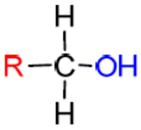
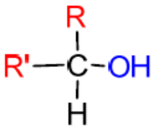
Chapter 8: Alcohols, phenols, ethers.

8.1. Definition:

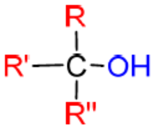
Alcohol is a compound that has a hydroxyl group bonded to a saturated, sp^3-hybridized carbon atom, R-OH. They are classified as **primary, secondary,** or **tertiary alcohols**.



Primary alcohol



Secondary alcohol



Tertiary alcohol

A phenol has a hydroxyl group bonded to an aromatic ring, Ar-OH; and an ether has an oxygen atom bonded to two organic groups, R-O-R′. The corresponding sulfur analogs are called thiols (R-SH), thio phenols (Ar-SH), and sulfides (R-S-R′).

8.2.Nomenclature of Alcohols, phenols and ethers:

a) Alcohols:

In the IUPAC system, the hydroxyl group in alcohols is indicated by the ending **-ol.**

In common names, the separate word *alcohol* is placed after the name of the alkyl group. The following examples illustrate the use of IUPAC rules, with common names given in parentheses.

CH_3OH

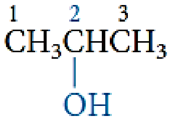
methanol
(methyl alcohol)

CH_3CH_2OH

ethanol
(ethyl alcohol)

$\overset{3}{CH_3}\overset{2}{CH_2}\overset{1}{CH_2}OH$

1-propanol
(*n*-propyl alcohol)

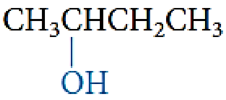


$\overset{1}{CH_3}\underset{\underset{OH}{|}}{\overset{2}{C}}H\overset{3}{CH_3}$

2-propanol
(isopropyl alcohol)

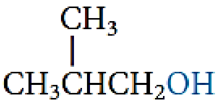
$CH_3CH_2CH_2CH_2OH$

1-butanol
(*n*-butyl alcohol)



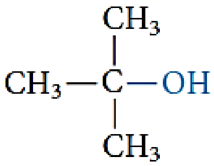
$CH_3\underset{\underset{OH}{|}}{C}HCH_2CH_3$

2-butanol
(*sec*-butyl alcohol)



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2OH$

2-methyl-1-propanol
(isobutyl alcohol)

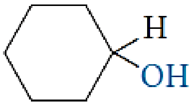


$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$

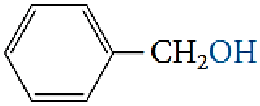
2-methyl-2-propanol
(*tert*-butyl alcohol)

$CH_2{=}CHCH_2OH$

2-propen-1-ol
(allyl alcohol)



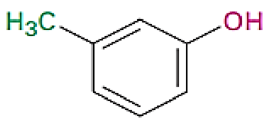
cyclohexanol
(cyclohexyl alcohol)



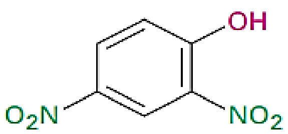
phenylmethanol
(benzyl alcohol)

b) phenols:

Phenols are usually named as derivatives of the parent compounds.

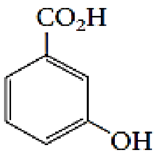


m-**Methylphenol**
(*m*-cresol)

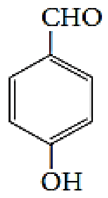


2,4-Dinitrophenol

The hydroxyl group is named as a substituent when it occurs in the same molecule with carboxylic acid, aldehyde, or ketone functionalities, which have priority in naming.

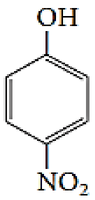


m-hydroxy
benzoic acid



p-hydroxybenzaldehyde

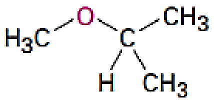
but



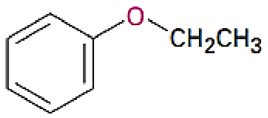
p-nitrophenol
(*not p*-hydroxynitrobenzene)

c) Ethers:

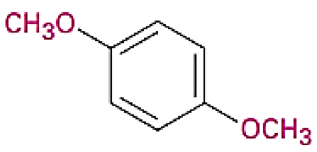
Simple ethers that contain no other functional groups are named by identifying the two organic groups and adding the word ether.



