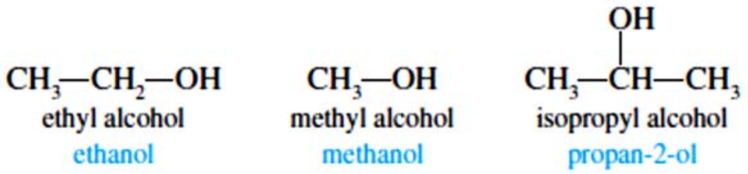
Alcohols

Are organic compounds containing hydroxyl (-OH) groups. They occur widely in nature and have many industrial and pharmaceutical applications. For example, methanol and ethanol are two industrially important alcohols.

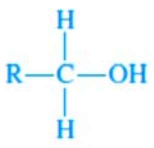


The structure of an alcohol resembles the structure of water, with an alkyl group replacing one of the hydrogen atoms of water. Both have sp^3-hybridized oxygen atoms.

Figure 10-1 Comparison of the structures of water and methyl alcohol.

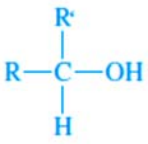
One way of organizing the alcohol family is to classify each alcohol according to the type of **carbinol carbon atom:** the one bonded to the -OH group. If this carbon atom is primary (bonded to one other carbon atom), the compound is a **primary alcohol.**
A **secondary alcohol** has the -OH group attached to a secondary carbon atom, and a **tertiary alcohol** has it bonded to a tertiary carbon.

Primary alcohol



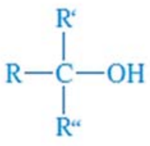
$$R-\underset{H}{\overset{H}{C}}-OH$$

Secondary alcohol



$$R-\underset{H}{\overset{R'}{C}}-OH$$

Tertiary alcohol

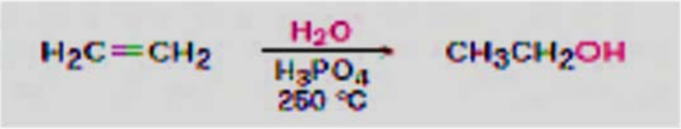


$$R-\underset{R''}{\overset{R'}{C}}-OH$$

Methanol is manufactured by catalytic reduction of carbon monoxide with hydrogen gas. Methanol is toxic to humans, causing blindness in small doses (15 mL) and death in larger amounts (100–250 mL). Industrially, it is used both as a solvent and as a starting material for production of formaldehyde (CH_2O) and acetic acid (CH_3CO_2H).

$$CO + 2H_2 \xrightarrow[\text{Zinc oxide/chromia catalyst}]{400\ °C} CH_3OH$$

Ethanol was one of the first organic chemicals to be prepared and purified. Its production by fermentation of grains and sugars and its purification by distillation . Ethanol for industrial use as a solvent or chemical intermediate is largely obtained by acid-catalyzed hydration of ethylene at high temperature.



$$H_2C{=}CH_2 \xrightarrow[H_3PO_4,\ 250\ °C]{H_2O} CH_3CH_2OH$$

Nomenclature of Alcohols:

1. Name the longest carbon chain that contains the carbon atom bearing the -OH group. Drop the final -*e* from the alkane name and add the suffix -*ol* to give the root name.

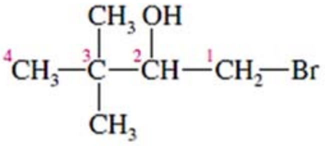
2. Number the longest carbon chain starting at the end nearest the hydroxyl group, and use the appropriate number to indicate the position of the -OH group.

(The hydroxyl group takes precedence over double and triple bonds.)

3. Name all the substituents and give their numbers, as you would for an alkane or an alkene.

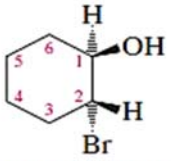
In the following example, the longest carbon chain has four carbons, so the root name is *butanol*. The group is on the second carbon atom, so this is a butan-2-ol.

The complete IUPAC name is 1-bromo-3,3-dimethylbutan-2-ol.

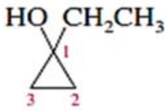


$$\overset{4}{C}H_3-\overset{3}{C}(CH_3)_2-\overset{2}{C}H(OH)-\overset{1}{C}H_2-Br$$

Cyclic alcohols are named using the prefix *cyclo*-; the hydroxyl group is assumed to be on C1.



trans-2-bromocyclohexanol

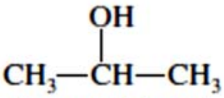


1-ethylcyclopropanol

Common Names of Alcohols

$CH_3—OH$
methyl alcohol
methanol

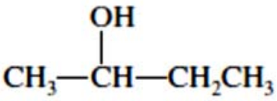
$CH_3CH_2CH_2—OH$
n-propyl alcohol
propan-1-ol



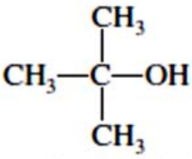
$CH_3—\overset{OH}{CH}—CH_3$
isopropyl alcohol
propan-2-ol

