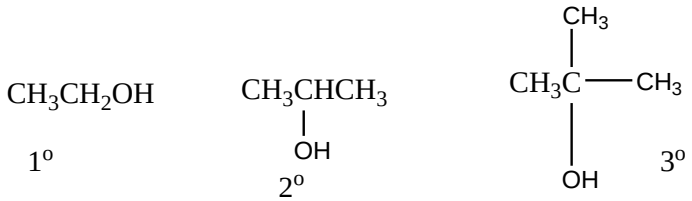
ALCOHOLS OR ALKANOLS

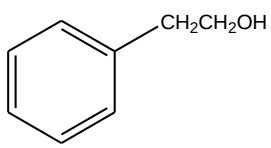
Introduction

Aliphatic Monohydric Alcohols are monohydroxyl derivatives of alkanes and have a general formula $C_nH_{2n+1}OH$ or $C_n H_{2n+2}O$

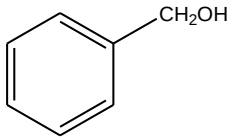
Aliphatic monools may be classified as 1°, 2° or 3° according to the nature of the carbon atom to which the hydroxyl group is attached i.e.



Aromatic Alcohols have aryl group attached to aliphatic portion of the alcohol separated by at least a methylene group. E.g.

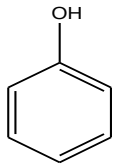


2-Phenylethanol

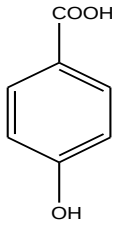


Phenylmethanol

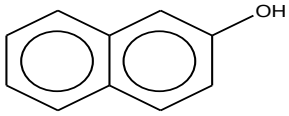
Compounds in which the hydroxyl group is attached directly to the benzene (Aromatic) ring are classified as **Phenol**. E.g.



Phenol

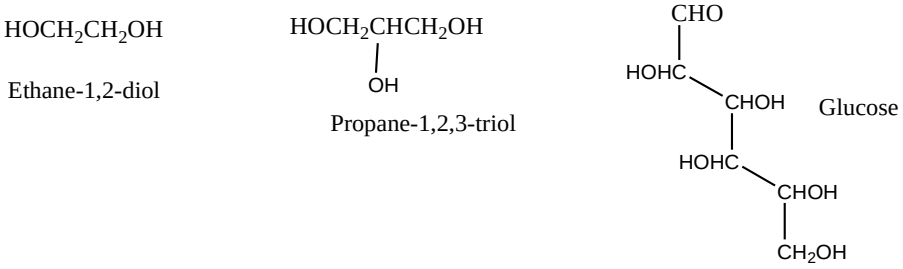


p-Hydroxybenzoic acid



2-Napthol

Alcohols containing two hydroxyl groups are described as **dihydric alcohols or diols** and those with three hydroxyl groups are **triols** while those containing many hydroxyl groups are **polyols**. E.g.



Nomenclature of Alcohols

The IUPAC Names are obtained by dropping the ending **"–e "**of alkane and replacing it with suffix **"-ol"**. The position of the hydroxyl group is indicated by inserting an appropriate number between the stem name and *ol.*

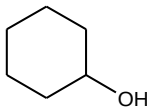
Example:

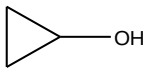
Name the following compounds using the IUPAC System

(a) CH_3OH (b) CH_3CH_2OH (c) $CH_3CH_2CH_2OH$ (d) $(CH_3)_3CCH_2OH$

(e) CH_3CHCH_2Br with OH

(f) $CH_3CH_2CH(CH_3)CH_2OH$

(g) 

(h) 

Solution

(a) Methanol (b) Ethanol (c) Propan-1-ol (d) 2, 2-dimethylpropan-1-ol

(e) 1-bromopropan-2-ol (f) 2-methylbutan-1-ol (g) Cyclohexanol (h) Cyclopropanol

Isomerism

Aliphatic monools have structural isomers .i.e. Chain, functional and Positional Isomers.

Ethers are functional isomers of monools.

Example:

A compound X has molecular formula C_3H_8O. Write down the structural formulae and names of the possible isomers of X.

Solution:

$CH_3CH_2CH_2OH$
Propan-1-ol

CH_3CHCH_3 with OH
Propan-2-ol

$CH_3OCH_2CH_3$
Methoxyethane

Physical Properties of Alcohols

a) Solubility

Lower members of the series are soluble, however, solubility decreases as the hydrocarbon portion increases. The miscibility of alcohols is due to ability of the formation of hydrogen bond with water molecule.

b) Boiling Points

Alcohols boil at higher temperatures expected because the molecules associate through hydrogen bonding which requires an extra energy to break. Within the series, boiling points increase with molecular mass.

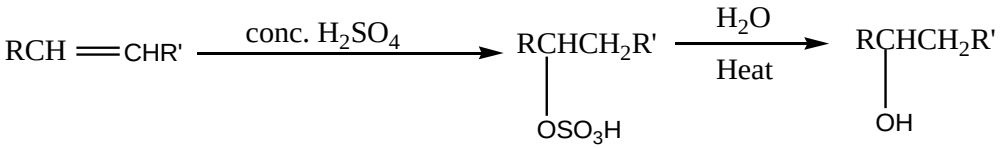
c) Density

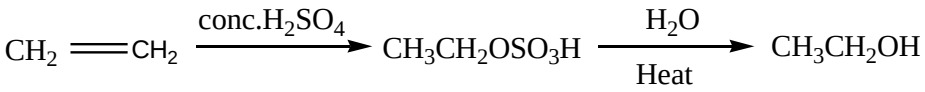
Density increases with increasing molecular mass although branching reduces the factor. Aliphatic alcohols are less dense than water while Aromatic alcohols tend to be slightly denser than water.

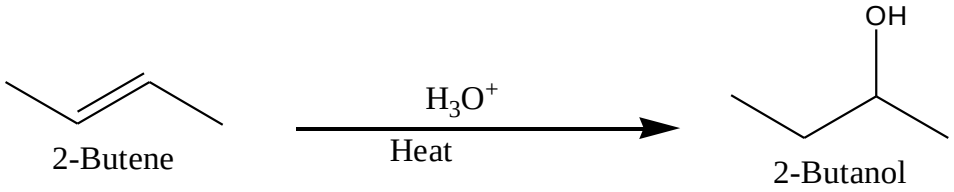
SYNTHETIC PREPARATION OF ALCOHOLS

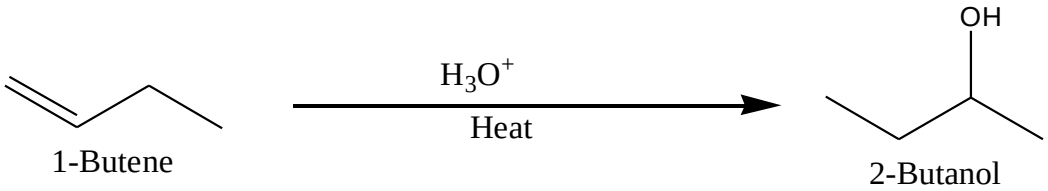
1. **From Alkenes**

   Hydration of alkenes in the presence of concentrated sulphuric or phosphoric acids. This reaction according to Markovnikov's rule.