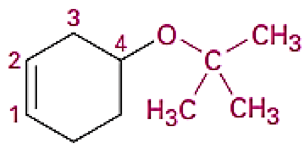
Isopropyl methyl ether



Ethyl phenyl ether



***p*-Dimethoxybenzene**



4-*tert*-Butoxycyclohex-1-ene

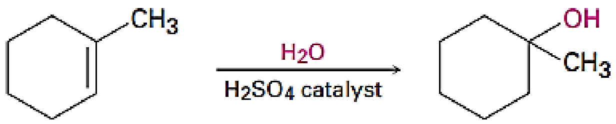
8.3. Physical properties:

- ✓ Acyclic alcohols are liquids up to C_{12}, and solids beyond that.
- ✓ The boiling points of alcohols are much higher than those of corresponding hydrocarbons and other functional compounds with the same number of carbon atoms. The high boiling points of alcohols are due to the presence of **intermolecular bonds called hydrogen bonds**.
- ✓ The longer the carbon chain of the alcohol, the lower its water solubility.

8.4. Preparation of alcohols:

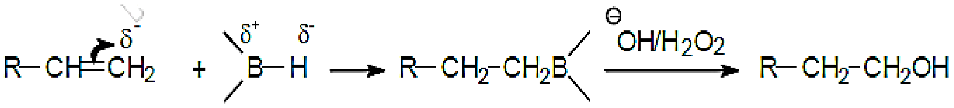
Alcohols occupy a central position in organic chemistry. They can be prepared from many other kinds of compounds (alkenes, alkyl halides, ketones, aldehydes, and esters, among others), and they can be transformed into an equally wide assortment of compounds.

8.4.1. Hydration of alkenes :



1-Methylcyclohexene **1-Methylcyclohexanol**

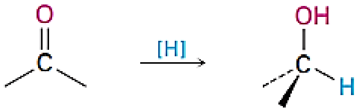
8.4.2. Hydroboration of alkenes (anti-Markovnikov addition):



8.4.3. Hydrolysis of halogen derivatives :

$$R-X + \overset{\ominus}{OH} \xrightarrow{SN_1 \text{ ou } SN_2} R-OH + \overset{\ominus}{X}$$

8.4. 4. Reduction of Carbonyl Compounds :



where [H] is a reducing agent

A carbonyl compound **An alcohol**

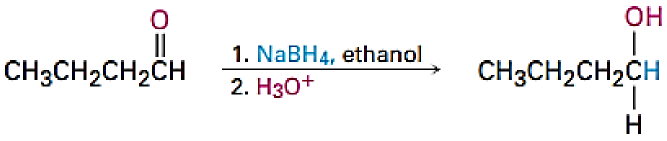
a. Reduction of Aldehydes and Ketones:

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

An aldehyde **A primary alcohol** **A ketone** **A secondary alcohol**

Many reducing reagents are available, but sodium borohydride, $NaBH_4$, is usually chosen because of its safety. It is a white, crystalline solid that can be weighed in the open atmosphere and used in either water or alcohol solution.

Aldehyde reduction

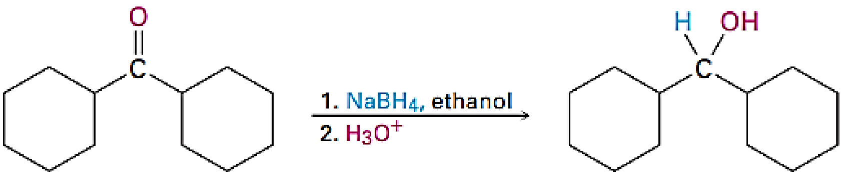


$$CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow[2.\ H_3O^+]{1.\ NaBH_4,\ ethanol} CH_3CH_2CH_2\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}H$$

Butanal

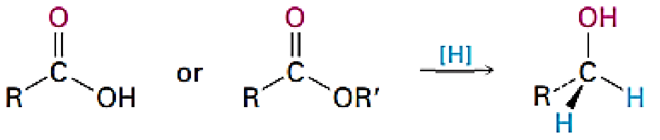
Butan-1-ol (85%)
(a 1° alcohol)

Ketone reduction



b. Reduction of Carboxylic Acids and Esters:

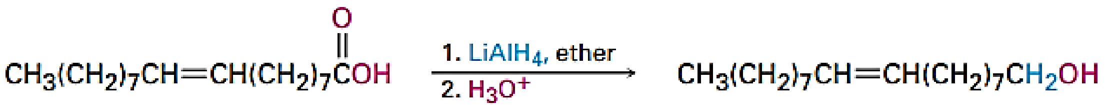
Esters and carboxylic acids are reduced to give primary alcohols.



