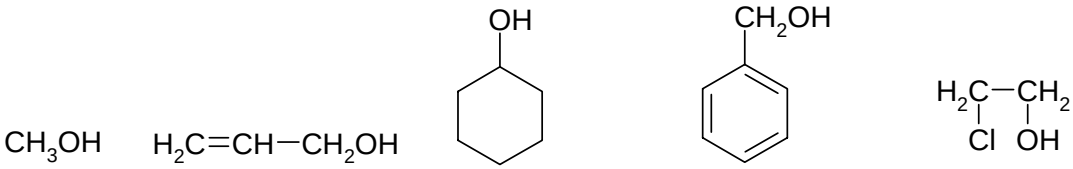
ALCOHOLS, PHENOLS, ETHERS AND EPOXIDES

Prof. S.C. Jain
Department of Chemistry
University of Delhi
University Road, Delhi - 110007

CONTENTS

Alcohols are compounds having general formula ROH, where R is alkyl or a substituted alkyl group. The group may be *primary*, *secondary* or *tertiary*. Alcohol may be open chain, or cyclic. It may also contain a double bond, a halogen atom or an aromatic ring. For example:

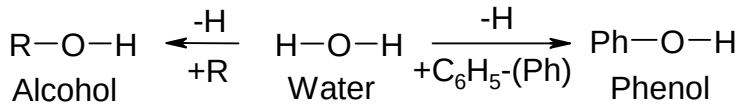


Methyl alcohol Allyl alcohol Cyclohexanol Benzyl alcohol Ethylene chlorohydrin

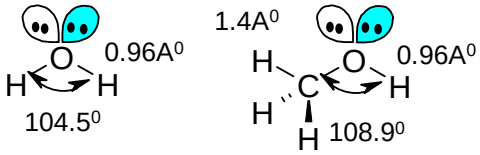
All alcohols contain hydroxyl (-OH) group which is a functional group and determines the properties of the family.

Alcohols as derivatives of water

The most familiar covalent compound is water. Replacement of one of the hydrogens in the water molecule by an alkyl group leads to the formation of alcohol. However, when the substituted alkyl group is an phenyl group (C_6H_5-), the resultant compound is phenol.



Alcohols as expected, show some of the properties of water. They are neutral substances. The lower ones are liquids and soluble in water. The structure of an alcohol resembles that of water having sp^3 hybridized oxygen atom.

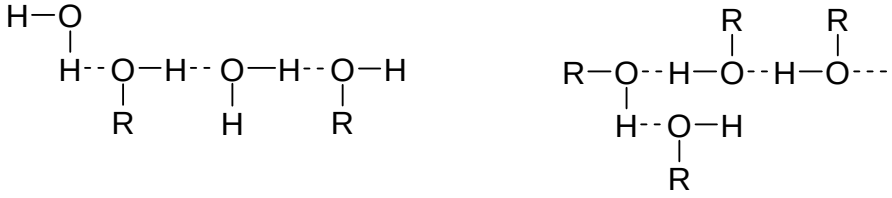


Water (a) Methanol (b)

Figures (a) & (b) shows the difference in H-O-H and C-O-H bond angle, in water and alcohol respectively. Presence of methyl group in place of hydrogen in methanol counter acts the bond angle compression caused by lone pair-lone pair repulsion in oxygen. Besides this, the O-H bond lengths are same in water and methanol.

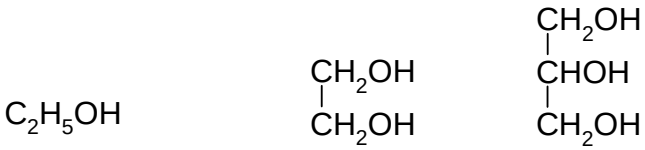
The apparent molecular weight of water is several times larger due to stronger intermolecular hydrogen bonding, and this is the reason why water has such a high boiling point (b.p.) as compared to compounds of similar molecular weight. In a similar manner, molecules in the lower alcohols associate through H- bonding resulting in higher b.p. than expected.

The solubility of lower alcohols in water may also be attributed to the formation of hydrogen bonds with water. Alcohol molecules get bonded with water and amongst themselves as shown below:



(Between water and alcohol) (Between alcohol molecules)

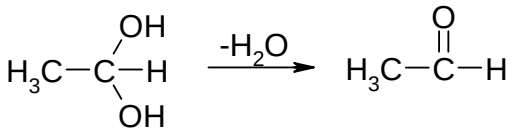
Alcohols are classified as *mono*-, *di*- and *trihydric* alcohols according to the number of hydroxyl groups present in them, *e.g.*,



Ethyl alcohol (Monohydric) Ethylene glycol (*Dihydric*) Glycerol (*Trihydric*)

Alcohols containing four or more than four hydroxyl groups are called **polyhydric alcohols**.

More than one –OH group cannot be present on the same carbon atom, as it is unstable and at once loses a molecule of water, *e.g.*,



(*unstable*)

Alcohols should not be confused with the inorganic bases or metallic hydroxides because of the presence of hydroxyl group in them because,

(i) alcohols are covalent compounds, while inorganic hydroxides are ionic,

(ii) alcohols do not ionize in water and are neutral to litmus, while inorganic hydroxides ionize and are alkaline towards litmus,

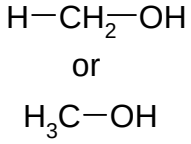
(iii) alcohols undergo molecular reactions while inorganic hydroxides, ionic reactions.

Monohydric Alcohols

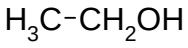
General Formula and Classification. As discussed above, monohydric alcohols contain one hydroxyl group in their molecule. They form a homologous series having general formula $C_nH_{2n+1}OH$ or simply ROH where R stands for an alkyl group.

Monohydric alcohols are further classified as *primary*, *secondary* and *tertiary* alcohol depending upon whether the hydroxyl group is attached to a primary, secondary, or a tertiary carbon atom.

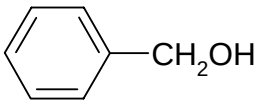
(i) **Primary alcohols**. They contain the monovalent group $-CH_2OH$ in their molecule. Hence, their general formula is $R\text{-}CH_2OH$, *e.g.*,



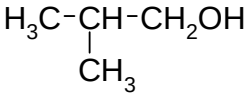
Methanol



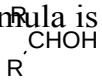
Ethanol

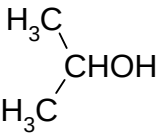


Benzyl alcohol

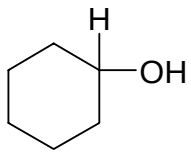


2-methylpropan-1-ol

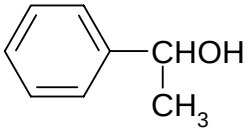
(ii) **Secondary alcohols**. They contain the bivalent group >CHOH in the molecule. Hence their general formula is  , *e.g.*,



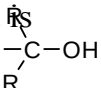
2-Propanol

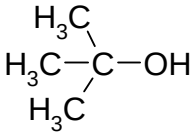


Cyclohexanol



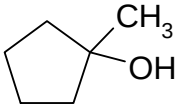
1-Phenylethanol

(iii) **Tertiary alcohol**. They contain the trivalent group  in their molecule. Hence, their general formula is  , *e.g.*,



2-Methylpropan-2-ol

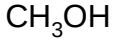
Triphenylmethanol



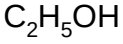
1-Methylcyclopentanol

Nomenclature. There are three systems of naming alcohols.

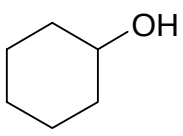
(i) Common system. According to this, the names of the lower members are derived by adding the word alcohol after the name of the alkyl group present in the molecule, *e.g.*



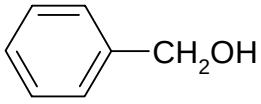
Methyl alcohol



Ethyl alcohol



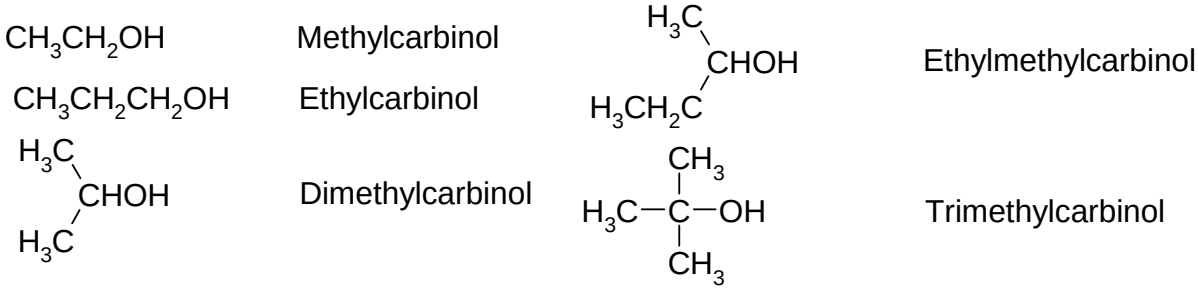
Cyclohexyl alcohol



Benzyl alcohol

(ii) Carbinol system. According to this, alcohols are considered to be derived from methyl alcohol by replacement of one or more hydrogen atoms by other

alkyl groups. We simply name the groups attached to the carbon bearing the –OH and then add the suffix- carbinol to include the C-OH portions.