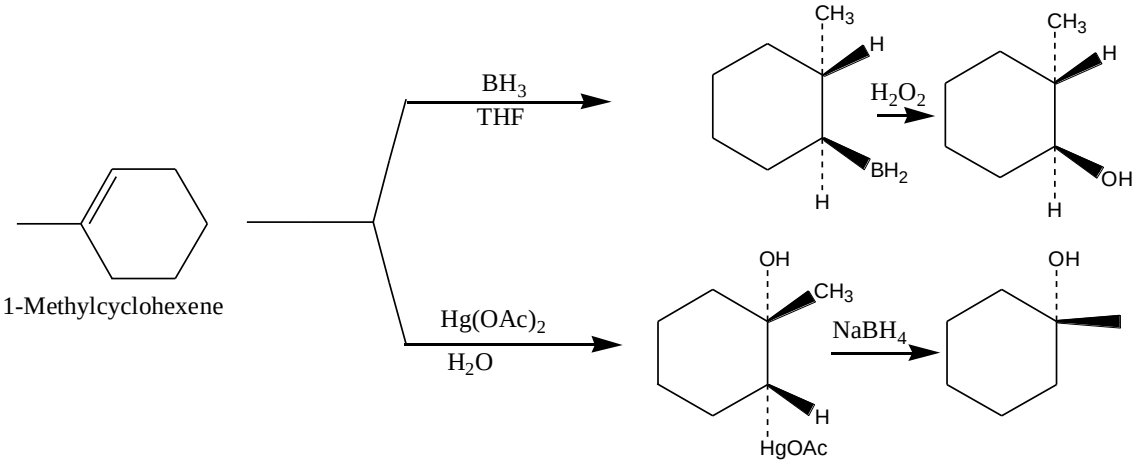




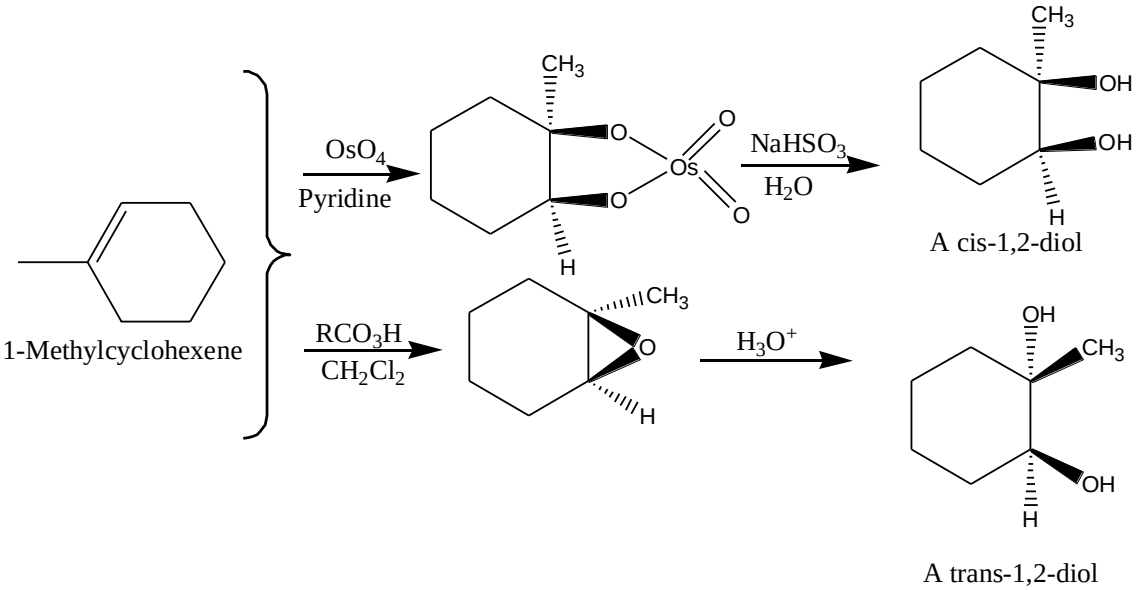




Also, hydroboration/oxidation yields the product of Syn Anti- Markovnikov hydration whereas Oxymercuration/reduction yields the product of Markovnikov hydration.



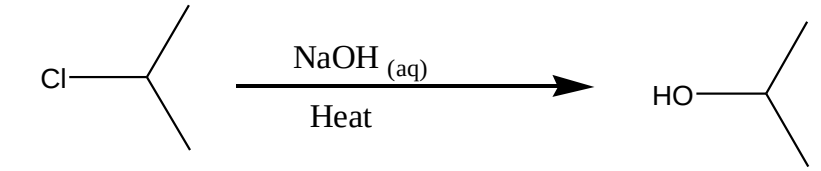
Diols can be prepared either by direct hydroxylation of an alkene with OsO_4 followed by reduction with $NaHSO_3$ or base- catalyzed hydrolysis of epoxides. The OsO_4 reaction occurs with Syn stereochemistry to give a **cis diol** whereas epoxide occurs with anti-stereochemistry to give a **trans- diol.**



2. From Alkyl halides

$$RX \xrightarrow[\text{heat}]{\text{NaOH (aq)}} ROH + NaX$$

$$CH_3CH_2Br \xrightarrow[\text{Heat}]{\text{NaOH (aq)}} CH_3CH_2OH$$

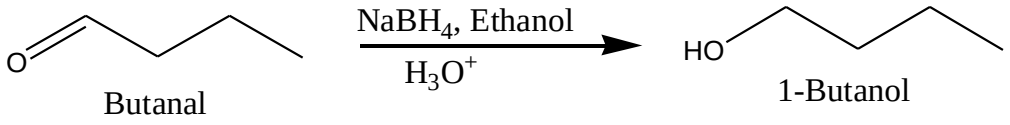


2-Chloropropane 2-Propanol

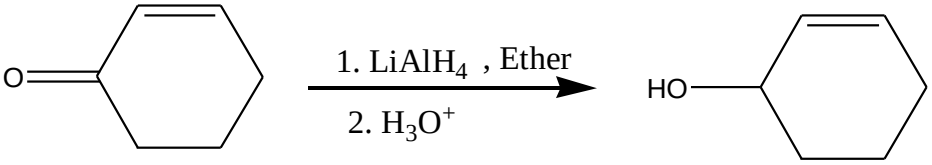
3. From Carbonyl compounds

Reduction of carbonyl compounds generates alcohol. Aldehydes are reduced to Primary Alcohol while Ketones to Secondary Alcohol.

The reducing agents commonly used are Na/ethanol, $LiAlH_4$ in dry ether, $NaBH_4$ and water, amalgamated Zinc and concentrated Hydrochloric acid, finely divided Ni or Pt with hydrogen gas.