A carboxylic acid **An ester** **A primary alcohol**

These reactions aren't as rapid as the reductions of aldehydes and ketones, so the more powerful reducing agent lithium aluminum hydride ($LiAlH_4$) is used rather than $NaBH_4$. ($LiAlH_4$ will also reduce aldehydes and ketones.)

Carboxylic acid reduction

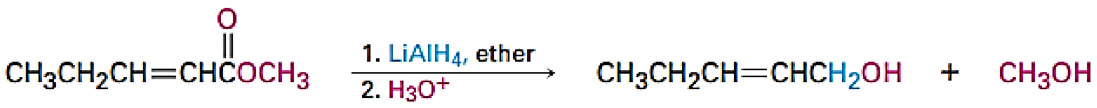


$$CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{\overset{O}{\|}}{C}OH \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4,\ ether} CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OH$$

Octadec-9-enoic acid
(oleic acid)

Octadec-9-en-1-ol (87%)

Ester reduction



$$CH_3CH_2CH{=}CH\overset{\overset{O}{\|}}{C}OCH_3 \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4,\ ether} CH_3CH_2CH{=}CHCH_2OH + CH_3OH$$

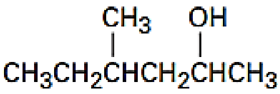
Methyl pent-2-enoate

Pent-2-en-1-ol (91%)

Exercise:

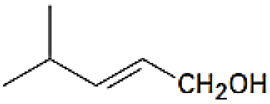
What carbonyl compound(s) might you reduce to obtain the following alcohols?

(a)

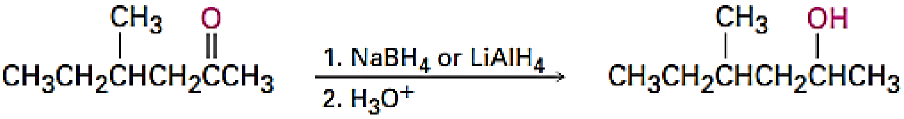


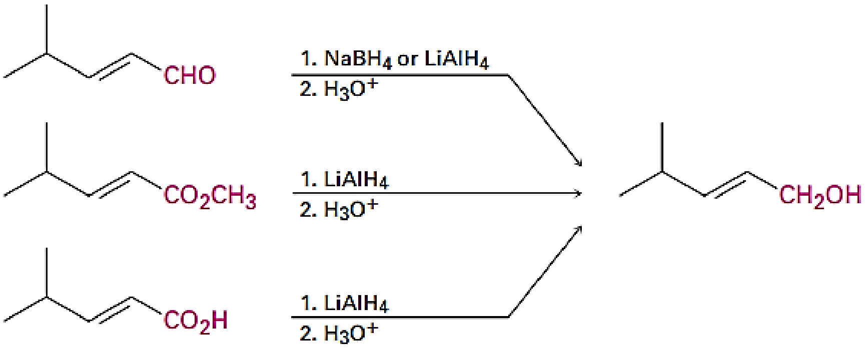
$CH_3CH_2CH(CH_3)CH_2CH(OH)CH_3$

(b)

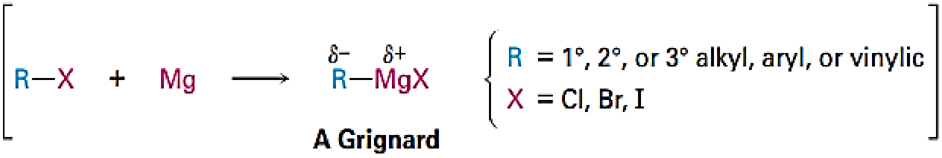


Solution:

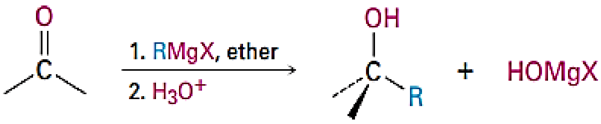




8.4. 5. Grignard Reactions of Carbonyl Compounds :

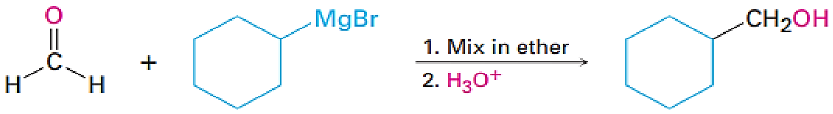


A Grignard reagent



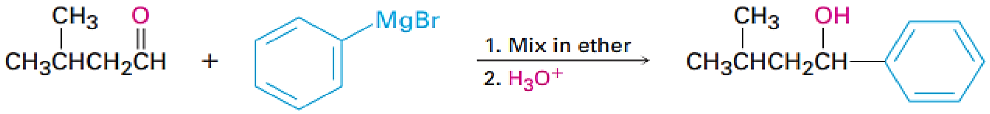
Examples:

Formaldehyde reaction



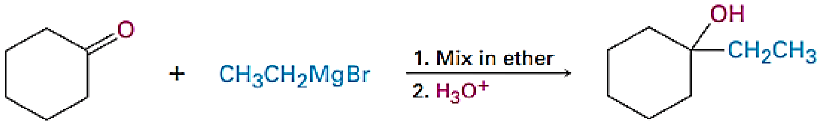
Formaldehyde **Cyclohexylmagnesium bromide** **Cyclohexylmethanol (65%) (a 1° alcohol)**

Aldehyde reaction



3-Methylbutanal **Phenylmagnesium bromide** **3-Methyl-1-phenyl-butan-1-ol (73%) (a 2° alcohol)**

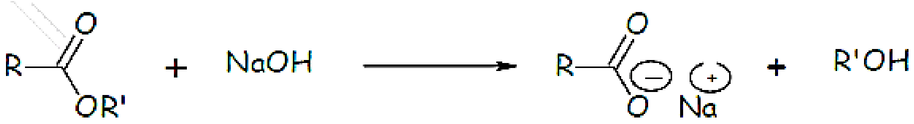
Ketone reaction



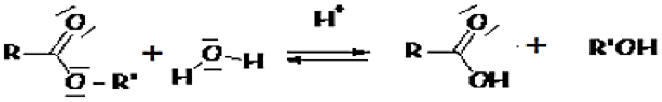
Cyclohexanone **Ethylmagnesium bromide** **1-Ethylcyclohexanol (89%) (a 3° alcohol)**

8.4. 6.Hydrolysis of Esters:

a. Saponification = Hydrolysis with NaOH (basic hydrolysis)



b. Hydrolysis under acidic conditions (H^+) :



8.5. Reactivity of Alcohols:

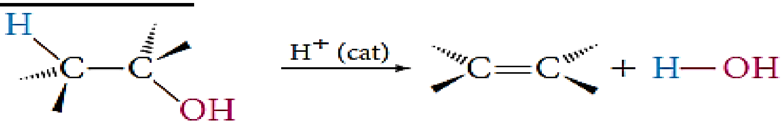
Two characteristics of the functional group in alcohols determine their reactivity: the polarization of the O-H and C-O bonds **(O-H bond: ΔEN = 1.24; C-O bond: ΔEN = 0.89),** due to oxygen's high electronegativity and the presence of two lone pairs on the oxygen atom.

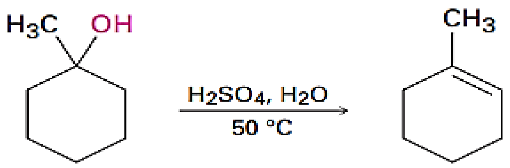
8.5.1. Conversion to Alkoxides :

$$2\,RO{-}H + 2\,Na \longrightarrow 2\,RO^- Na^+ + H_2$$

$$RO{-}H + NaH \longrightarrow RO^- Na^+ + H_2$$

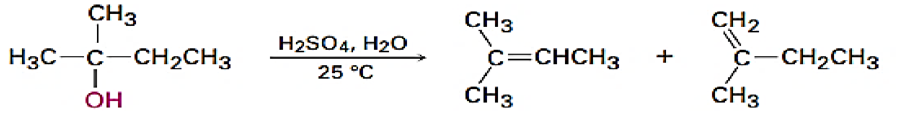
8.5.2. Dehydration to Alkenes :





1-Methylcyclohexanol **1-Methylcyclohexene (91%)**

Acid-catalyzed dehydrations usually follow Zaitsev's rule and yield the more highly substituted alkene as the major product. Thus, 2-methyl butan-2-ol gives primarily 2-methylbut-2-ene (trisubstituted) rather than 2-methylbut-1-ene (disubstituted).