$H_2C{=}CH—CH_2—OH$
allyl alcohol
prop-2-en-1-ol

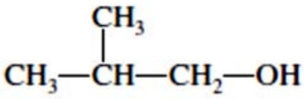
$CH_3CH_2CH_2CH_2—OH$
n-butyl alcohol
butan-1-ol



$CH_3—\overset{OH}{CH}—CH_2CH_3$
sec-butyl alcohol
butan-2-ol

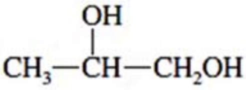


$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—OH$
tert-butyl alcohol
2-methylpropan-2-ol



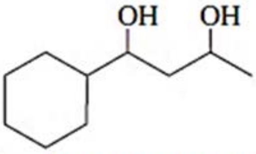
$CH_3—\overset{CH_3}{CH}—CH_2—OH$
isobutyl alcohol
2-methylpropan-1-ol

Alcohols with two -OH groups are called **diols** or **glycols.**

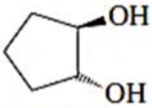


$CH_3—\overset{OH}{CH}—CH_2OH$

propane-1,2-diol

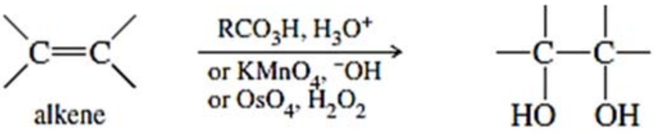


1-cyclohexylbutane-1,3-diol



trans-cyclopentane-1,2-diol

The term *glycol* generally means a 1,2-diol, or **vicinal diol,** with its two hydroxyl groups on adjacent carbon atoms. Glycols are usually synthesized by the hydroxylation of alkenes, using peroxyacids, osmium tetroxide, or potassium permanganate.



vicinal diol (glycol)

Physical Properties:

The electronegativity of oxygen is more than that of hydrogen. Therefore, in alcohols, the O–H bond is polar in nature. In other words, oxygen has a slight negative charge on it whereas hydrogen has a slight positive charge. This bond polarity alone cannot explain the higher boiling points of alcohols as compared to hydrocarbons or similar haloalkanes. Normally, hydrogen bonding is responsible for higher boiling points of alcohols. Hydrogen bonding amongst alcohol molecules is depicted in Fig.10.2.

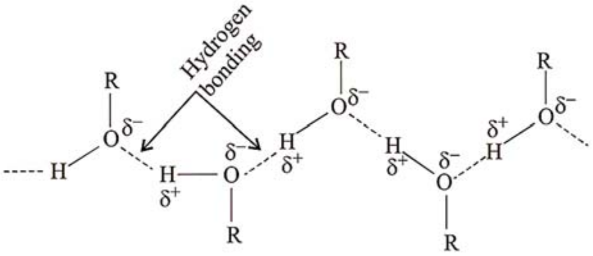
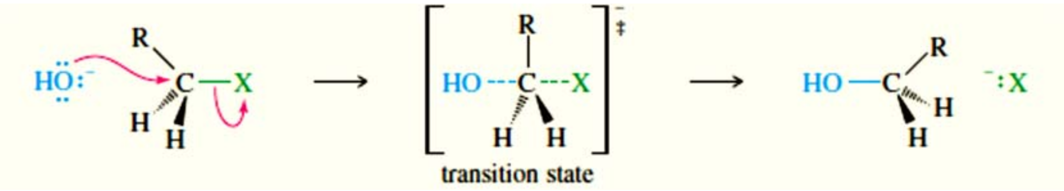


Fig.10.2: Hydrogen bonding in alcohol molecules

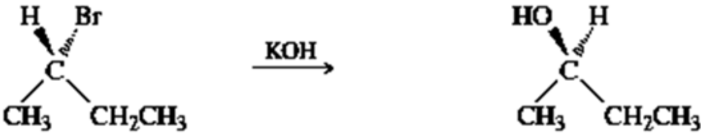
Synthesis of Alcohols:

1. Nucleophilic Substitution on an Alkyl Halide

Usually via the **SN2 mechanism**; competes with elimination.