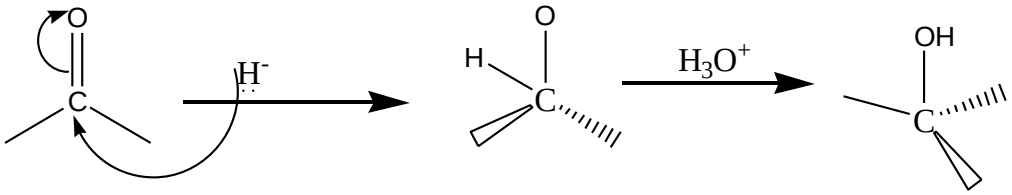


Butanal 1-Butanol



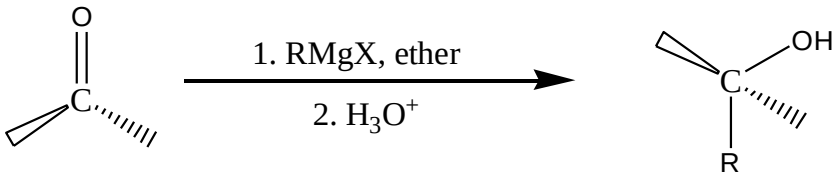
2-Cyclohexenone 2-Cyclohexenol

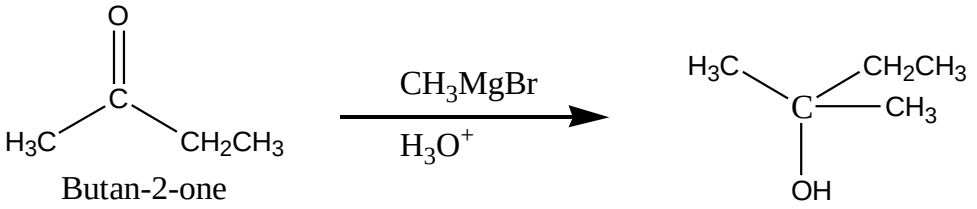
Mechanism



4. Grignard Reagent Synthesis

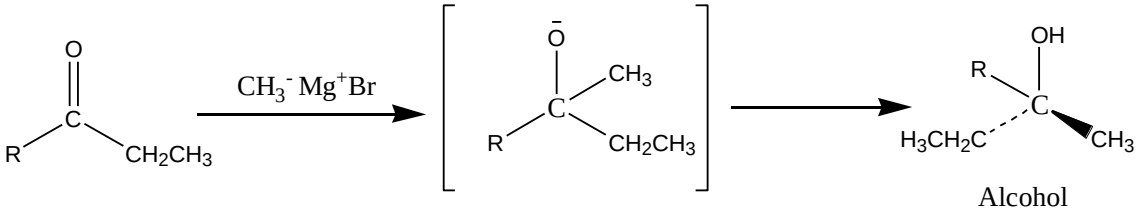
See Reactions of Haloalkanes.





Butan-2-one

Mechanism



Ketone/Aldehyde

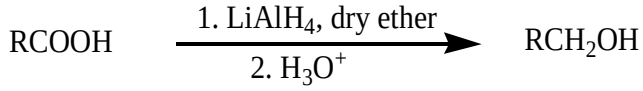
Tetrahedral intermediate

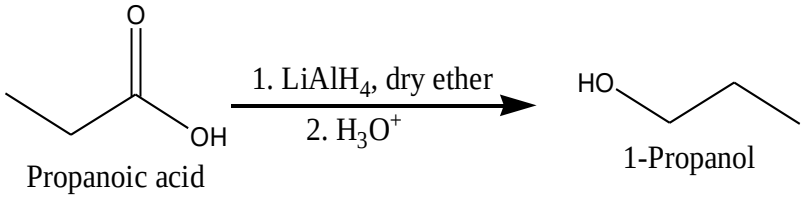
Alcohol

(R = H or alkyl group)

5. Reduction Of Carboxylic acids

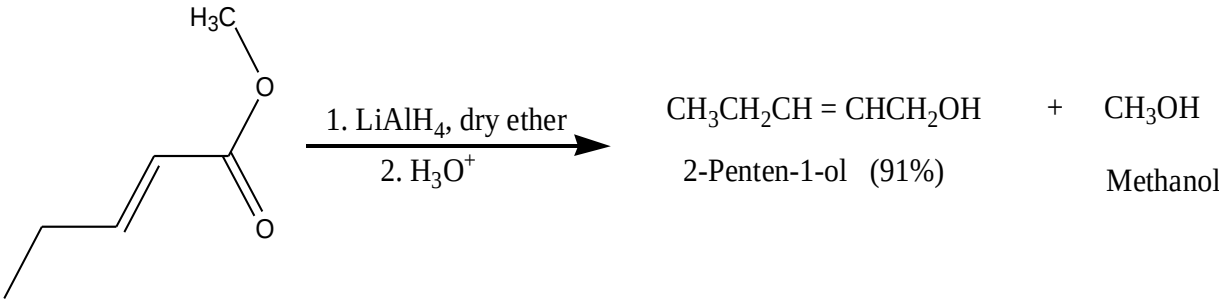
Carboxylic acids are reduced to Primary Alcohols using $LiAlH_4$ in dry ether and hydrolyzing the product.





Propanoic acid

1-Propanol



2-Penten-1-ol (91%)

Methanol

Pent-2-enoic acid methyl ester

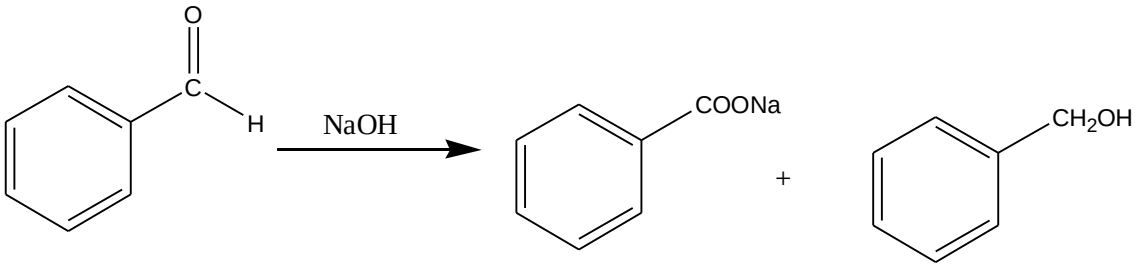
6. From Esters

Esters are hydrolyzed by aqueous sodium hydroxide solution to generate an alcohol. However this is not usually done since esters are obtained from alcohols.

$$RCO_2R' \xrightarrow[\text{heat}]{OH^-(aq)} RCOO^-(aq) + R'OH$$

7. Cannizzaro Reaction

Aromatic Aldehydes without α -hydrogen atoms undergo self-reduction and oxidation in sodium hydroxide solution.



DOMESTIC PRODUCTION OF ETHANOL

Ethanol is mainly prepared by fermentation process. Fermentation is a process where starch or sugar is converted to ethanol by yeast enzymes.

The main sources of the starch materials include maize, millet, cassava, sorghum, potatoes, banana, rice, molasses, etc.

The enzymes that participate in the fermentation process and their stages include:

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)n} + n\,H_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CH_3CH_2OH + 2CO_2$$

Question:

a) Describe the processes involved in the production of ethanol from a named material domestically

b) State briefly how the purification of the ethanol produced can be done

c) State four uses of ethanol

d) State two effects of over consumption of ethanol on the human body.

REACTIONS OF ALCOHOLS

1. With Electropositive Metals

Although Alcohols are neutral to neutralization indicators, the hydroxyl group can be replaced by metals of Group I and II of the periodic table. The products are hydrogen gas and metal alkoxides.

$$2ROH + Na \longrightarrow 2RO^-Na^+ + H_2$$

$$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^-Na^+ + H_2$$

2. Halogenation

This can be done by:

a) Using Hydrogen Halide

They react with hydrogen halides to form alkyl halides. The order of reactivity for alcohols is $3^o>2^o>1^o$ while for hydrogen halides is HI>HBr>HCl.

$$ROH \xrightarrow{HX} RX + H_2O$$

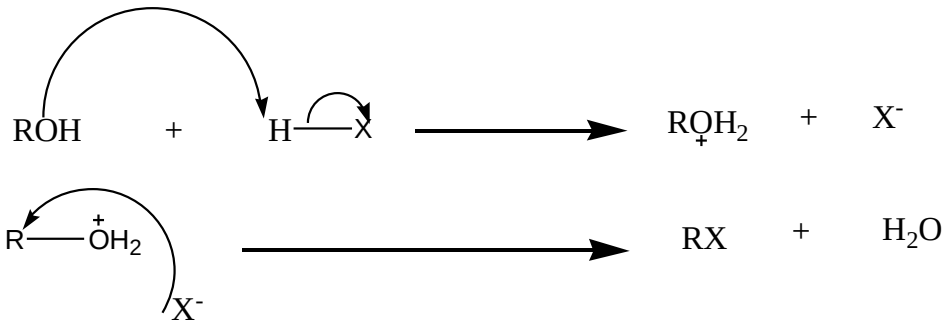
1^o Alcohols undergo bromination with hydrogen bromide which is generated from sodium bromide and concentrated sulphuric acid.