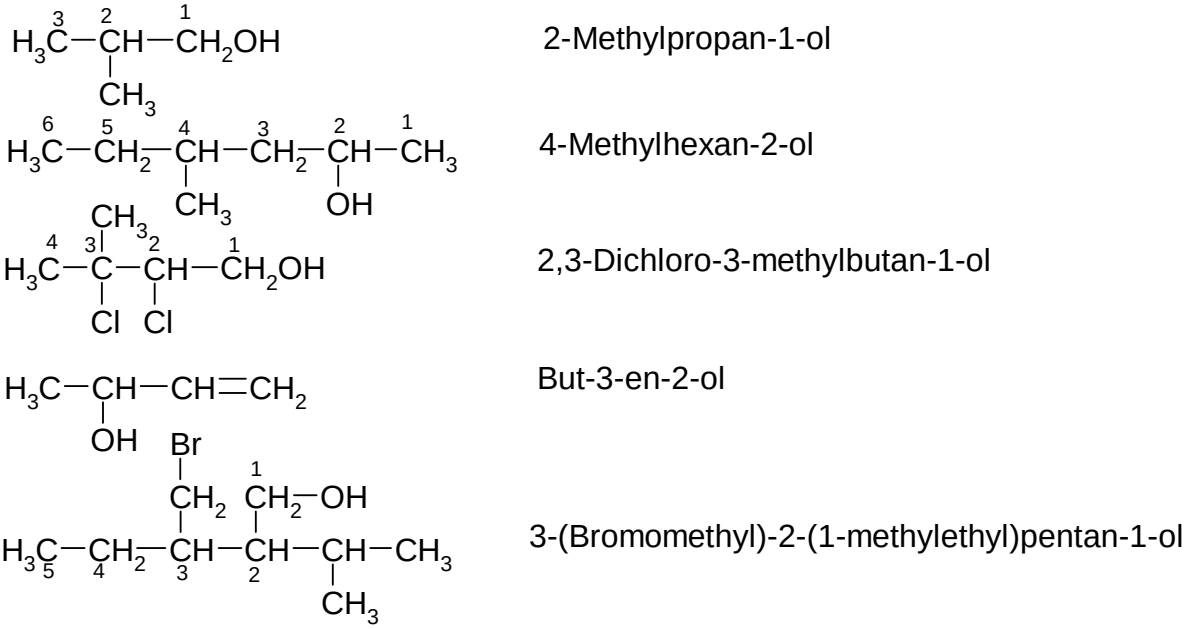


(iii) I.U.P.A.C. system. According to this system, alcohols are named as alkanols and the name of the particular alcohol is derived by substituting the terminal 'e' of the parent alkane by 'ol'

CH_3OH	C_2H_5OH	C_3H_7OH
Methanol	Ethanol	Propanol

1. For naming higher alcohols, the longest carbon chain that contains the –OH group is selected as the parent alkane. The position of the –OH group is indicated by a number.

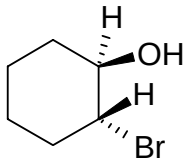
2. Longest chain selected is numbered in such a way so that the carbon carrying –OH group gets the lowest number.



3. The hydroxyl group takes precedence over double and triple bonds.

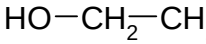
4. All the substituents are assigned their numbers, as in the case of alkane or an alkene.

5. Cyclic alcohols are named using the prefix cyclo-, the hydroxyl group is assumed to be on C-1.



trans-2-bromocyclohexan-1-ol

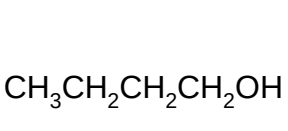
6. The –OH functional group will be treated as a substituent and named as a "hydroxy" substituent, when it appears on a structure with a higher priority functional group.



3-Hydroxypropanoic acid

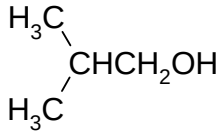
Isomerism. Higher aliphatic alcohols exhibit two types of isomerism:

(a) **Chain isomerism.** This isomerism is due to the difference in the nature of the chain, *e.g.*,



n-Butyl alcohol

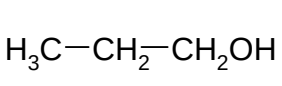
and



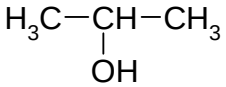
iso-Butyl alcohol

Both of these are primary alcohols due to the presence of $–CH_2OH$ group but the former has a straight chain formula and is called *n*-butyl alcohol, while the latter has a branched-chain formula and is called *iso*-butyl alcohol.

(b) **Position isomerism**. This isomerism is due to the different position of the hydroxyl group in the same chain, *e.g.*,



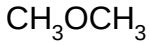
Propan-1-ol



Propan-2-ol

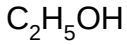
In the former case, the hydroxyl group is attached to the first carbon atom, while in the latter case, it is attached to the middle carbon atom.

(c) **Functional isomerism**. Alcohols show functional isomerism with ethers having the same molecular formula, *e.g.*,



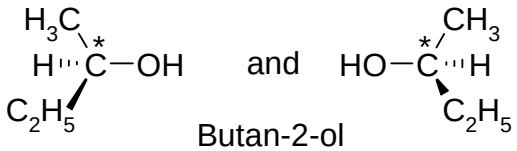
Dimethyl ether

and



Ethyl alcohol

(d) **Optical isomerism**. Monohydric alcohols containing chiral centres exhibit optical isomerism and thus exist as a pair of enantiomers (nonsuperimposable) *e.g.*



Butan-2-ol

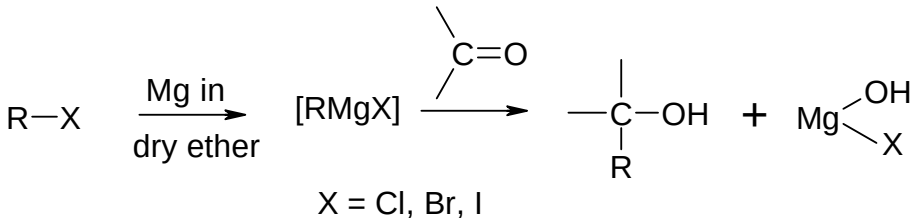
* represent the chiral centre

Preparation of Alcohols.

(i) **From Grignard's reagent** (RMgX). All the three types of alcohols, *i.e.*, primary, secondary and tertiary alcohols can be prepared with the help of Grignard's reagent by reacting it with appropriate aldehyde or ketone. The Grignard

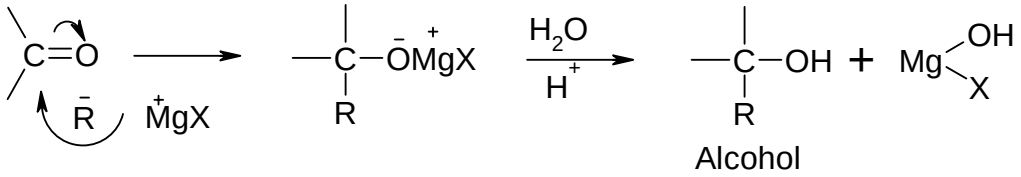
reaction is an important reaction and is used for the formation of new carbon-carbon bond.

Usually the Grignard's reagent is not isolated and is prepared in *situ* by reacting pure and dry magnesium metal with alkyl or arylhalide in dry ether. The aldehyde or ketone is then added to its ethereal solution. The addition product formed, is hydrolysed by treating the reaction mixture with dilute acid or ammonium chloride solution.



X = Cl, Br, I

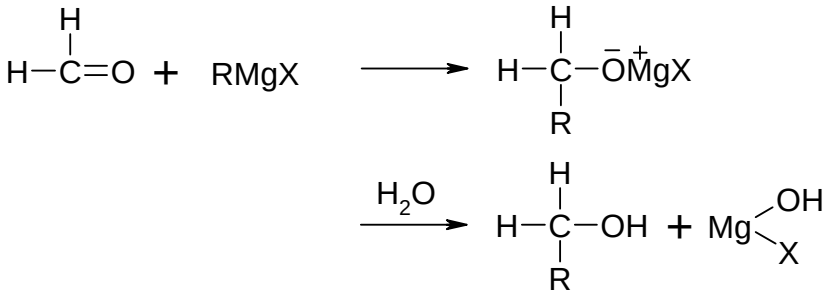
Mechanism of Grignard's reaction. This reaction is an example of nucleophilic addition reaction and is represented as follows:



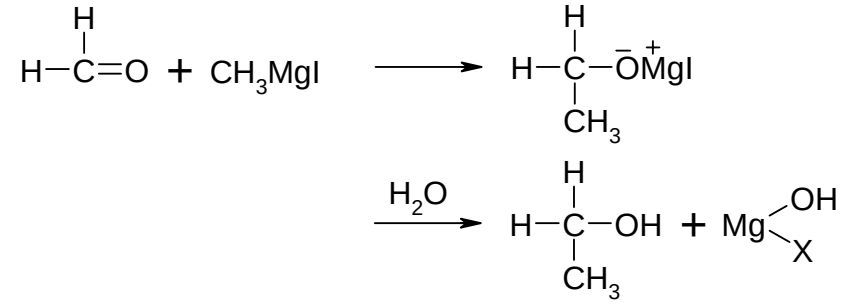
Alcohol

The product is the magnesium salt of the weakly acidic alcohol and is easily hydrolysed to alcohol by the addition of acid or even water.

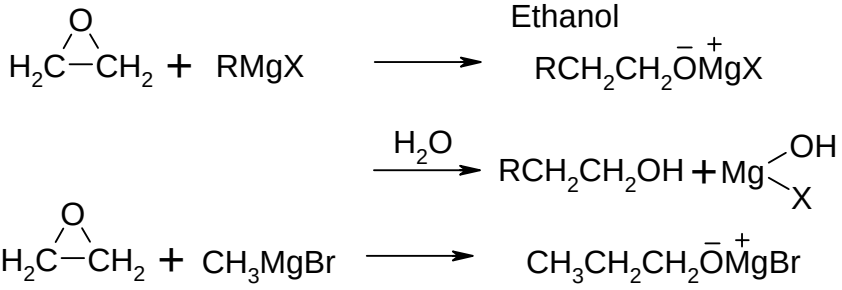
(a) **Primary alcohols**. They are obtained by treating Grignard's reagent with (i) formaldehyde (ii) ethylene oxide (iii) passing dry oxygen or (iv) ethylene chlorohydrin, followed by hydrolysis of the addition product.

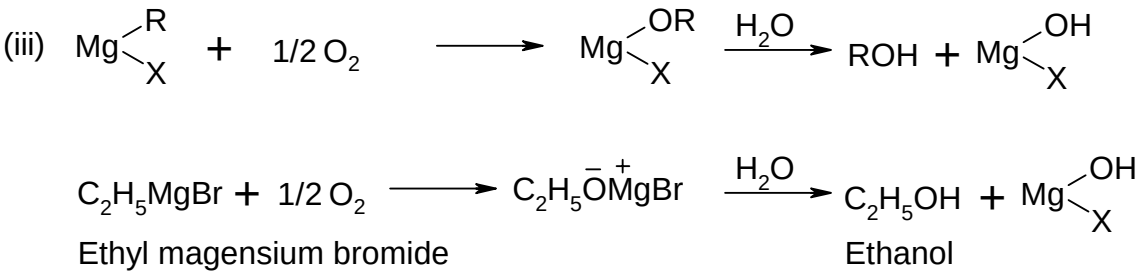
(i) 

