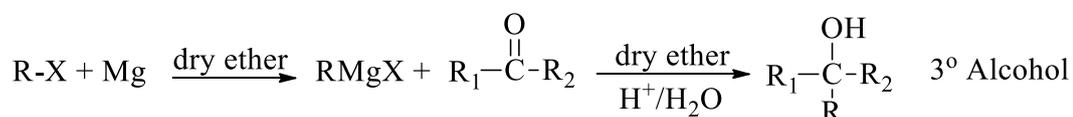
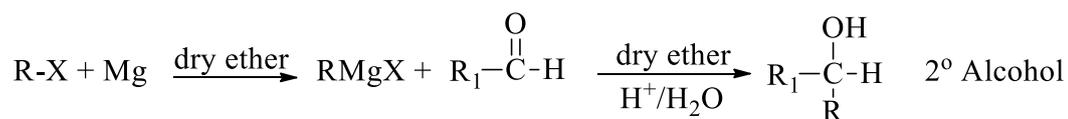
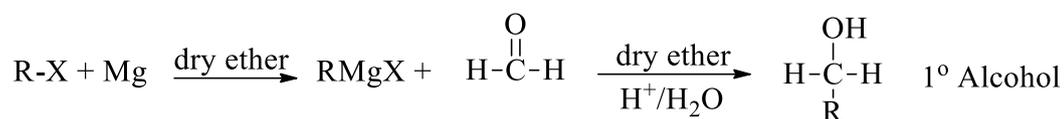
### 5.3.3.2 Alcohols from Aldehyde and Ketones



Reducing reagents :  $\text{H}_2/\text{Pt}$ ,  $\text{LiAlH}_4$  or  $\text{NaBH}_4$

### 5.3.4 Alcohols from Grignard Reagent

The Grignard reaction is the only simple method available that is capable of producing primary, secondary, and tertiary alcohols.



## 5.4 Reactions of Alcohols

Alcohols are converted to metal salts, alkyl halides, esters, aldehydes, ketones, and carboxylic acids.

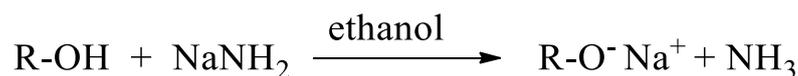
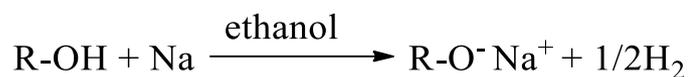
### 5.4.1 Combustion Reactions

Alcohols burn in oxygen to produce carbon dioxide and heat.



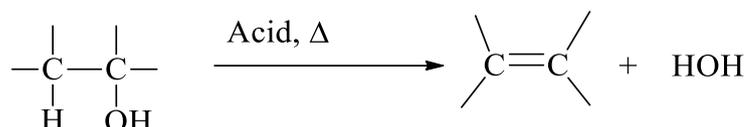
## 5.4.2 Deprotonation

Alcohols are slightly weaker acids than water, with a  $pK_a$  value of approximately 16. The reaction of ethanol with sodium metal (or a base) produces sodium ethoxide and hydrogen gas.



## 5.4.3 Dehydration of Alcohols

See "Alkenes" section for details.



## 5.4.4 Alkyl Halide Formation

### 5.4.4.1 Reaction with Halogen Acids

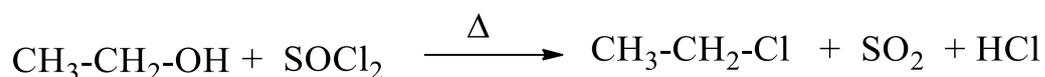
Alcohols are converted to alkyl halides by nucleophilic substitution ( $S_N$ ) reactions with halogen acids.



X: I, Br, Cl (needs catalyst (e.g.  $ZnCl_2$ ))

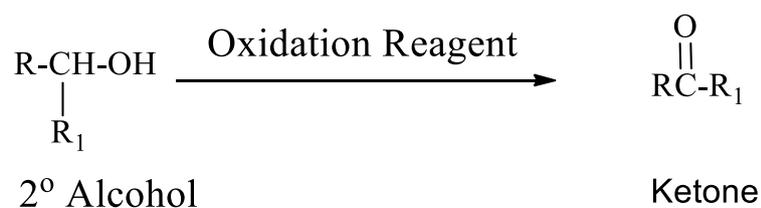
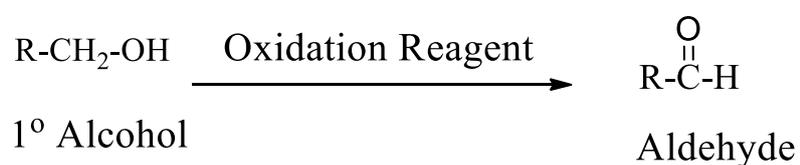
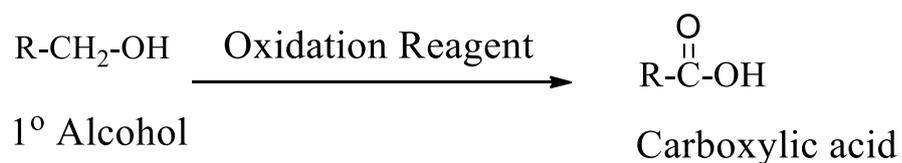
### 5.4.4.2 Reaction with Phosphorus tri or pentahalide, Thionyl chloride

A more efficient method of preparing alkyl halides from alcohols involves reactions with thionyl chloride ( $SOCl_2$ ).



### 5.4.5 Oxidation of Alcohols

The oxidation of alcohols can lead to the formation of aldehydes and ketones. Aldehydes are formed from primary alcohols, while ketones are formed from secondary alcohols.



Oxidation reagents: pyridinium chlorochromate (PCC),  
 $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ,  $\Delta$