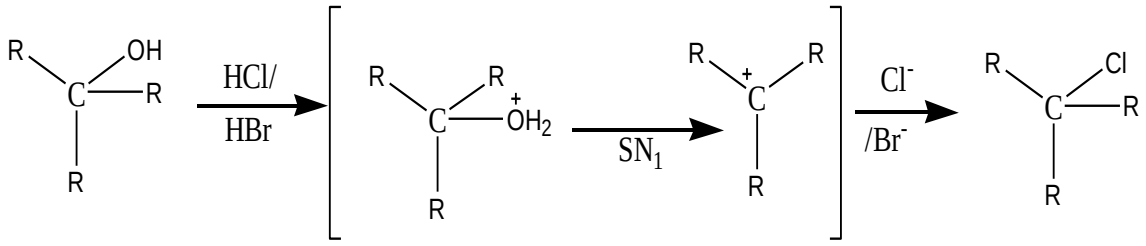
In case of hydrogen chloride, the reaction is carried by using anhydrous Zinc chloride and concentrated hydrochloric acid. (Luca's Reagent)

The reagent is used to distinguish the classes of monools i.e.

- 3^0 Alcohol forms a cloudy solution immediately
- 2^oAlcohols forms cloudiness between 5-10minutes
- 1^o Alcohols show no observable change.

Mechanism



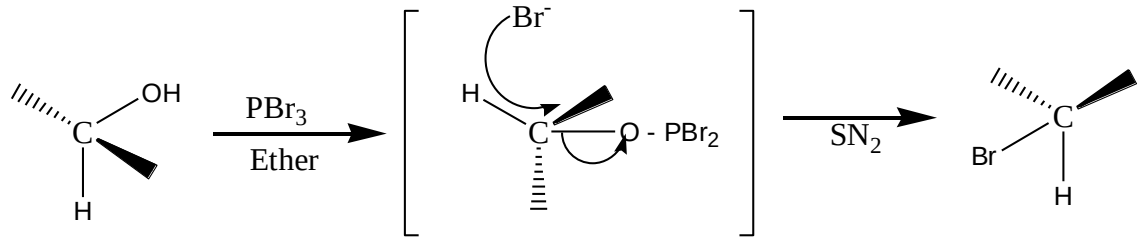


b) Using Phosphorous Halides

Phosphorus trihalides react with alcohols to form alkyl halides and phosphoric acid.

$$3ROH \xrightarrow[Ether]{PX_3} 3RX + H_3PO_3$$

Mechanism



Phosphorus pentahalides on the other hand react with alcohols to produce alkyl halides, phosphoryl chloride and hydrogen chloride

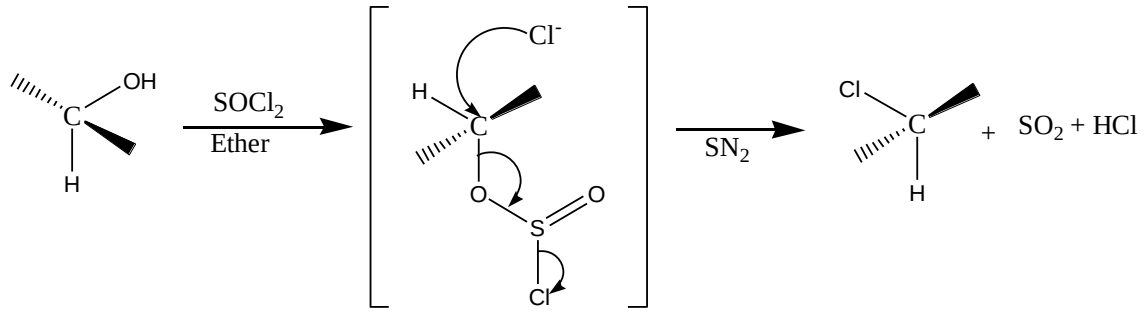
$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

c) Using Thionyl chloride

Thionyl Chloride also generates alkyl chloride.

$$ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$$

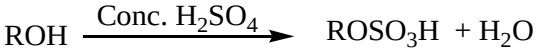
Mechanism



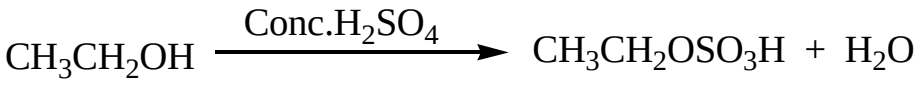
3. With concentrated Sulphuric acid

The products of the reaction depend on the conditions of the reaction under which it is carried out.

a) At lower temperatures (below 140°C), alkyl hydrogen sulphate is obtained



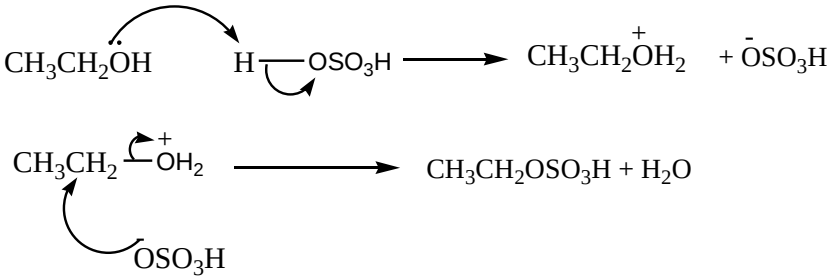
$$ROH \xrightarrow{\text{Conc. } H_2SO_4} ROSO_3H + H_2O$$



$$CH_3CH_2OH \xrightarrow{\text{Conc.}H_2SO_4} CH_3CH_2OSO_3H + H_2O$$

(Ethyl hydrogen sulphate)

Mechanism

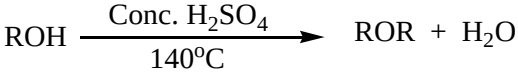


$$CH_3CH_2\ddot{O}H \quad H\text{—}OSO_3H \longrightarrow CH_3CH_2\overset{+}{O}H_2 + \overset{-}{O}SO_3H$$

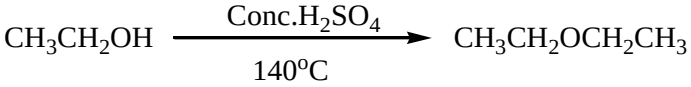
$$CH_3CH_2\text{—}\overset{+}{O}H_2 \longrightarrow CH_3CH_2OSO_3H + H_2O$$

OSO_3H

b) At about 140°C when excess alcohol, ether is obtained.