Primary alcohol

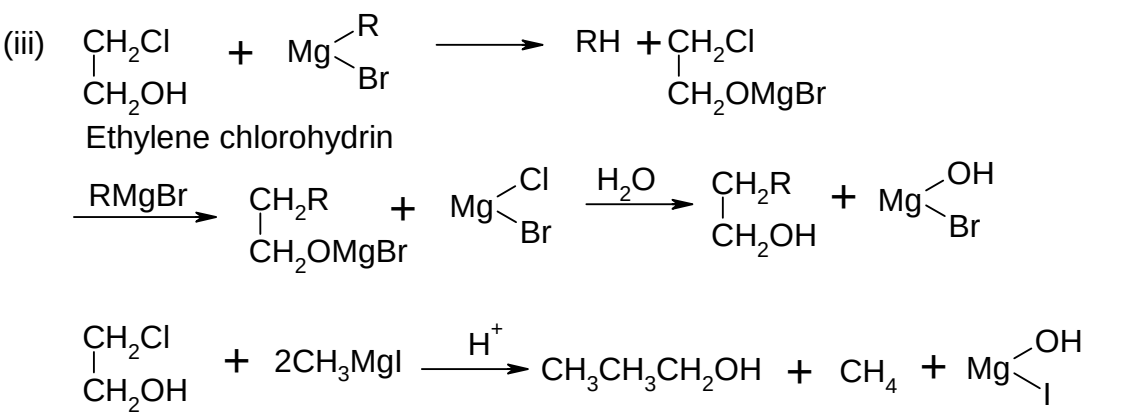


Ethanol

(ii) 

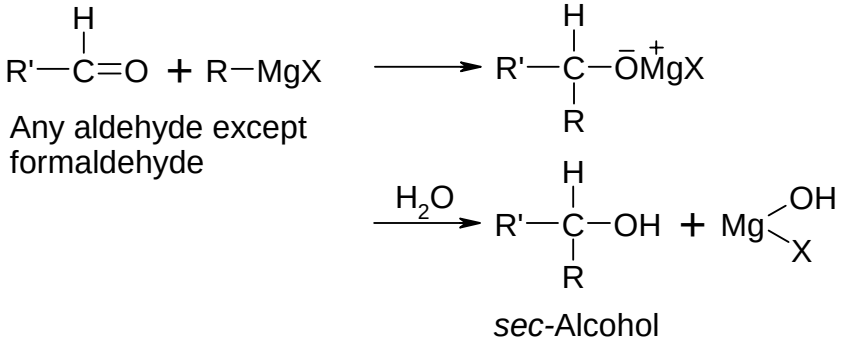
(iii) 

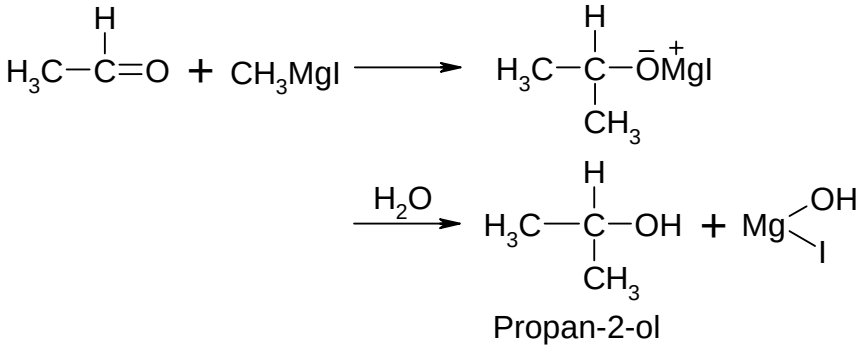
Propanol

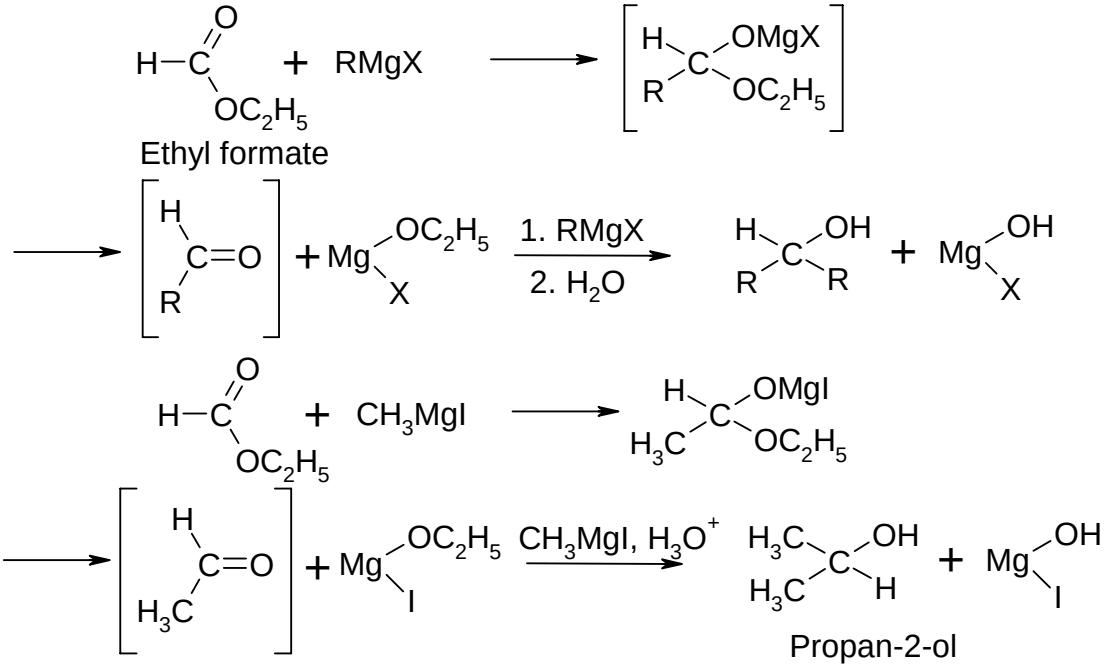
(iii) 

Ethylene chlorohydrin

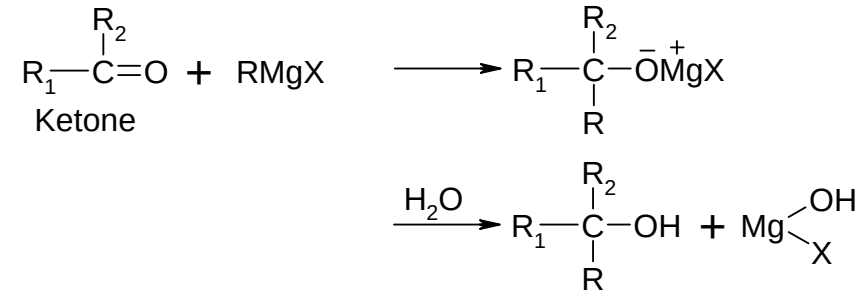
(b) **Secondary alcohols**. They are obtained by treating Grignard's reagent with aldehydes other than formaldehyde or one molecule of ethyl formate, followed by hydrolysis of the addition product.





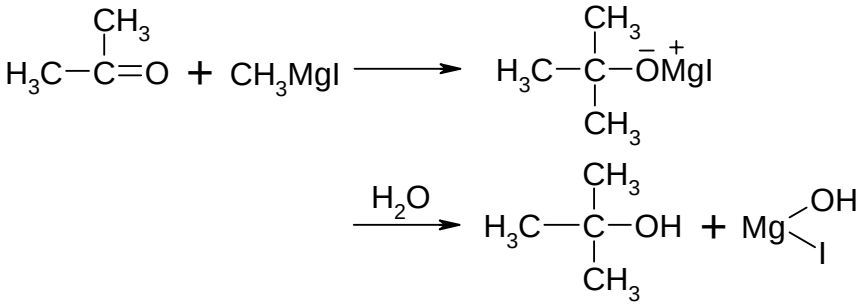


(c) **Tertiary alcohols**. They are obtained by treating Grignard's reagent with ketones or esters followed by hydrolysis of the addition product.

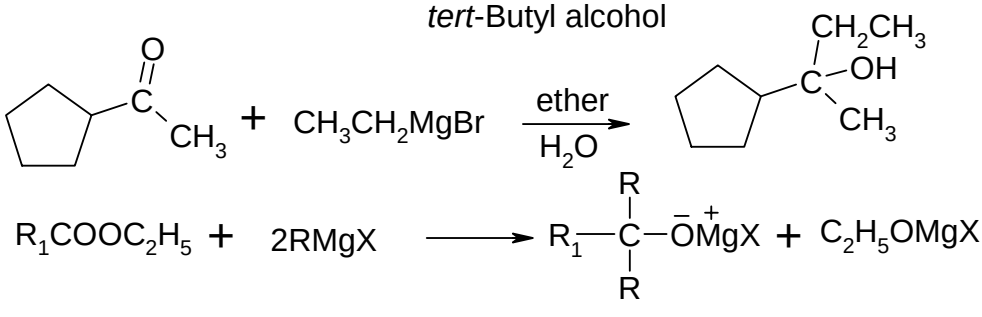


Ketone

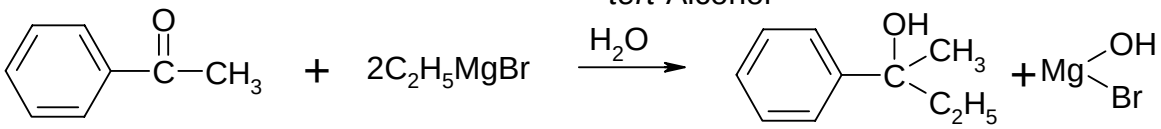
tert-Alcohol

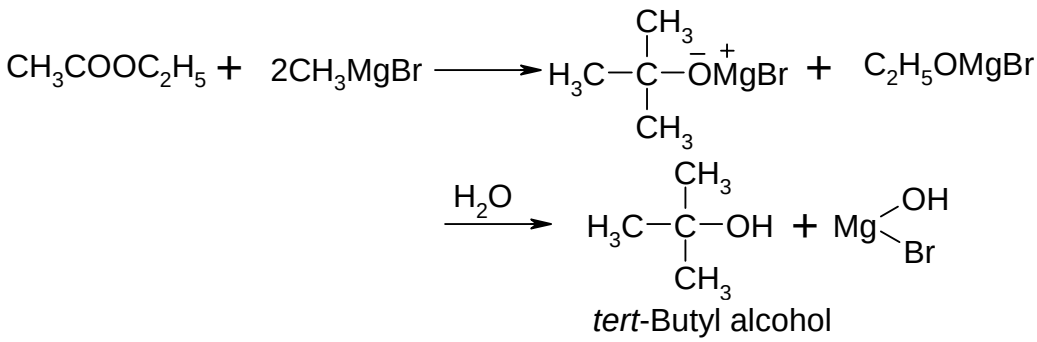


tert-Butyl alcohol



tert-Alcohol

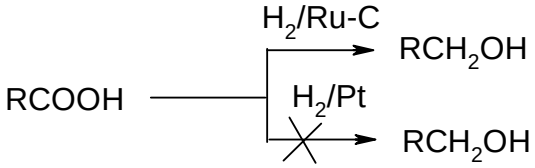




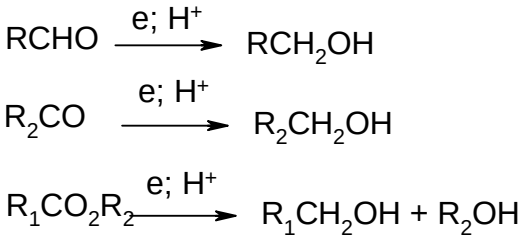
tert-Butyl alcohol

(ii) **From carbonyl compounds by reduction**. Aldehydes and ketones can be reduced to primary and secondary alcohols respectively either by catalytic hydrogenation (H_2, Ni) or by the use of chemical reducing agents like sodium and ethanol, lithium aluminium hydride ($LiAlH_4$) in ethereal solution. Tertiary alcohols can not be prepared by this method.