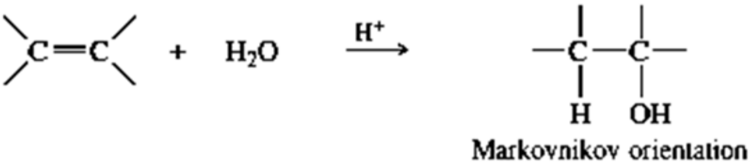


***Example*:**

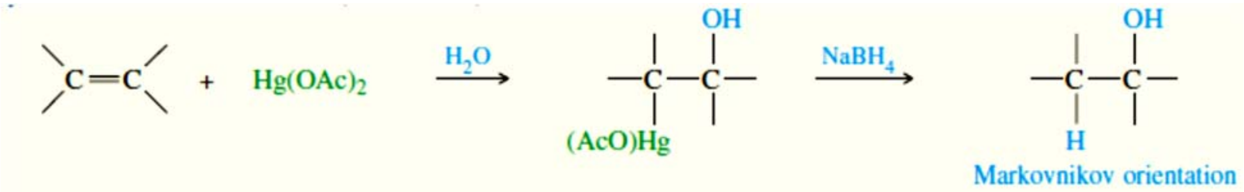


2. Synthesis of Alcohols from Alkenes

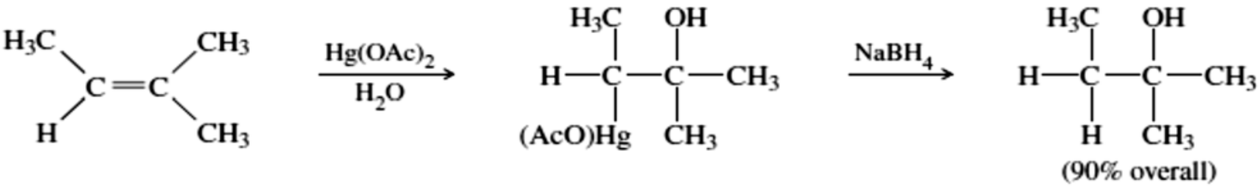
1. Acid-catalyzed hydration



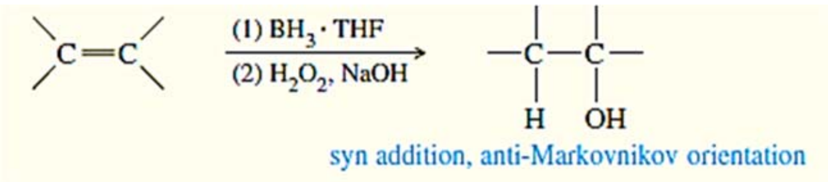
2. Oxymercuration–demercuration



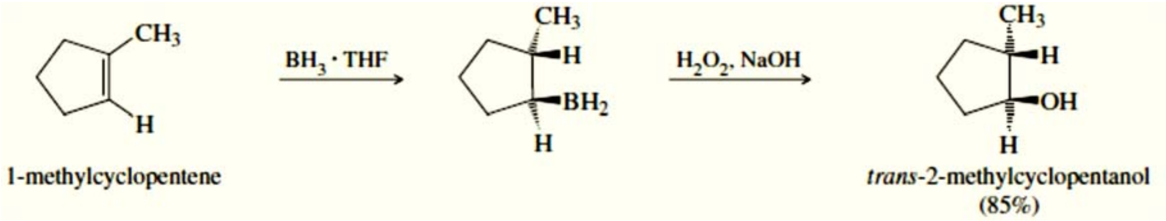
Example:



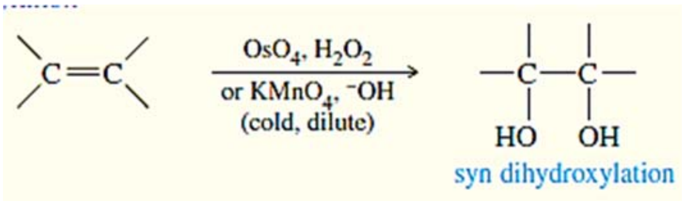
3. Hydroboration–oxidation:



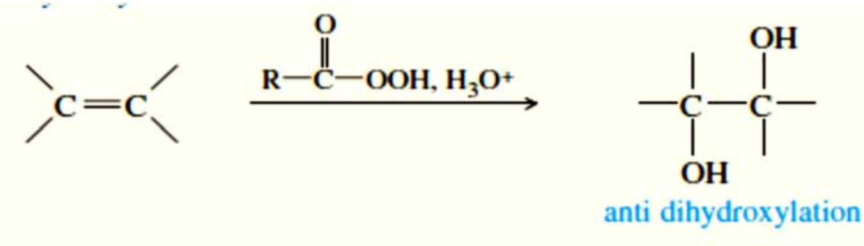
Example:



4. Dihydroxylation: synthesis of 1,2-diols from alkenes (*Syn Dihydroxylation*):

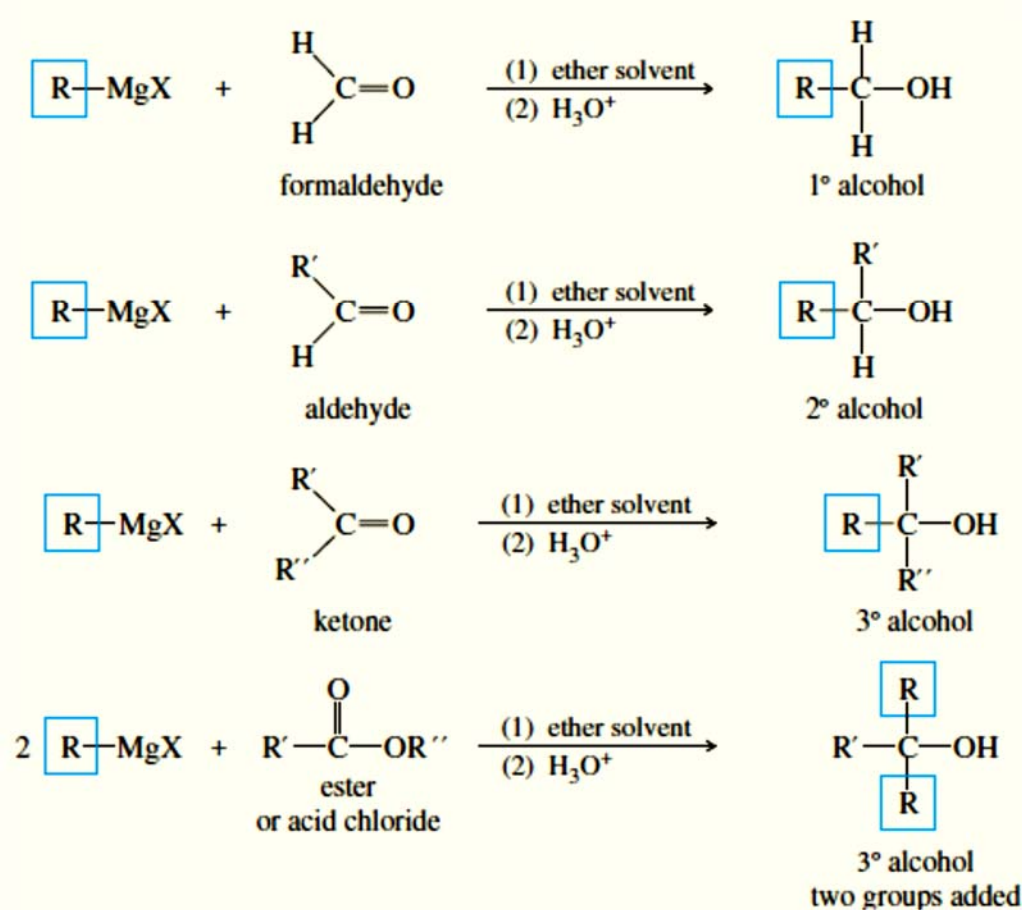


Anti Dihydroxylation:



Grignard Reactions:

1. Nucleophilic Additions to Carbonyl Compounds

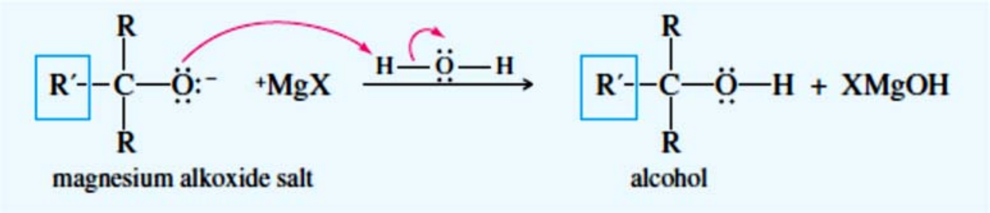


1.Formation of the Grignard reagent: Magnesium reacts with an alkyl halide in an anhydrous ether solution.

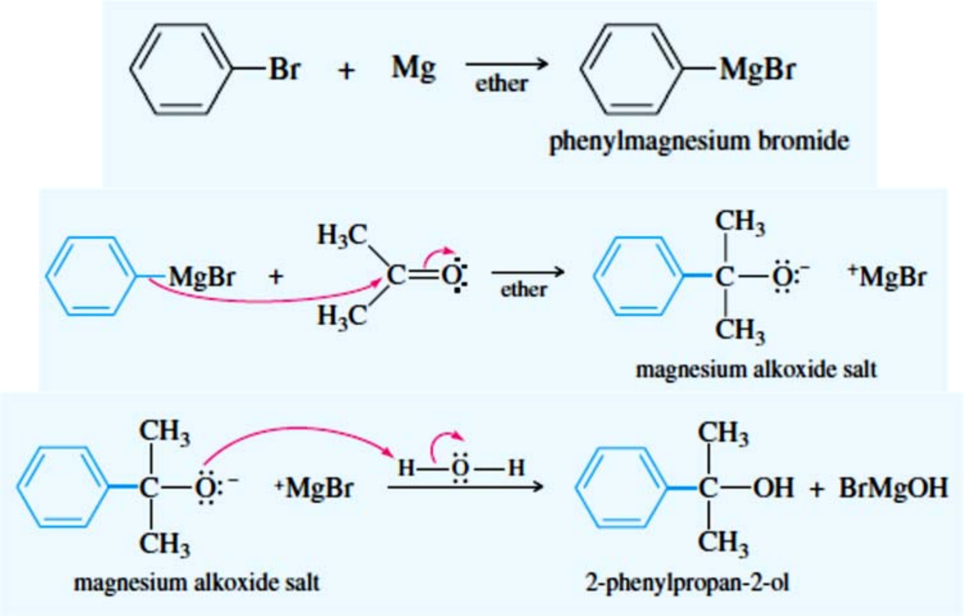
$$R'{-}X + Mg \xrightarrow[\text{ether}]{} R'{-}MgX$$

Reaction 1: The Grignard reagent attacks a carbonyl compound to form an alkoxide salt.