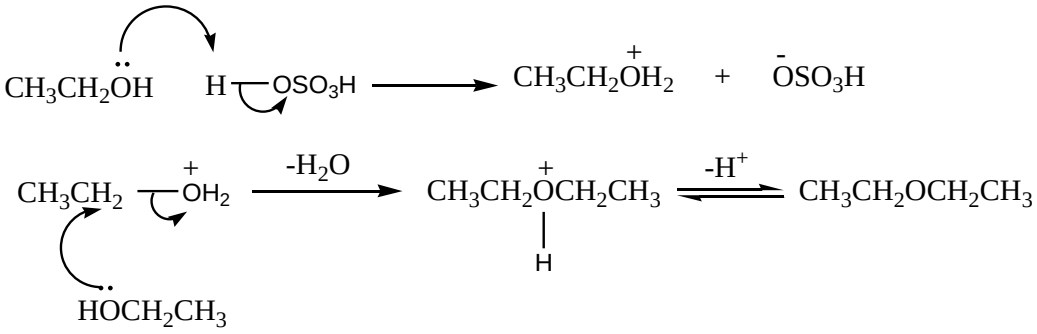


$$ROH \xrightarrow[140^oC]{\text{Conc. } H_2SO_4} ROR + H_2O$$



$$CH_3CH_2OH \xrightarrow[140^oC]{\text{Conc.}H_2SO_4} CH_3CH_2OCH_2CH_3$$

Mechanism

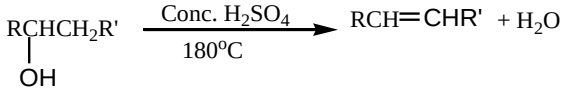


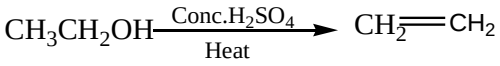
$$CH_3CH_2\ddot{O}H \quad H\text{—}OSO_3H \longrightarrow CH_3CH_2\overset{+}{O}H_2 + \overset{-}{O}SO_3H$$

$$CH_3CH_2\text{—}\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3CH_2\overset{+}{O}CH_2CH_3 \xrightleftharpoons{-H^+} CH_3CH_2OCH_2CH_3$$

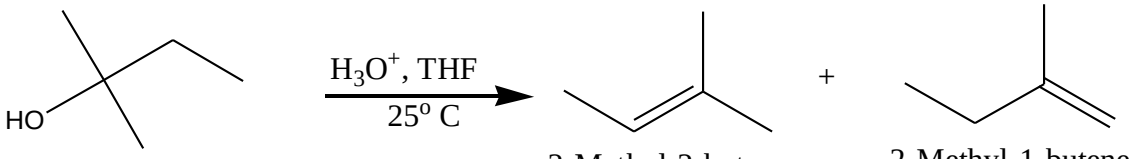
$HOCH_2CH_3$

c) When the reaction is carried out at about 180°C, an alkene is obtained. Aluminum Oxide at 350°C or concentrated orthophosphoric acid can be used.





Acid catalyzed dehydrogenation reactions usually follow Zaitsev's rule and yield more stable alkene as the major product. According to this rule, based induced elimination reactions generally (although not always) give the more stable alkene product, that is, the alkene with more alkyl substituent on the double bond carbon atoms.

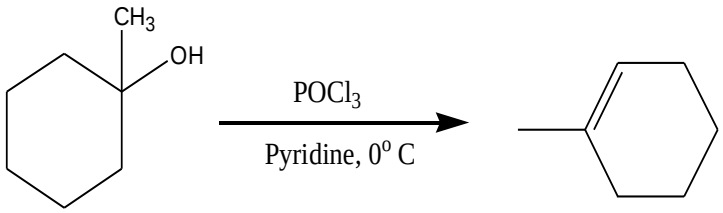


2-Methylbutan-2-ol

2-Methyl-2-butene
Major product

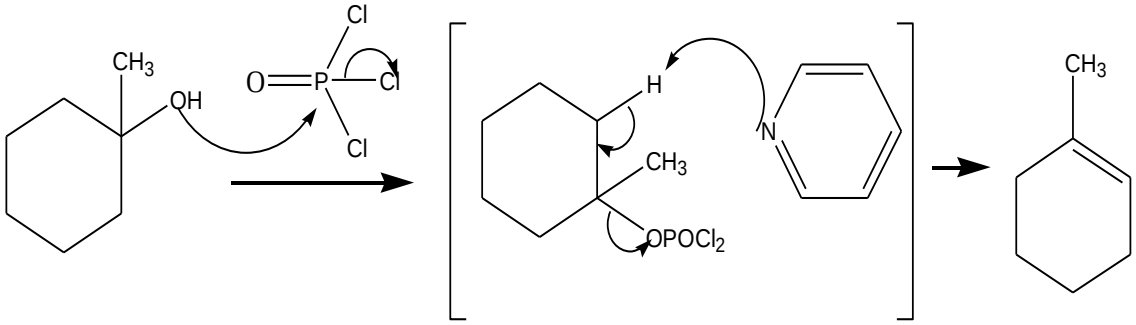
2-Methyl-1-butene
Minor product

Also phosphoryl chloride with pyridine catalyst can cause dehydration of alcohol.



1-Methylcyclohexene

Mechanism

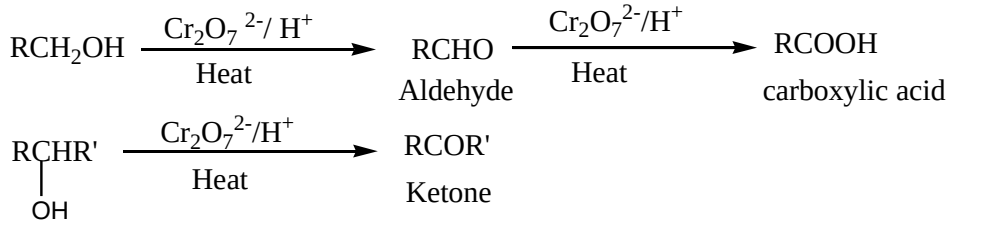


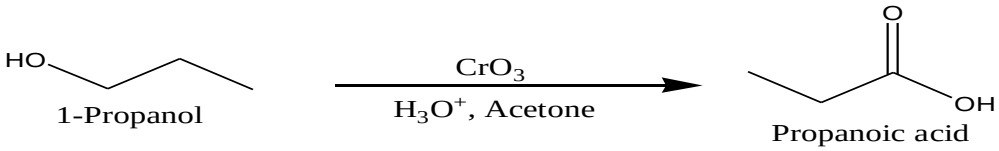
4. Oxidation reaction

The product of oxidation of alcohol depends on the type of alcohol and partly the power of oxidizing agent.

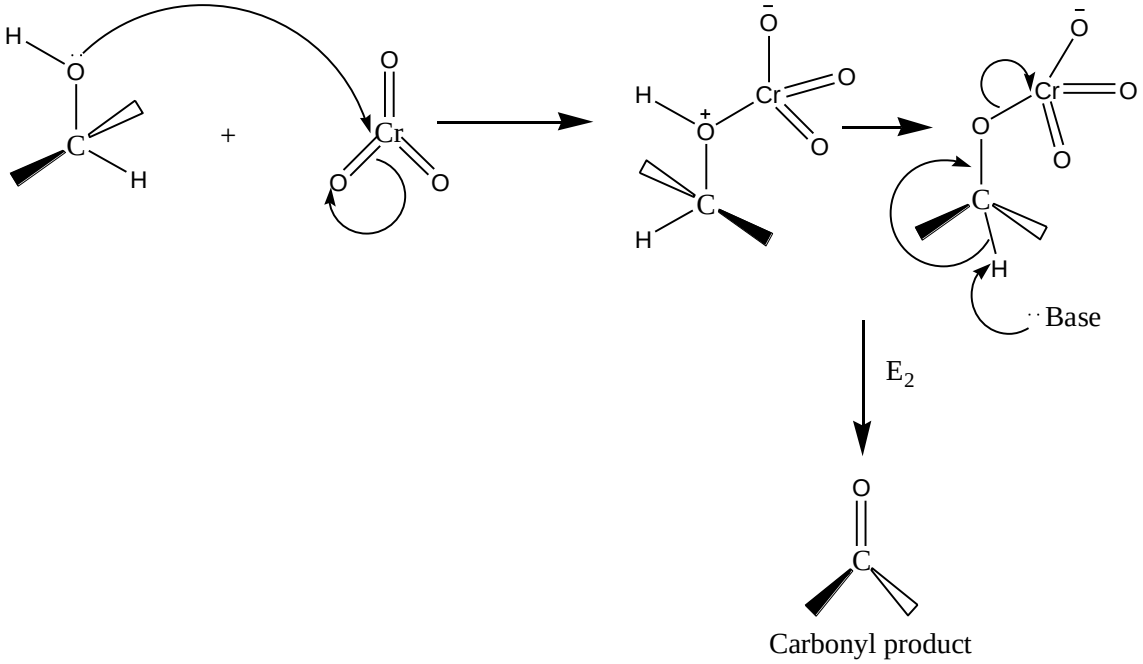
Reactions using mild oxidizing agents, such as chromium trioxide in aqueous acid oxidizes primary alcohols to carboxylic acids. Aldehydes are involved as intermediates in this reaction, but cannot usually be isolated because it is further oxidized too rapidly. Primary Alcohols are oxidized to Aldehydes and the reaction proceeds to carboxylic acid while Secondary Alcohols are oxidized to Ketones. Tertiary Alcohols are resistant to oxidation.