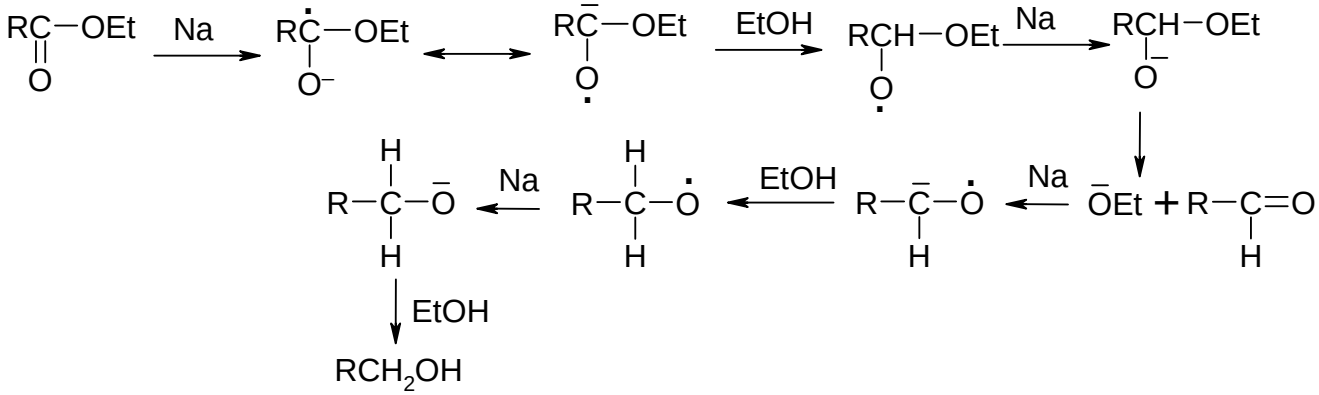
(a) **Catalytic hydrogenation**: Many functional groups are reduced catalytically by metals like Ni, Pt, Pd, Rh and Ru. The catalytic activity of a given metal is dependent on its method of preparation, presence of promoters or inhibitors and nature of solvent.



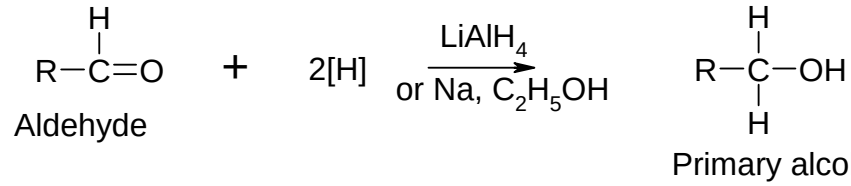
(b) **Bouveault –Blanc reduction**: Aldehydes, ketones, esters can be reduced by means of excess of Na and ethanol or *n*-butanol (Bouveault-Blanc reagent), ***e.g.***,

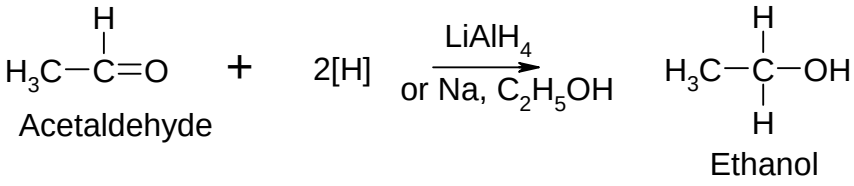


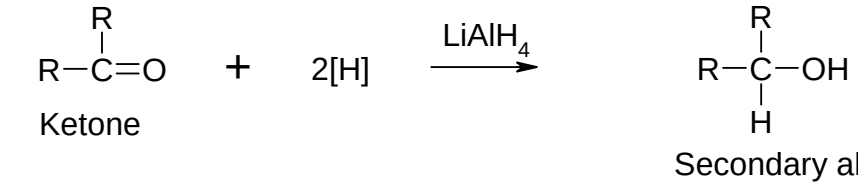
Mechanism: Reaction is believed to occur in steps involving the transfer of one electron (e) at a time, ***e.g.***,

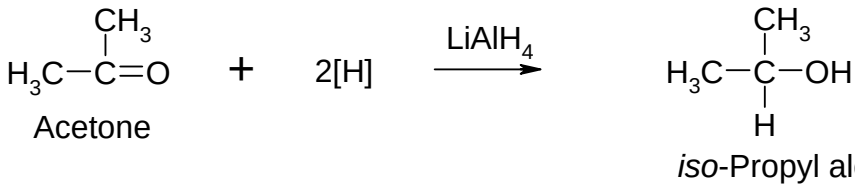


(c) **Reduction with metallic hydrides**: Many complex metallic hydrides like $LiAlH_4$ (LAH), $NaBH_4$ or $LiAlH(Obut)_3$ reduce functional group like >C=O to give alcohol.

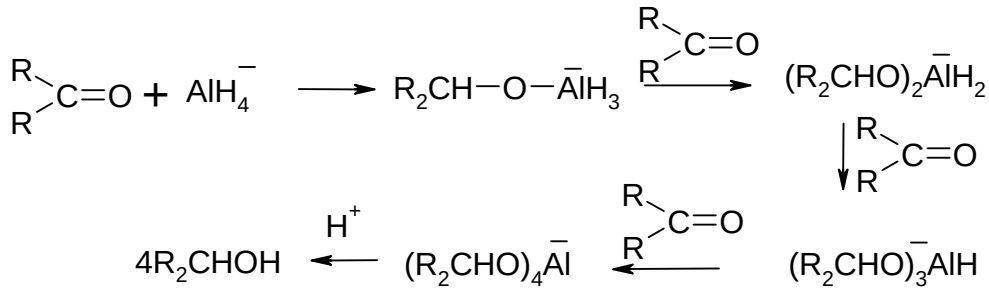




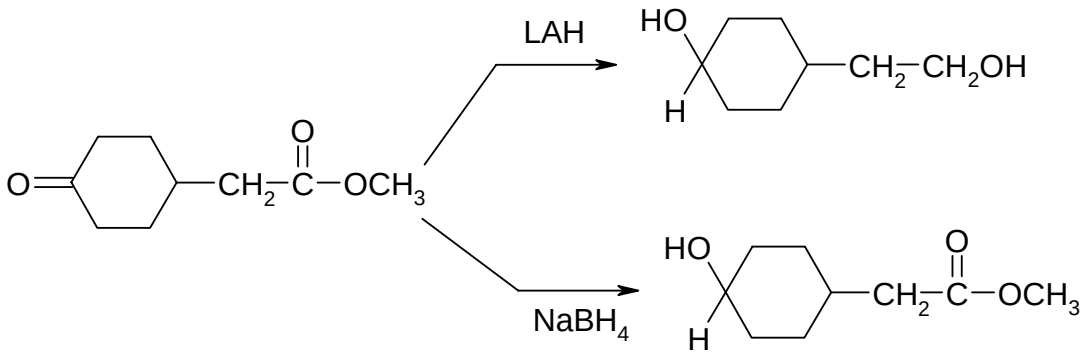




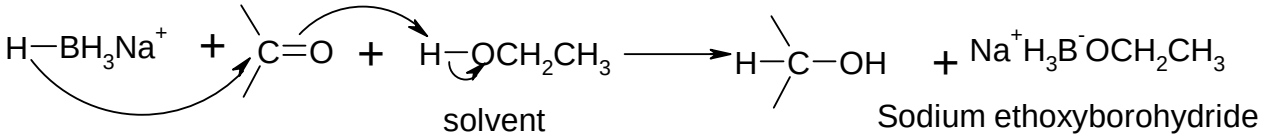
Mechanism



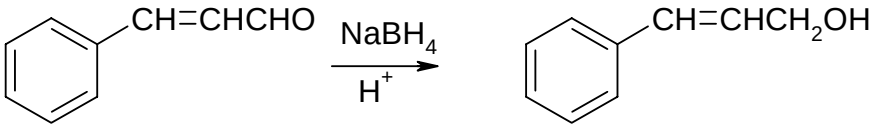
LAH is much stronger reducing agent than $NaBH_4$. However, $NaBH_4$ is more selective and does not reduce less active carbonyl group in acids, esters and amides. Hence, the ketonic and aldehydic group can be selectively reduced in the presence of an acid or an ester group using $NaBH_4$.



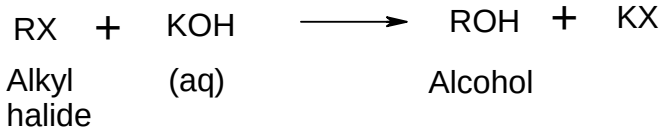
Mechanism of $NaBH_4$ reduction

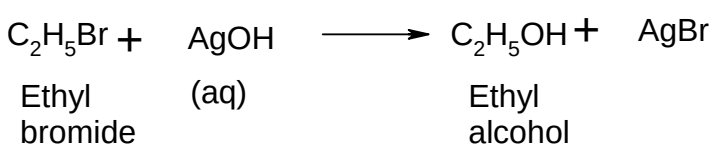


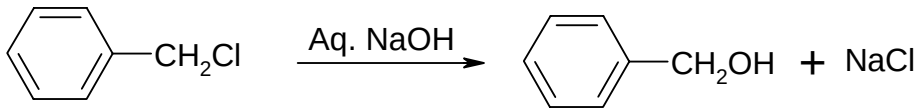
Unsaturated carbonyl compounds can be reduced to unsaturated alcohols by $NaBH_4$ or $LiAlH_4$. However, α, β-unsaturated carbonyl compounds can be only reduced to the corresponding unsaturated alcohols by $NaBH_4$ because $LiAlH_4$ reduces double bond as well, *e.g.*,

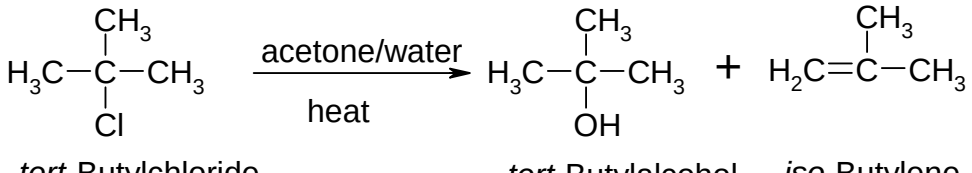


(iii) **By hydrolysis of alkyl halides**. Alkyl halides on hydrolysis with aqueous alkalies or moist silver oxide give alcohols. In general, alkyl halides are prepared from alcohols as the latter are easily available. It is a nucleophilic substitution reaction in which hydroxide ion substitutes halide ions. Among alkyl halides, alkyl Iodides undergo nucleophilic substitution at the fastest rate. The mode of mechanism S_N1 and S_N2 depends on the nature of alkyl group. Tertiary alkyl halides prefers to proceed via S_N1 mechanism, while primary alkyl halides follows S_N2 mechanism. Secondary alkyl halides can follow either of the mechanism depending upon the reagent used.