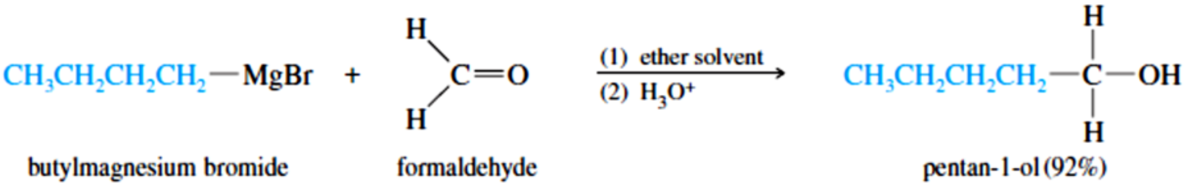
Reaction 2: After the first reaction is complete, water or dilute acid is added to protonate the alkoxide and give the alcohol.

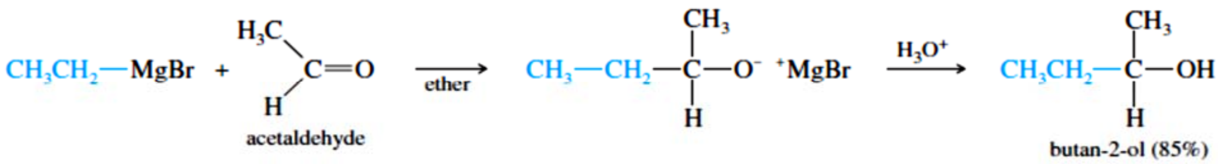


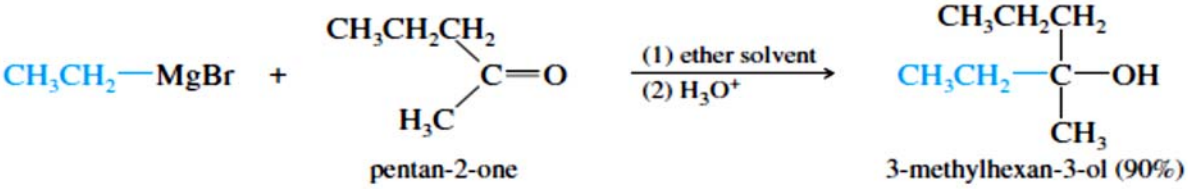
EXAMPLE: Addition of phenylmagnesium bromide to acetone.



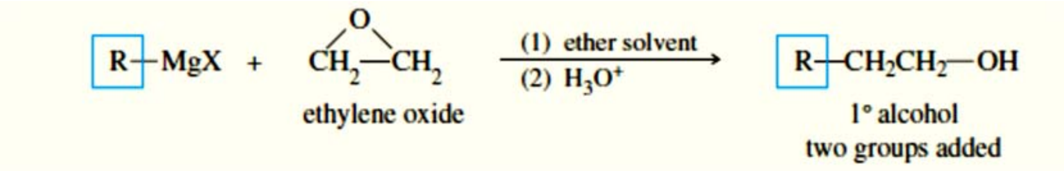
Examples:

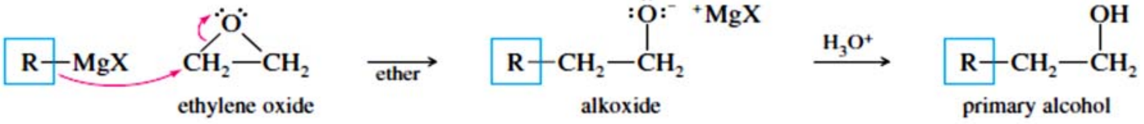






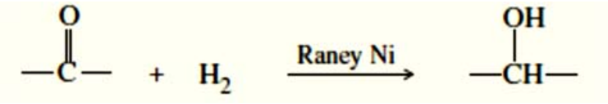
2. Nucleophilic Displacement of Epoxides