The oxidizing agents commonly used are acidified potassium dichromate or acidified chromium (VI) oxide





Mechanism



To produce aldehydes only, Pyridinium chlorochromate, PCC in dichloromethane solvent is employed.

$$RCH_2OH \xrightarrow[CH_2Cl_2]{PCC} RCHO$$

5. Esterification reaction

The process whereby a primary alcohol reacts with a monocarboxylic acid is known as esterification.

The reaction usually takes place in presence of concentrated sulphuric acid and it is reversible reaction.

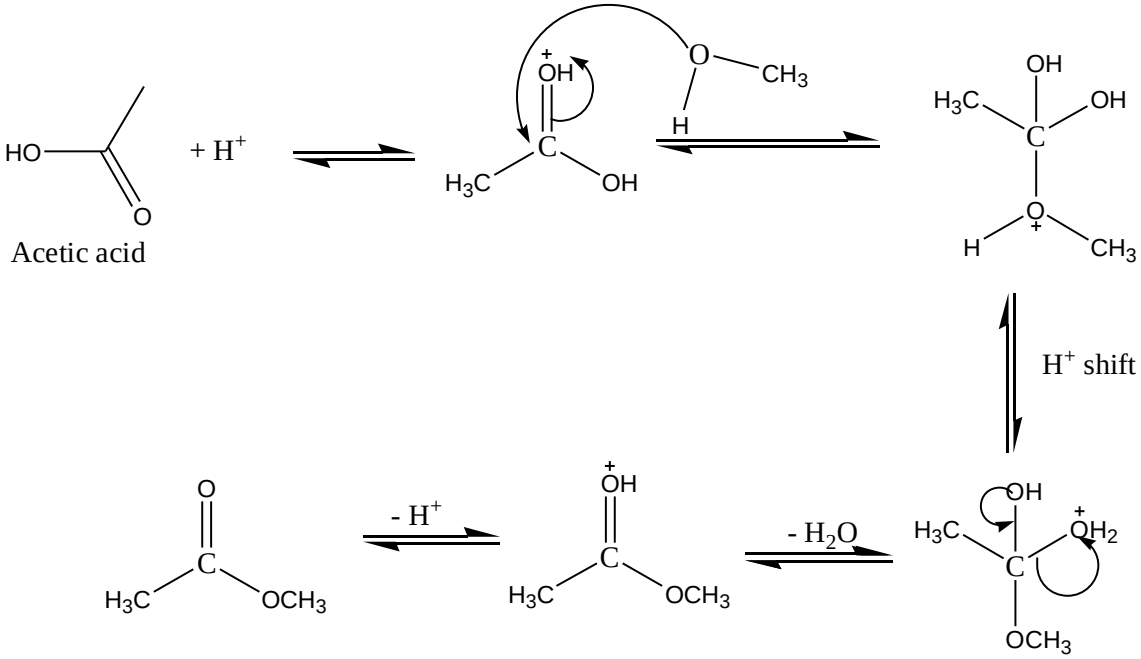
$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

Example:

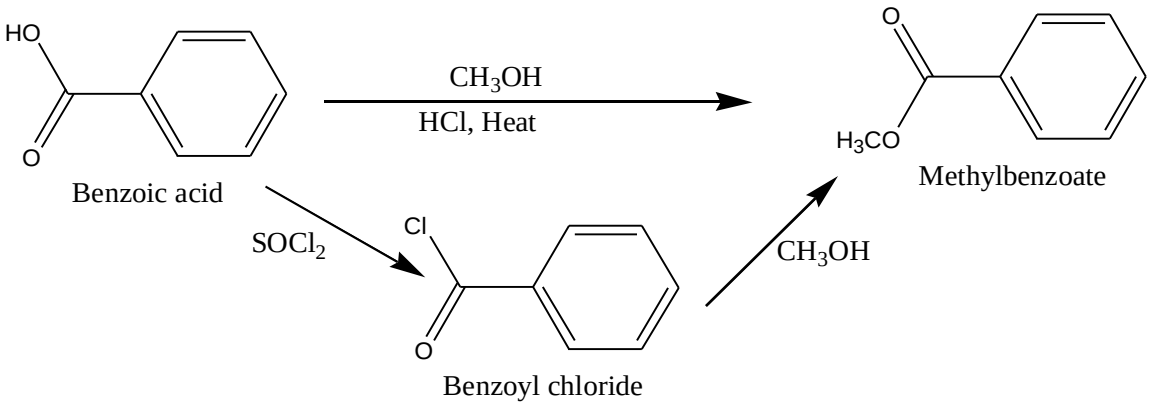
$$CH_3CO_2H + CH_3OH \rightleftharpoons CH_3CO_2CH_3 + H_2O$$

Mechanism:

This was determined using radioactive Oxygen (18). The primary alcohol containing oxygen-18 is reacted with monocarboxylic acid. The mass spectrometer is used to analyze the ester and water formed. The oxygen-18 is found in the ester only and not water indicating that carbon-oxygen single bond in the acid and oxygen-hydrogen bond in the alcohol are bonded.



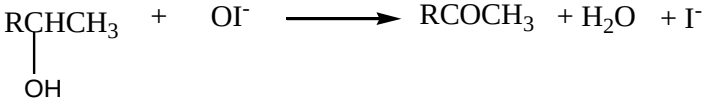
Also,



6. **Iodoform reaction**

Alcohols of the form $CH_3CH(OH)R$ react with iodine in presence of sodium hydroxide solution to form a yellow solid.

Iodine is an oxidizing agent and can oxidize alcohols to Aldehydes or Ketones.



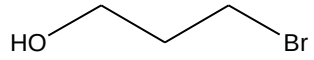
OR

Ethanol is the only primary alcohol which gives a positive test here.

N.B. Chlorine forms chloroform which is colourless liquid, Bromine forms bromoform which is reddish-brown.

7. **Protection of Alcohol group**

The reaction is very useful in organic synthesis.

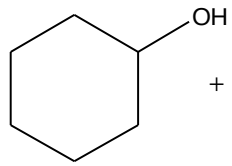


3-Bromopropanol

$\xrightarrow[\text{Ether}]{Mg}$ $HOCH_2CH_2CH_2MgBr$

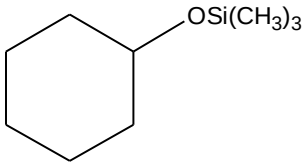
NOT formed

$ROH + (CH_3)_3SiCl \xrightarrow{(CH_3CH_2)_3N} RO-Si(CH_3)_3 + (CH_3CH_2)_3NH^+Cl^-$



Cyclohexanol

$+ \quad (CH_3)_3SiCl \xrightarrow{(CH_3CH_2)_3N}$

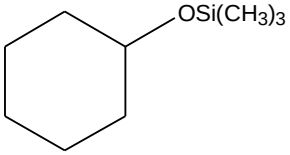


Cyclohexyltrimethylsilyl ether

(94%)

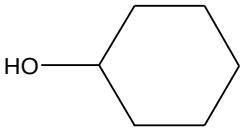
The product formed can then be subjected to Grignard synthesis.