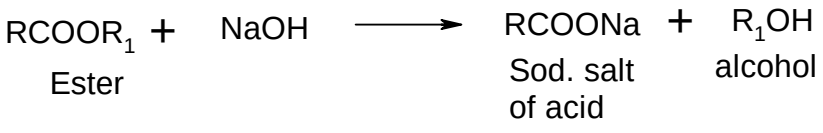


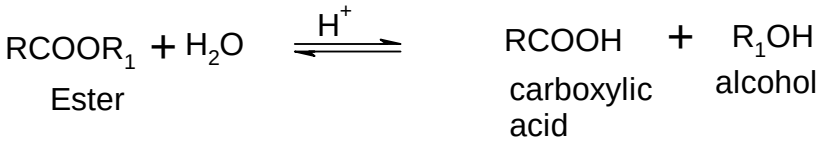


For those halides that can undergo elimination, the formation of alkene must always be considered as a possible side reaction. Selection of solvent permits some control: aqueous

solution favours substitution while alcoholic solution favours elimination. Tertiary alkyl halides and to a lesser extent secondary alkyl halides, are prone to dehydrohalogenation and yield an alkene even when aqueous solution is used. For these halides, simple hydrolysis with water is best, although even here considerable alkene is obtained.

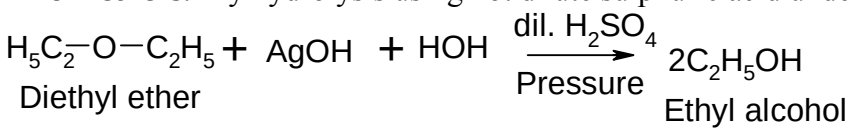
(iv) **From esters**. By acidic or basic hydrolysis.





This method is of industrial importance for preparation of certain alcohols which occur naturally as esters.

(v) **From ethers**. By hydrolysis using hot dilute sulphuric acid under pressure, *e.g.*,



(vi) **From acid chlorides, acid anhydrides and esters**.

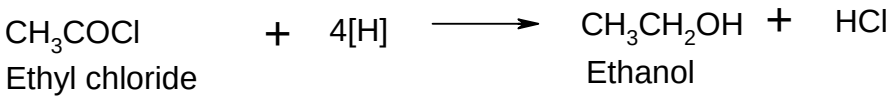
By reduction with the following reagents:

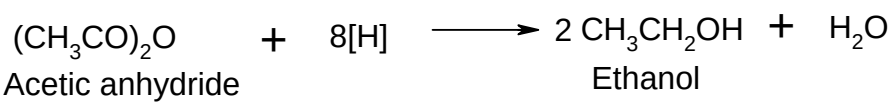
(a) Sodium and alcohol

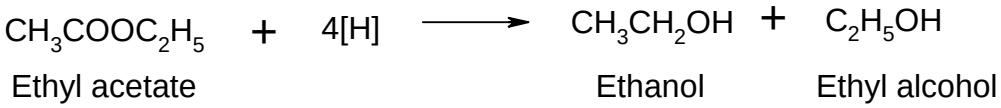
(b) Hydrogen and a metal catalyst (catalytic reduction)

(c) Lithiumaluminium hydride in ethereal solution.

Examples:



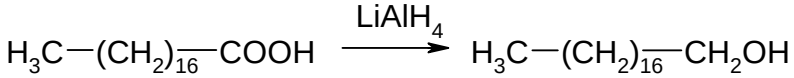




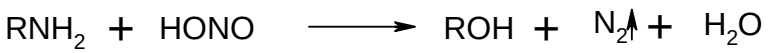
Reduction by reagents (a) and (c) is carried out by nascent hydrogen.

Reduction of ester by catalytic method requires more severe conditions. High pressure and elevated temperatures are needed. The catalyst used is a mixture of oxides, known as copper chromite, $CuO.CuCr_2O_4$.

Lithium aluminium hydride can reduce an acid directly to an alcohol, *e.g.*, stearic acid is reduced to octadecan-1-ol.

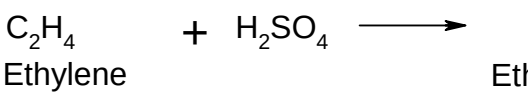


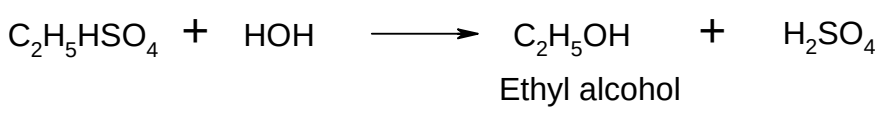
(vii) **From primary amines**. Primary amines on treatment with nitrous acid (a mixture of sodium nitrite and dilute mineral acid HCl or H_2SO_4) yield alcohols. Thus:

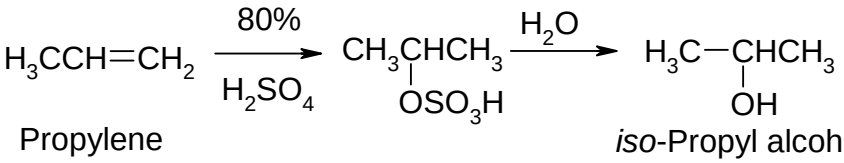


This reaction can be used as a test for primary amines, since none of the other classes of amines liberate nitrogen.

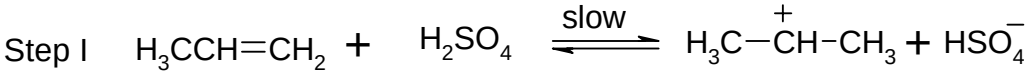
(viii) **From alkenes** (a) Alkenes, when passed through 98% sulphuric acid, are absorbed giving alkyl hydrogen sulphate, which when boiled with water yields alcohols. The addition of H_2SO_4 occurs *via* Markownikoff's rule *e.g.*,

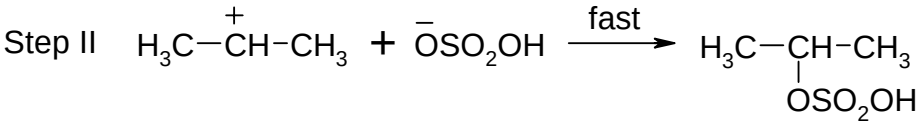




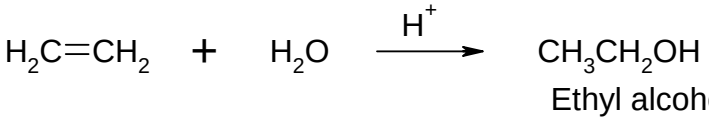


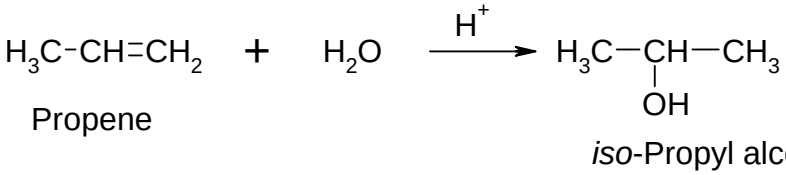
Mechanism:

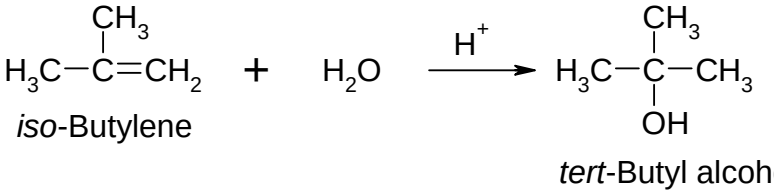


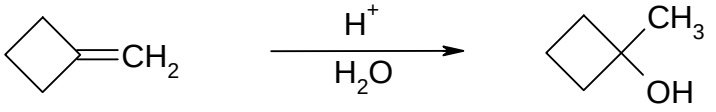


(b) **Direct hydration of alkenes.** Alkenes combine directly with water at low temperature and high pressure in the presence of acids to yield ethyl alcohol.



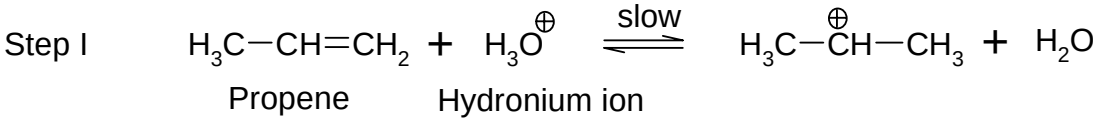


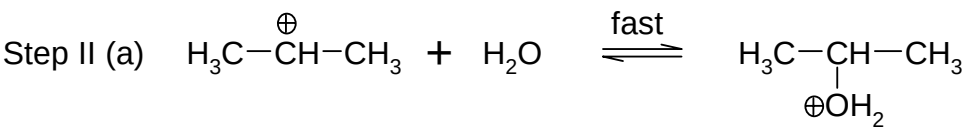


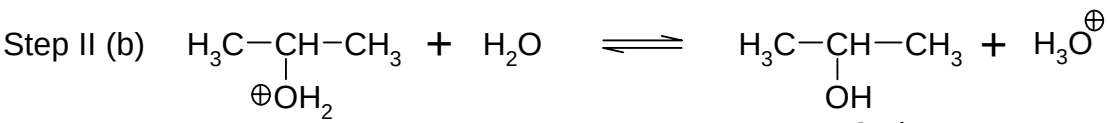


Methylenecyclobutane 1-Methylcyclobutanol

Since this addition follows Markownikoff's rule, the alcohols are the same as obtained by the two-step mechanism as under:

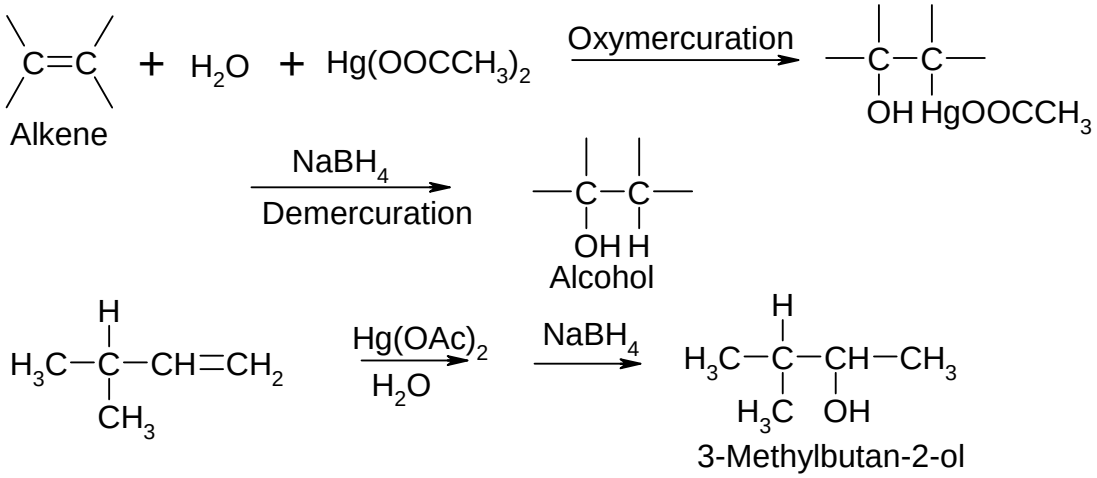






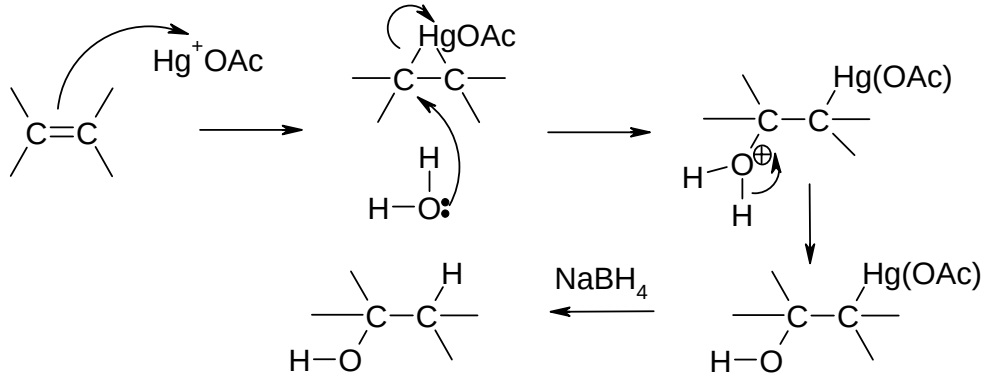
This method is a popular method for the manufacture of primary alcohols.

(c) **Oxymercuration-demercuration**. Alkenes react with mercuric acetate in the presence of water following Markownikoff's rule to give hydroxyl-mercurial compounds, which on reduction by sodium borohydride yield alcohols.



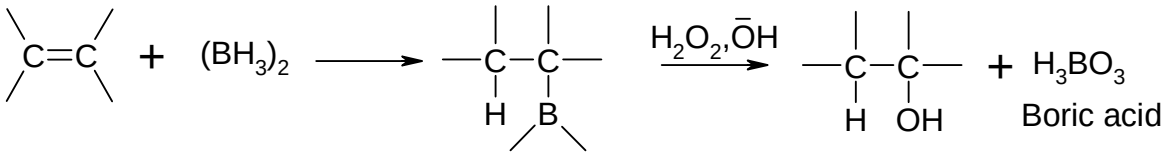
This process is very fast and covenient and gives excellent results. The alkene is added at room temperature to an aqueous solution of mercuric acetate diluted with solvent tetrahydrofuran (THF). The reaction is generally complete within minutes. The organo mercurial compound is then immediately reduced by sodium borohydride in demercuration. The reaction sequence amounts to hydration of the alkene following Markownikoff's rule.

Mechanism



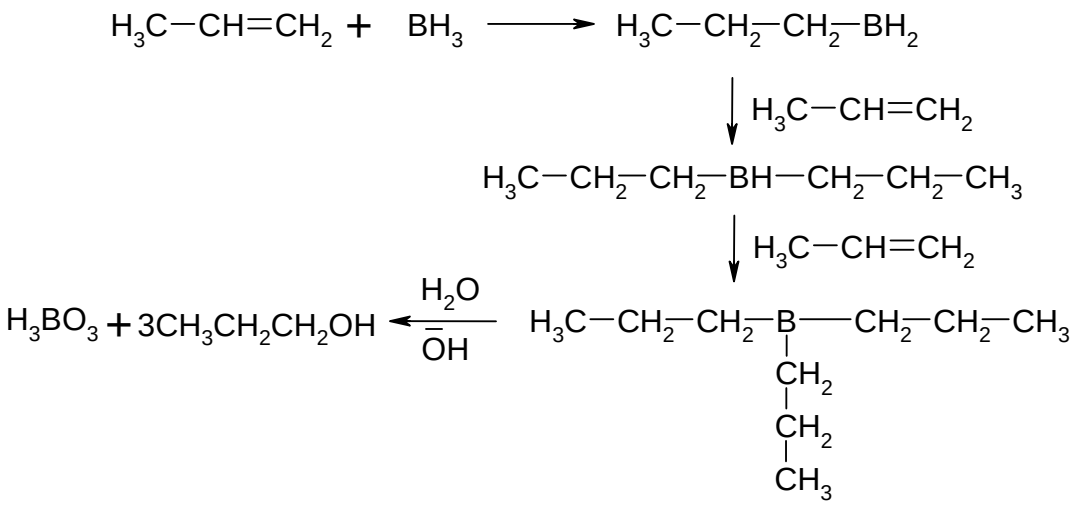
Oxymercuration involves elecrophilic addition to the carbon-carbon double bond, with the mercuric ion as electrophile. It has been proposed that a cyclic mercurinium ion is formed. This is attacked by nucleophilic solvent like H_2O to yield addition product.

(d) **By hydroboration-oxidation of alkenes**. Alkenes undergo hydroboration with diborane $(BH_3)_2$ to form alkyl boranes, R_3B, which on oxidation give alcohols.

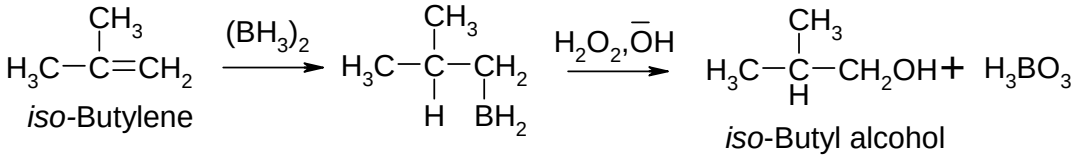


It involves addition of BH_3 to the double bond. The alkyl borane can then undergo oxidation in which boron is replaced by –OH group. The reaction is not a single step but proceeds in a series of steps in which each hydrogen atom of Borane is substituted by alkyl group. It may be noted here that in this case the addition of H and OH at the double bond follows antiMarkownikoff's rule.

For example:

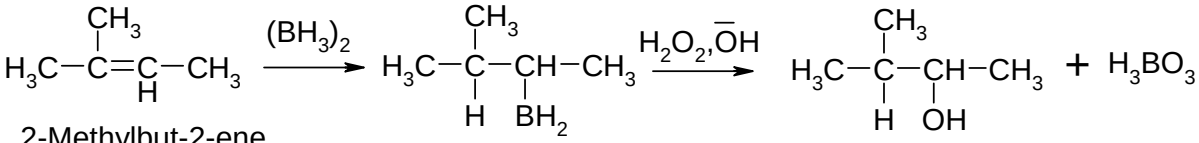


The medium for carrying out the hydroboration-oxidation reaction is ether or tetrahydrofuran. The oxidation is carried out with alkaline hydrogen peroxide. Diborane is the dimer of hypothetical BH_3 but in reaction it acts as BH_3.



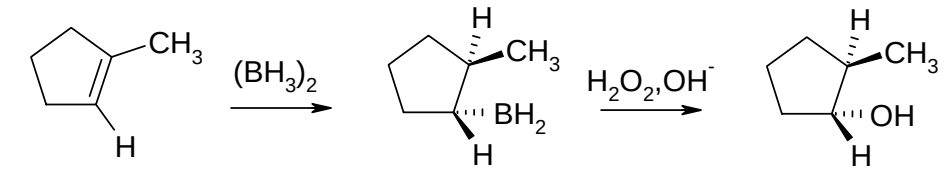
iso-Butylene

iso-Butyl alcohol



2-Methylbut-2-ene

3-Methylbutan-2-ol

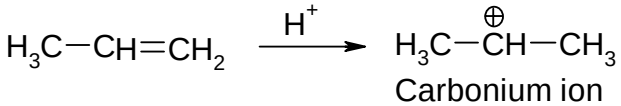


1-Methylenecyclopentane

trans-2-Methylcyclopentanol

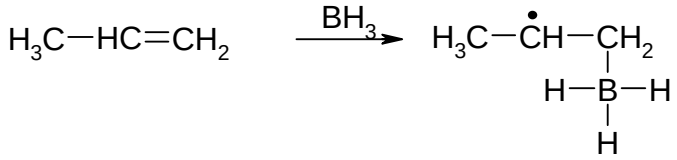
In the last example, H and OH adds to the same surface of the double bond i.e. *syn* addition. Only primary and secondary alcohol can be obtained by this method. Rearrangements do not occur in hydroboration because no carbonium ions are formed as intermediates. In most cases, where two isomeric products are possible, one of them generally predominates, *i.e.*, as envisages against the Markownikoff's rule.

Mechanism. In ordinary electrophilic addition reactions at the double bond, the nucleophilic part of the reagent attaches itself to that carbon atom which is attached to the least number of hydrogen atoms. Thus

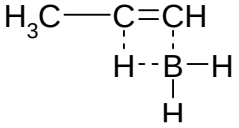


Carbonium ion

Since boron itself is acidic, being deficient in electrons, it withdraws the π electrons of the double bond and attaches itself to carbon. In doing so, the best possible attachment is such that the positive charge can develop on the carbon which can accommodate it more comfortably.