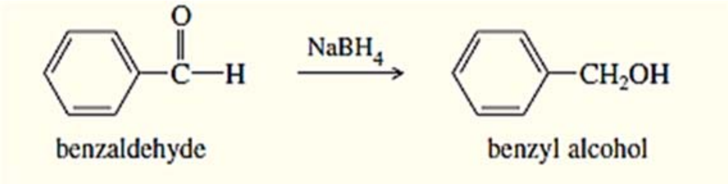
3. Reduction of carbonyl compounds

a. *Catalytic hydrogenation of aldehydes and ketones*

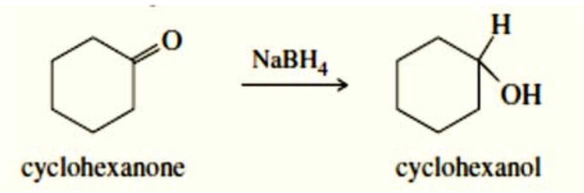


b. *Use of hydride reagents*

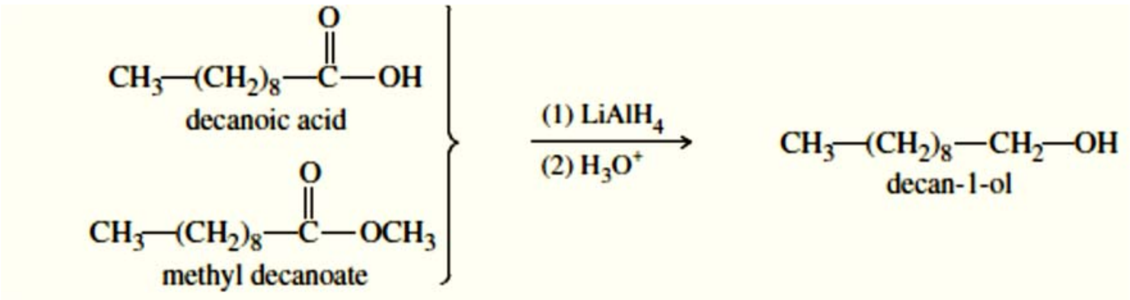
(1) Reduction of an aldehyde gives a primary alcohol



(2) Reduction of a ketone gives a secondary alcohol



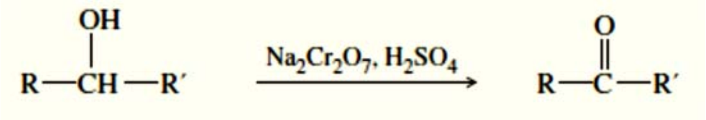
(3) Reduction of an acid or ester gives a primary alcohol



Reactions of Alcohols:

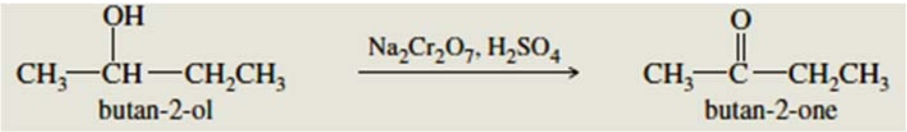
1. Oxidation–reduction reactions

a. *Oxidation of secondary alcohols to ketones*



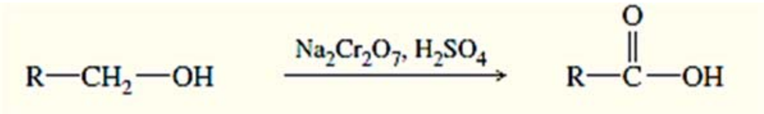
$$R-\underset{}{\overset{OH}{\overset{|}{CH}}}-R' \xrightarrow{Na_2Cr_2O_7,\ H_2SO_4} R-\overset{O}{\overset{\|}{C}}-R'$$

Example



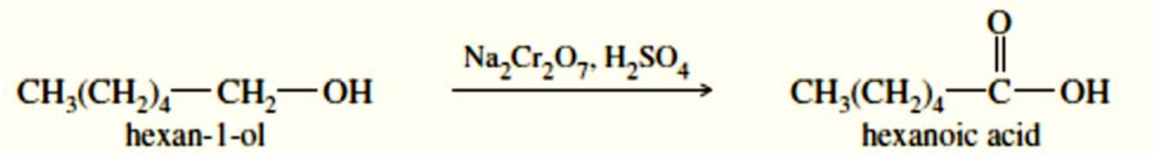
$$\underset{\text{butan-2-ol}}{CH_3-\overset{OH}{\overset{|}{CH}}-CH_2CH_3} \xrightarrow{Na_2Cr_2O_7,\ H_2SO_4} \underset{\text{butan-2-one}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3}$$

b. *Oxidation of primary alcohols to carboxylic acids*



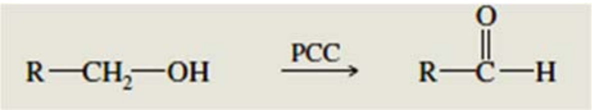
$$R-CH_2-OH \xrightarrow{Na_2Cr_2O_7,\ H_2SO_4} R-\overset{O}{\overset{\|}{C}}-OH$$