Acid hydrolysis removes the trimethylsilyl group.



Cyclohexyltrimethylsilyl ether

$\xrightarrow{H_3O^+}$



Cyclohexanol

$+ \quad (CH_3)_3SiOH$

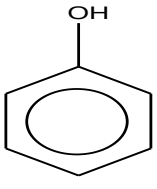
PHENOL

Introduction

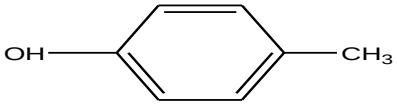
These are compounds containing a hydroxyl group attached directly to aromatic nucleus (Benzene) and have a general formula *ArOH*. Phenols are also called carbolic acids.

Like alcohols, they may be monools or polyols depending on the number of the hydroxyl groups they contain.

Examples include:



Phenol



4-Methylphenol

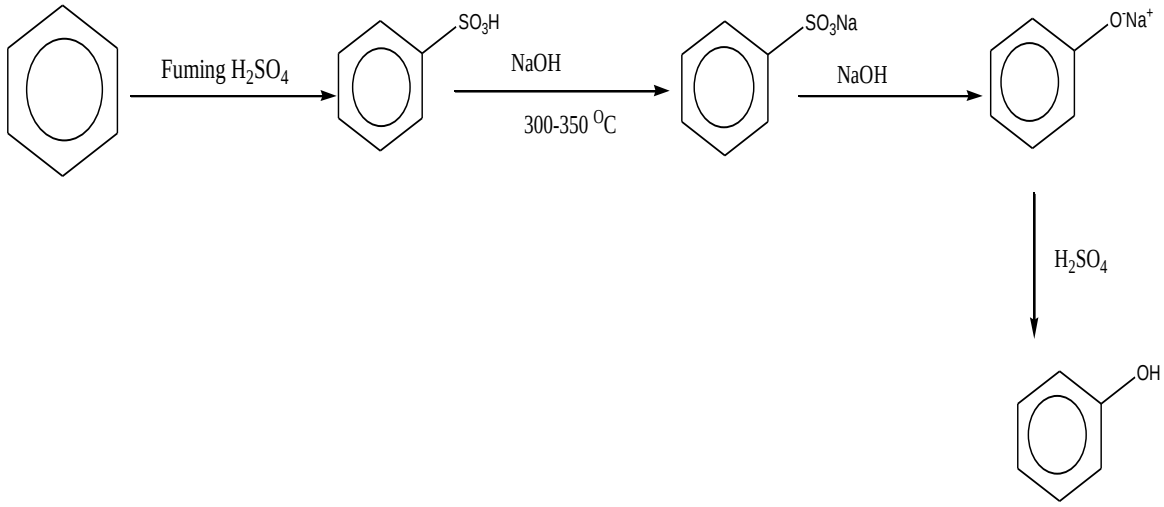
Physical Properties

Phenol is colourless crystalline solid although often found red tint due to presence of oxidation products. It is slightly soluble in water but very soluble in organic solvents.

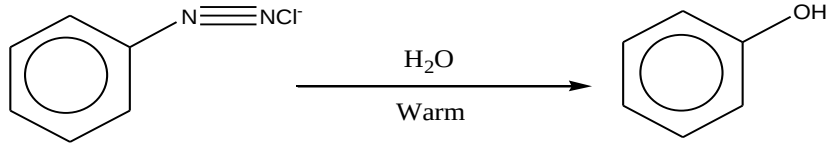
N.B. The introduction of the hydroxyl group into an already substituted aromatic ring especially in position-4 produces a marked increase in the boiling point. E.g. the greater volatility of 2-nitrophenol is attributed to intramolecular hydrogen bonding while the higher boiling points of 3- and 4- isomers are direct result of intermolecular hydrogen bonding.

Preparation of Phenol

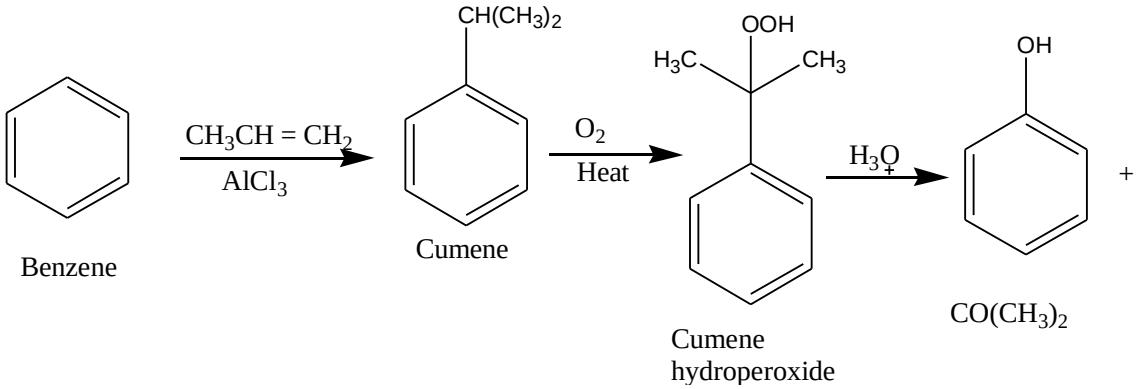
a) From Benzene sulphonic acid



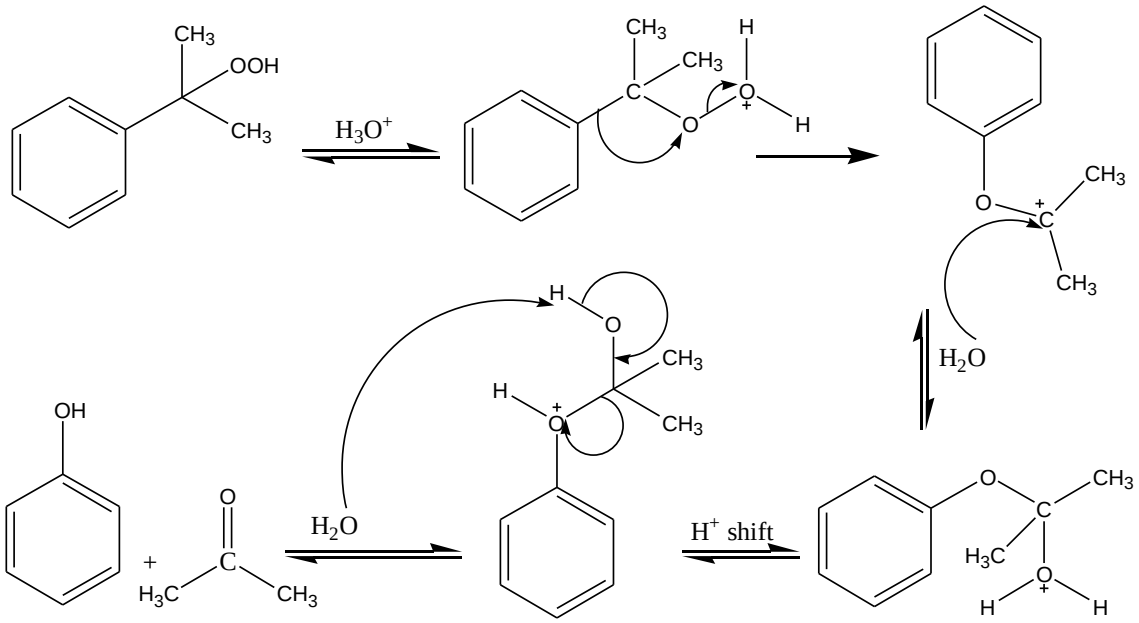
b) From Benzene Diazonium salt.



c) Cumene process



Mechanism



Reactions of Phenol

Phenol undergoes two distinct reactions i.e.

a) Side-chain substitution reactions which generally involves replacement of the acidic proton

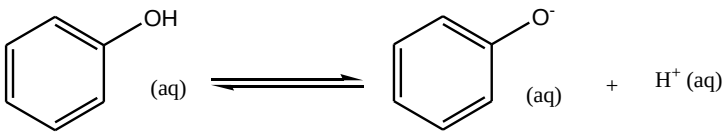
b) Electrophilic substitution in the ring.