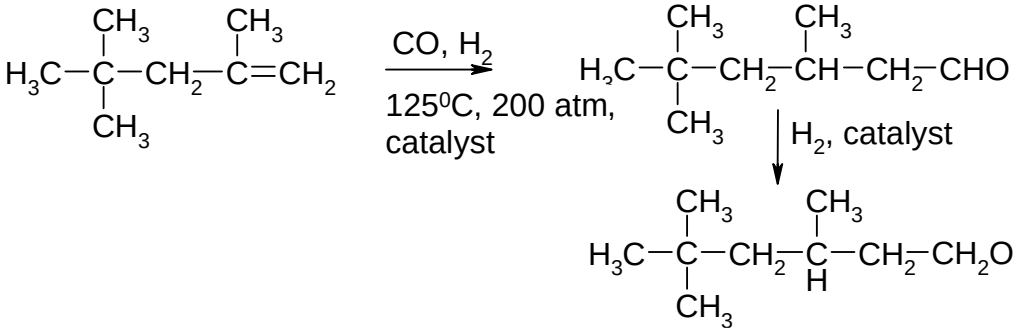
In this case, no intermediate carbonium ion is formed as in ordinary electrophilic addition at the double bond. Thus when the transition state is approached, both the carbon atom and the electron-deficient boron atom become acidic. Since boron has a hydrogen atom bonded to it by a pair of electrons, therefore the electron-deficient carbon takes this hydrogen and boron loses it at the expense of the gained π electrons. Thus:



Transition state

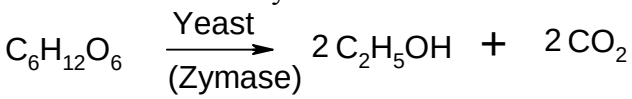
The loss of π electron by C_2 to the C_1-bond exceeds its gain of electron from hydrogen and thus C_2 attains a partial positive charge. Thus the reactions involves a single step with only one transition state in which hydrogen and boron both add to the carbon-carbon double bond. It is hence a four centre transition state.

(d) **Oxo-process** (Hydroformylation or carbonylation reaction). In this process, carbon monoxide and hydrogen are added to olefins at 125-145°C and 200 atm pressure in the presence of a catalyst to yield aldehydes and ketones which can be reduced to alcohols. The catalyst consists of cobalt, thoria, kieselguhr.



3,5,5-Trimethylhexan-1-ol

(ix) **From carbohydrates**. Certain carbohydrates on fermentation yield alcohols under the influence of suitable enzymes under anaerobic conditions. Thus:



This method is of great commercial importance and is described in detail later.

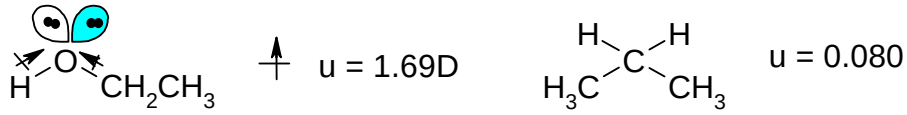
Physical Properties. (i) The lower members are colourless volatile liquids having characteristic alcoholic smell and burning taste. The higher member are colourless solids.

(ii) The first three members are completely miscible with water due to their tendency to form hydrogen bonding with water molecules. The solubility rapidly decreases with the increasing number of carbon atoms. The higher members are practically insoluble in water.

(iii) The specific gravity and boiling points increase as the molecular weight increases. The primary alcohol has a higher boiling point than the corresponding secondary alcohol and the latter has a higher boiling point than the corresponding tertiary alcohol.

(iv) **Association among alcohols (Hydrogen bonding)**. It is known that whenever hydrogen is covalently bonded to a highly electronegative atom such as oxygen in alcohols, the shared pair of electrons is partially shifted towards oxygen atom. Thus, the hydrogen atom acquires slight positive charge and the oxygen atom acquires sight negative charge.

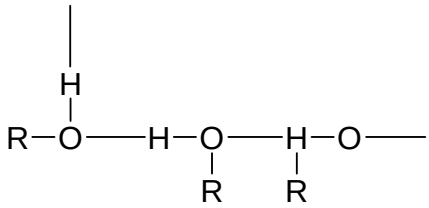
This accounts for the high dipole moment of alcohols. For example: the polarized C-O & H-O bonds and the nonbonding electrons add to produce a dipole moment of 1.69 in ethanol, compared to the dipole moment of only 0.8 in propane. In liquid ethanol, the positive and negative ends of these dipoles align to produce additive interactions.



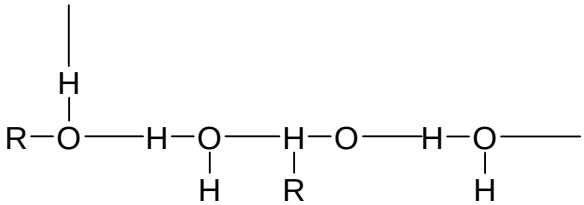
Mol. wt. 46	Mol. wt. 44
b.p. 78^0C	b.p. 42^0C

Dipole-dipole interactions and association of molecules through H-bonding accounts for the much higher boiling point of ethanol (b.p. 78°C) in comparison to propane (b.p. 42°C).

The hydrogen atom of one molecule of alcohol gets attracted to the oxygen atom of the second OH group of the other molecule and the two molecules are held together by a weak bond called the hydrogen bond which is electrostatic in nature.



Lower alcohols like methanol, ethanol, etc., are soluble in water in all proportions because of the existence of a hydrogen bond between molecules of water and molecules of alcohol.



In the lower alcohols, the hydroxyl group being polar, constitutes a large part of the molecule, but as the molecular weight of the alcohol increases, the hydrocarbon character of the molecule increases and hence the solubility in water decreases. The structure of carbon chain also plays its own role, *e.g.*, *n*-butanol is fairly soluble in water, (18 g/100g water) but *tert*-butanol is miscible with water in all proportions. Cyclohexyl alcohol is more soluble than n-hexylalcohol due to its compact hydrophobic chain.

Table I lists solubility of some simple alcohols.

Table I: Solubility of alcohols in water(at 25°C)

Alcohol	**Solubility in water**
Methyl	Miscible
Ethyl	Miscible
n-Propyl	Miscible
t-Butyl	Miscible
iso-Butyl	10.0%
n-Butyl	9.1%
Cyclohexyl	3.6%
n-Hexyl	0.6%
Hexane-1,6-diol	Miscible

Chemical Properties

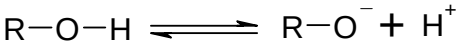
The chemical properties of alcohols can be studies under the following headings:

I. Reactions involving the cleavage of O-H bond
II. Reactions involving the cleavage of C-OH bond
III. Reactions involving oxidation
IV. Reactions with Lucas reagent

I. **Reactions involving the cleavage of O-H bond (Acidic nature of alcohols)**: Some examples are as follows:

Acidic nature of alcohols

Alcohols can be acidic in nature as the hydrogen atom is attached to the strongly electronegative oxygen atom and can be removed as a proton. This can be done by using a strong base than the alkoxide formed.



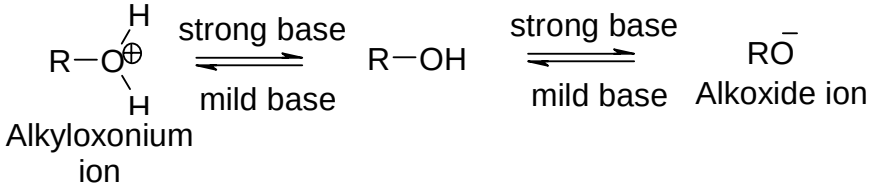
In alcohols, alkyl groups have +I effect (electron donating groups) i.e., there will be an increased electron displacement towards the oxygen atom, which causes difference in the acidic strength of the primary, secondary and tertiary alcohols.

This is because the presence of three alkyl groups release electrons in *tert*-alcohol, two in *sec.* and one in primary, to the carbon bearing the –OH group. As a result, the oxygen atom in each has a different electron density. The greater the negative charge on the oxygen atom, the closer is the covalent pair in the O-H bond and release of proton becomes increasingly difficult. Thus the acid strength of alcohols will be in the order

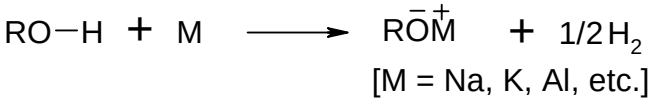
CH_3OH > primary > secondary > tertiary

Strongest acid — Weakest acid

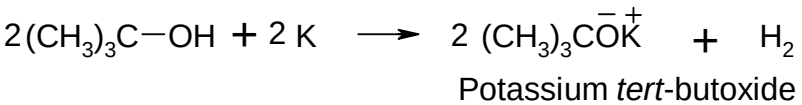
Alcohols may also be basic, although weakly. Very strong acids are required to protonate the OH group, as indicated by the low pKa values of their conjugate acids, alkyloxonium ions. Thus, in strong acids they exist as alkyloxonium ions, in neutral media as alcohols, and in strong bases as alkoxides. The alcohols can be called amphoteric. The amphoteric nature of the hydroxyl functional group characterizes the chemical reactivity of alcohols.



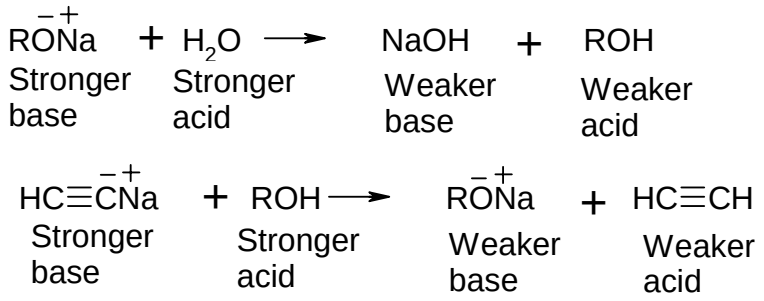
(i) **Reactions with active metals**. The hydrogen atom of OH can be replaced by an electropositive metal, indicating that alcohols are acidic in nature.