Example



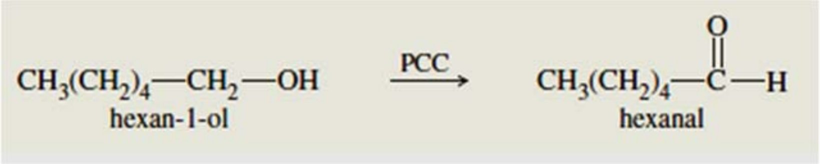
$$\underset{\text{hexan-1-ol}}{CH_3(CH_2)_4-CH_2-OH} \xrightarrow{Na_2Cr_2O_7,\ H_2SO_4} \underset{\text{hexanoic acid}}{CH_3(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH}$$

c. *Oxidation of primary alcohols to aldehydes*



$$R-CH_2-OH \xrightarrow{PCC} R-\overset{O}{\overset{\|}{C}}-H$$

Example

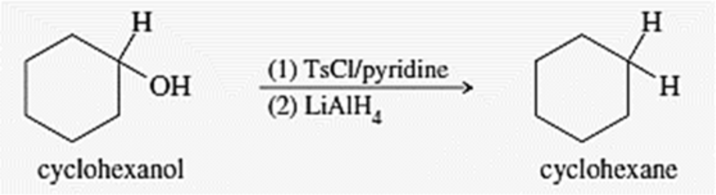


$$\underset{\text{hexan-1-ol}}{CH_3(CH_2)_4-CH_2-OH} \xrightarrow{PCC} \underset{\text{hexanal}}{CH_3(CH_2)_4-\overset{O}{\overset{\|}{C}}-H}$$

d. *Reduction of alcohols to alkanes*

$$R-OH \xrightarrow[\text{(2) LiAlH}_4]{\text{(1) TsCl/pyridine}} R-H$$

Example



2. Cleavage of the alcohol hydroxyl group

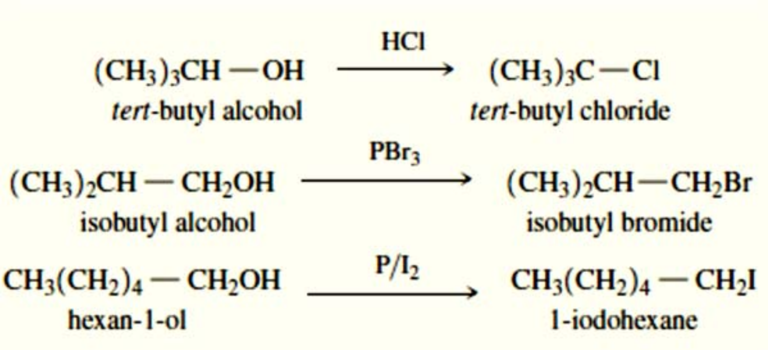
a. *Conversion of alcohols to alkyl halides*

$$R{-}OH \xrightarrow{HCl \text{ or } SOCl_2/\text{pyridine}} R{-}Cl$$

$$R{-}OH \xrightarrow{HBr \text{ or } PBr_3} R{-}Br$$

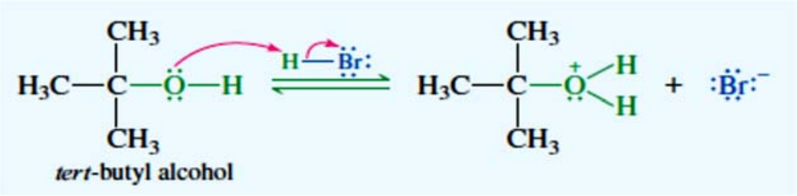
$$R{-}OH \xrightarrow{HI \text{ or } P/I_2} R{-}I$$

Examples

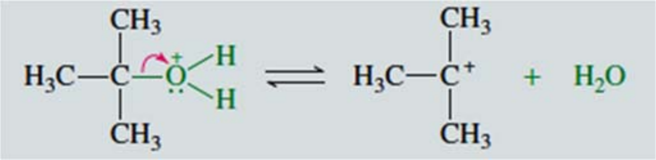


Reaction of a Tertiary Alcohol with HBr (SN1)

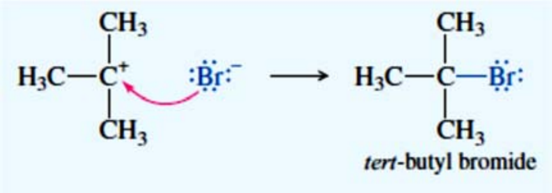
Step 1: Protonation converts the hydroxyl group to a good leaving group.



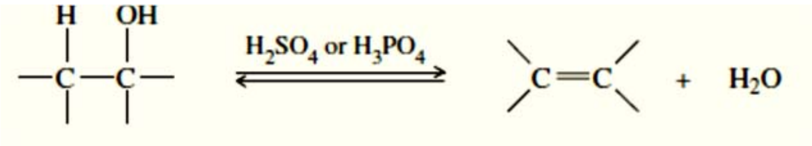
Step 2: Water leaves, forming a carbocation.