Phenol as an acid

Phenol is a stronger acid than alcohols but weaker acid compared to carboxylic acid.

Question: Explain briefly why phenol is more acidic compared to Ethanol

Solution: In phenol, the lone pair of electrons on the oxygen atom interacts with delocalized electrons of the benzene ring. This strengthens the carbon- oxygen bond while weakening the oxygen-hydrogen bond consequently; phenol loses a proton easily making it acidic.



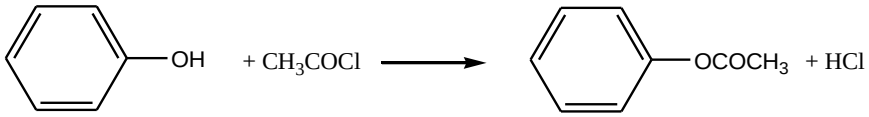
In ethanol, the oxygen-hydrogen bond is not weakened and the proton is not easily lost. This is because there are no delocalized electrons to interact with lone pairs of electrons on the electrons.

Note: Due to the above reason, phenol differs from alcohols in that it does not react with halogen acids or Phosphorus halides and does not undergo elimination reaction

a) **Side-chain reactions include**:

1) Esterification reaction

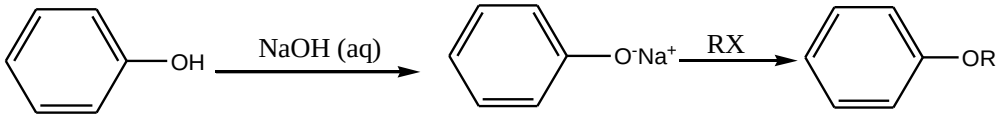
Phenol reacts with acid chlorides and acid anhydrides to form esters



Phenylethanoate

2) Ether Formation

Sodium phenate (Sodium phenoxide) reacts with alkyl halides to form ethers



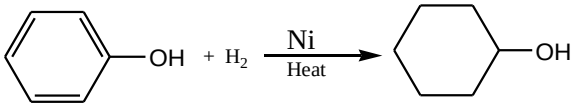
3) With Neutral Iron (III)chloride solution

Phenol reacts with neutral Iron (III) chloride solution to form a violet colouration due to a complex formed.

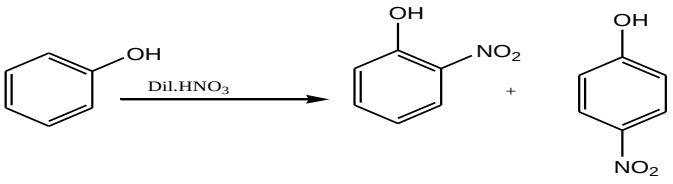
b) Electrophilic Substitution of the ring

Phenol is more reactive towards Electrophilic reagent than Benzene since it activates position 2- and 4- therefore the products formed at those positions.

1) Reduction reaction



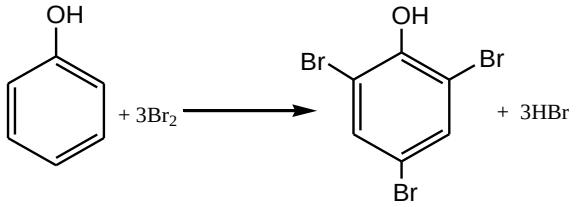
2) Nitration reaction



3) Bromination

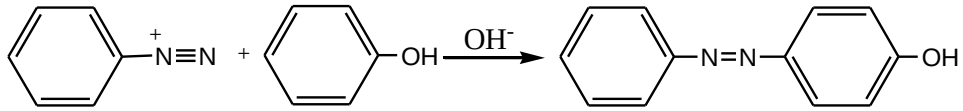
In aqueous solution, phenol reacts with bromine to form a white precipitate of 2, 4, 6-tribromophenol.

This reaction is used also to test for presence of phenol and estimate phenol quantitatively.



4) Coupling with Benzene Diazonium salts

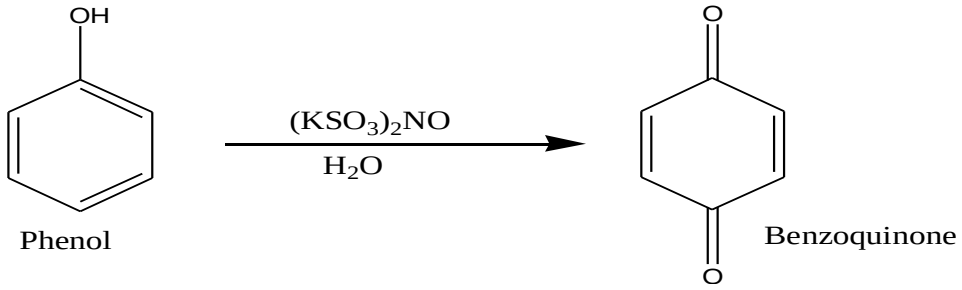
Benzene Diazonium salt solution is added to alkaline solution of phenol to generate bright yellow precipitate of 4-hydroxyphenylazobenzene.



4-hydroxphenylazobenzene

c) Oxidation of phenol

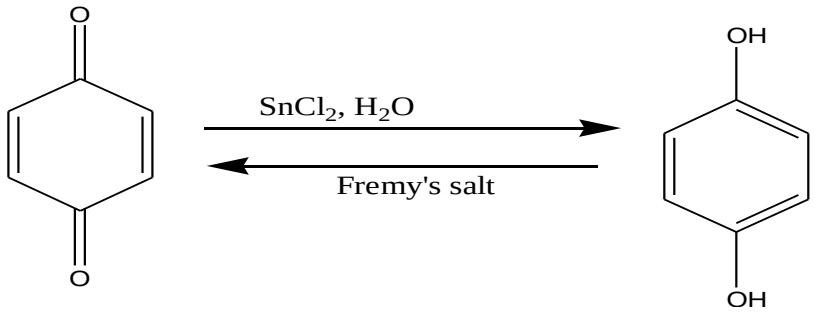
This reaction produces quinones. This uses Potassium nitrosodisulonate = Fremy's salt.



Phenol

Benzoquinone

Benzoquinone can be reduced to hydroquinone using $NaBH_4$ and $SnCl_2$ and hydroquinone can be re-oxidized back to quinones by Fremy's salt.



Question

1. Explain the following observation:
   a) Ethanol is more acidic than 2-methylpropan-2-ol but less acidic than phenol
   b) Phenol is easily nitrated using nitric acid whereas Benzene is nitrated using a mixture of concentrated nitric acid and sulphuric acid
   c) Butan-1-ol is more soluble in 5M hydrochloric acid than in water
   d) The boiling point of ethanol (78^oC) is greater than Ethoxyethane (35^oC)
2. Write the half and overall equation of reaction for:
   a) Ethanol and acidified potassium dichromate solution
   b) Ethene and acidified potassium manganate (VII) solution