2-Methylbutan-2-ol **2-Methylbut-2-ene (trisubstituted)** **2-Methylbut-1-ene (disubstituted)**

Major product **Minor product**

8.5.3. Conversion to Alkyl Halides:

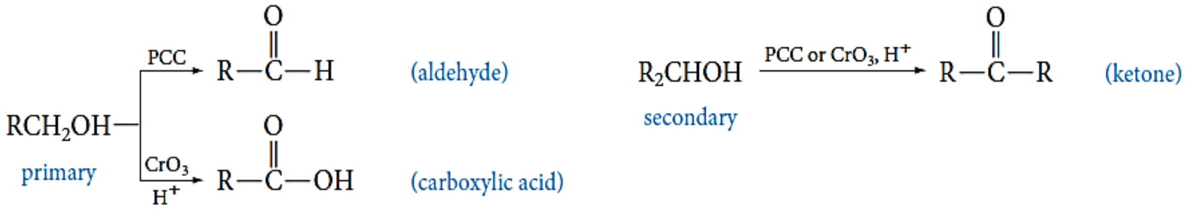
$$R{-}OH + HX \longrightarrow R{-}X + H_2O\ (X{=}Cl, Br, I)$$

$$R{-}OH + SOCl_2 \longrightarrow R{-}Cl + HCl + SO_2$$

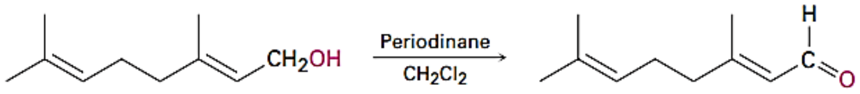
$$3\ R{-}OH + PX_3 \longrightarrow 3\ R{-}X + H_3PO_3\ (X{=}Cl, Br)$$

8.5.4. Oxidation of Alcohols :

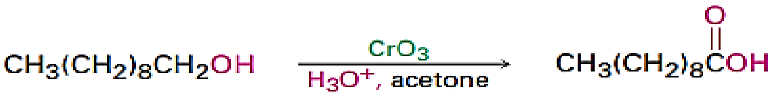
Primary alcohols yield aldehydes or carboxylic acids, and secondary alcohols yield ketones, but tertiary alcohols don't normally react with oxidizing agents.



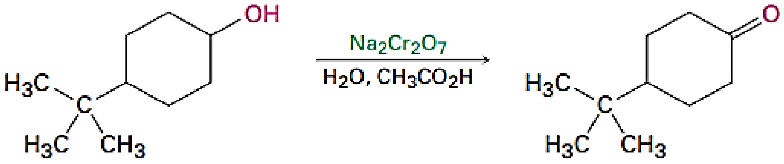
Examples:



Geraniol **Geranial (84%)**

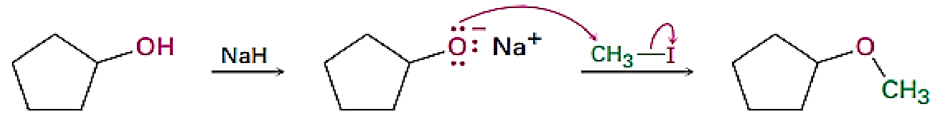


Decan-1-ol **Decanoic acid (93%)**



4-*tert*-Butylcyclohexanol **4-*tert*-Butylcyclohexanone (91%)**

8.5.5. Conversion into Ethers :



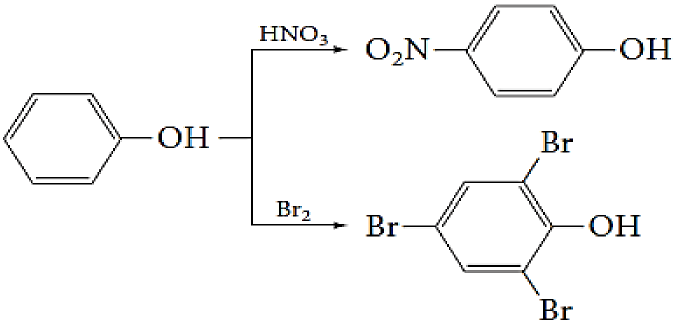
Cyclopentanol Alkoxide ion Cyclopentyl methyl ether (74%)

8.6. Reactivity of phenols:

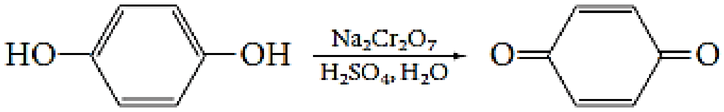
8.6.1. Preparation of Phenoxides:

$$\mathrm{ArO{-}H} + \mathrm{NaOH} \longrightarrow \mathrm{ArO^- \, Na^+} + \mathrm{H_2O}$$

8.6.2. Electrophilic Aromatic Substitution :



8.6.2. Oxidation to Quinones :



quinone