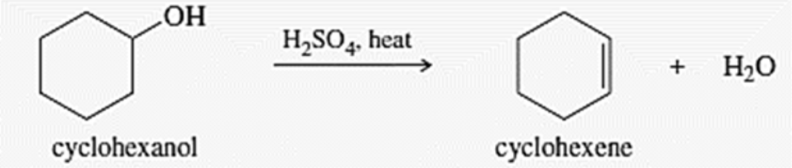
Step 3: Bromide ion attacks the carbocation.



b. *Dehydration of alcohols to form alkenes*

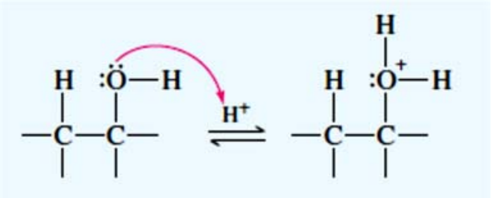


Example

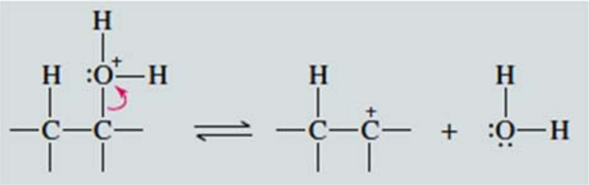


Mechanism:

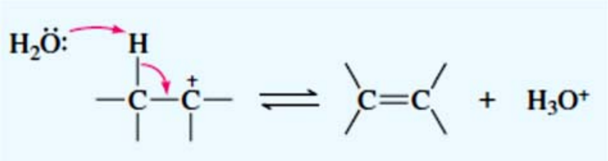
Step 1: Protonation converts the hydroxyl group to a good leaving group.



Step 2: Water leaves, forming a carbocation.



Step 3: Loss of a proton gives the alkene.



c. *Industrial condensation of alcohols to form ethers*

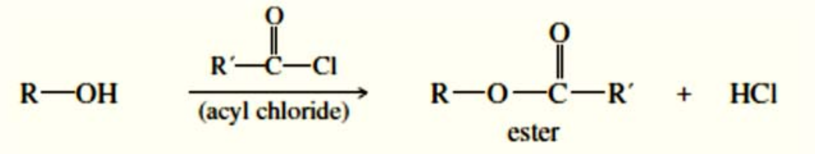
$$2\,R{-}OH \xrightleftharpoons{H^+} R{-}O{-}R + H_2O$$

Example

$$\underset{\text{ethanol}}{2\,CH_3CH_2OH} \xrightarrow[140\,^\circ C]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3CH_2-O-CH_2CH_3} + H_2O$$

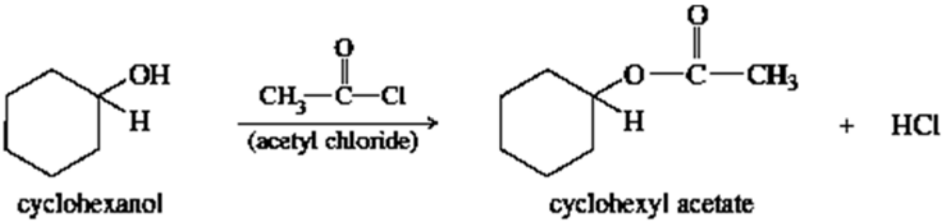
3. *Cleavage of the hydroxyl proton*

a. *Acylation to form esters*



$$R-OH \xrightarrow[\text{(acyl chloride)}]{R'-\overset{O}{\overset{\|}{C}}-Cl} \underset{\text{ester}}{R-O-\overset{O}{\overset{\|}{C}}-R'} + HCl$$

Example



c. *Deprotonation to form an alkoxide*

$$R-OH + Na\ (\text{or } K) \longrightarrow R-O^-\ Na^+ + \tfrac{1}{2}H_2\uparrow$$
$$R-OH + NaH \longrightarrow R-O^-\ Na^+ + H_2\uparrow$$

Example

$$\underset{\text{ethanol}}{CH_3-CH_2-OH} + Na \longrightarrow \underset{\text{sodium ethoxide}}{Na^+\ {}^-O-CH_2-CH_3}$$

d. *Williamson ether synthesis*

$$R-O^- + R'X \longrightarrow R-O-R' + X^-$$

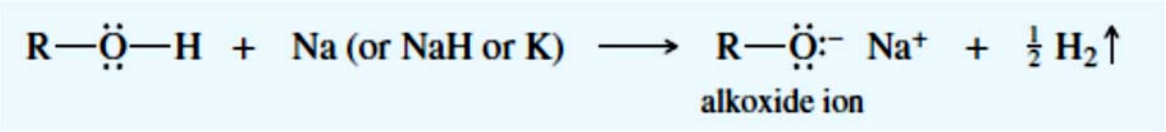
(R′ must be unhindered, usually primary)

Example

$$\underset{\text{sodium ethoxide}}{Na^+\ {}^-O-CH_2CH_3} + \underset{\text{methyl iodide}}{CH_3I} \longrightarrow \underset{\text{ethyl methyl ether}}{CH_3CH_2-O-CH_3} + NaI$$

Mechanism:

Step 1: Form the alkoxide of the alcohol



Step 2: The alkoxide displaces the leaving group of a good SN_2 substrate.