The compound formed is known as alkoxide and hydrogen is liberated, *e.g.*,

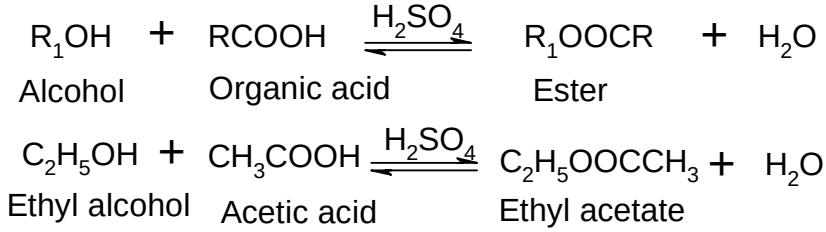


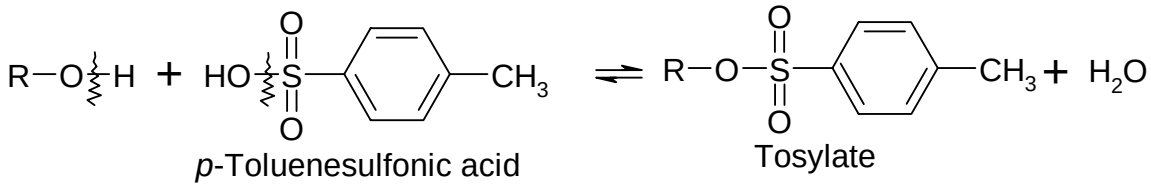
Alcohols are weaker acids than water but stronger than acetylene.



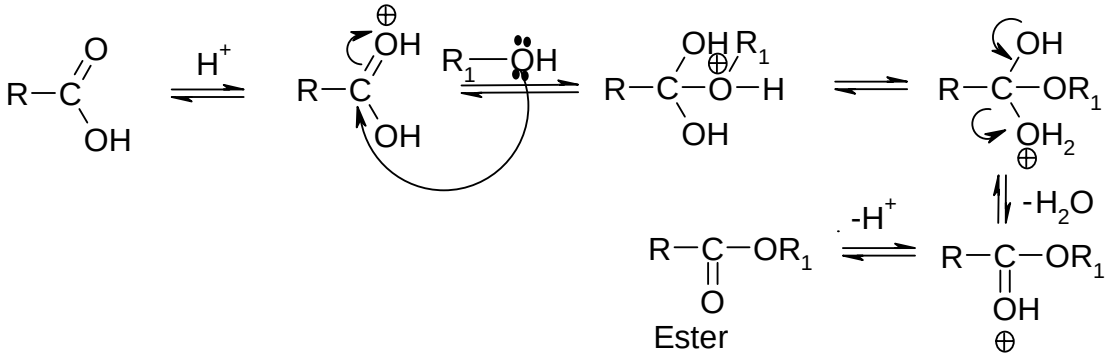
(ii) **Ester formation**. Alcohols react with acids to form esters. This process is called esterification.

The reaction is carried out in the presence of dehydrating agent like, concentrated sulphuric acid or dry hydrogen chloride. Esterification is a reversible reaction and therefore, water is removed as soon as it is formed in order to prevent the reaction from going in the backward direction. The reaction is an example of nucleophilic substitution reaction with respect to acid.

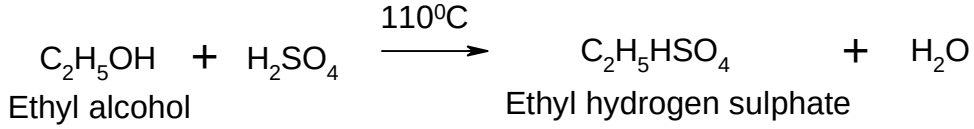




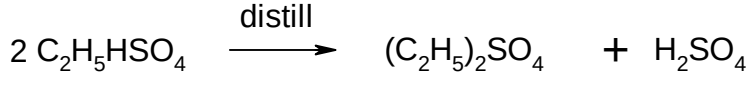
It has been proved beyond doubt that esterification with organic acid involves cleavage at the O-H bond of alcohol and C-OH of the acid.



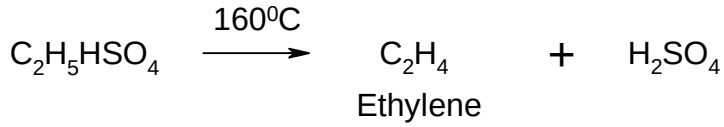
The action of concentrated sulphuric acid on alcohols is very interesting as it gives different products under different experimental conditions. In the first step, alkyl hydrogen sulphate is formed which under different conditions form different products. Thus:



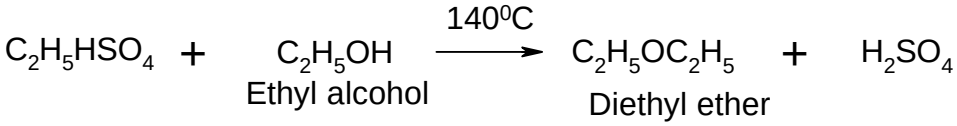
(a) When heated alone, diethyl sulphate is obtained.



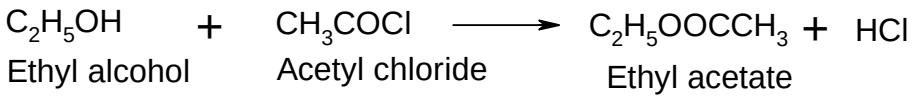
(b) When heated with excess of sulphuric acid at 160°, ethylene is obtained.

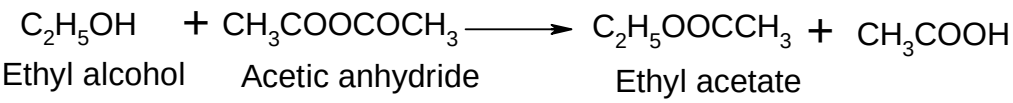


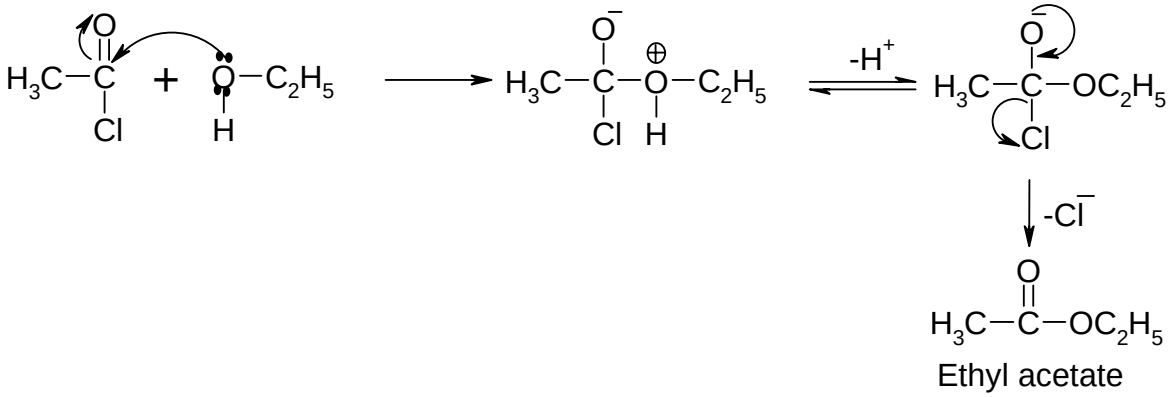
(c) When heated with excess of alcohol at 140°, diethyl ether is obtained.



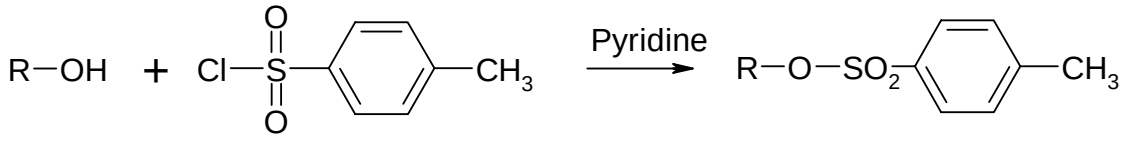
(ii) **Acylation**. When an alcohol is treated with an acid chloride or acid anhydride, the H-atom of –OH is replaced by an acyl (RCO-) group and an ester is formed. The process is called acylation.







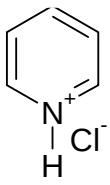
(iii) **Tosylation**. Tosylates are obtained from alcohols using tosyl chlorides (TsCl) in pyridine.



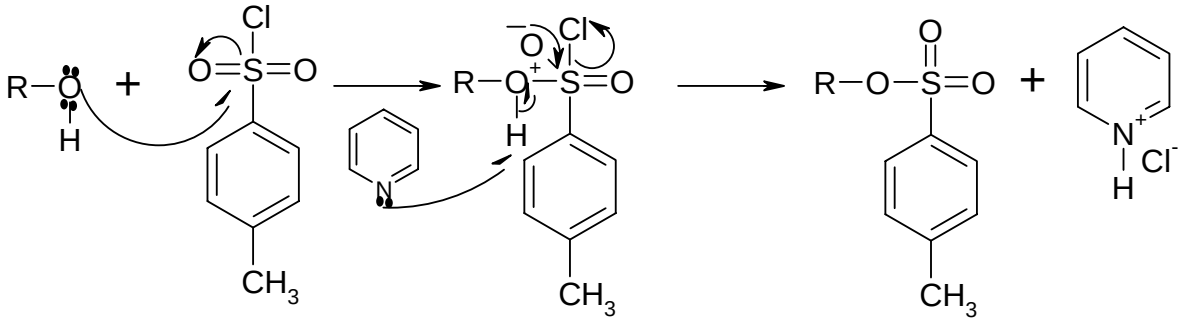
p-Toluenesulfonyl chloride

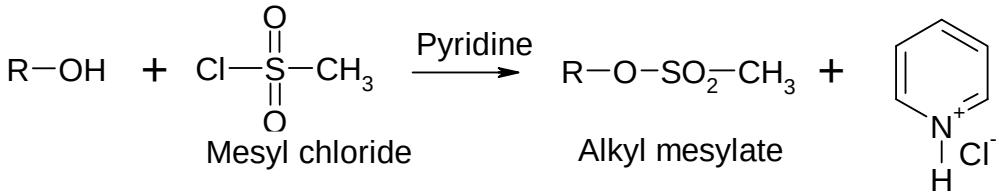
Tosylate ester

+



Mechanism





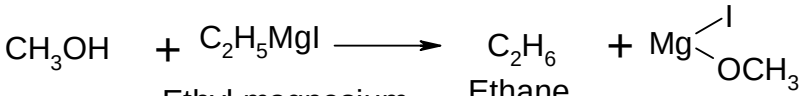
Mesyl chloride

Alkyl mesylate

(iv) **Action of Grignard reagent**. Alcohols react with Grignard's reagents forming alkanes. In this case, the hydrogen atom of the hydroxyl group combines with the alkyl group of the Grignard reagent forming an alkane.

Grignard reagent

Alkane



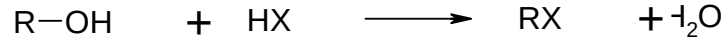
Ethyl magnesium iodide

Ethane

II. **Reactions involving the cleavage of C-OH bond**: C-O bond is broken when OH is lost as a nucleophile and another nucleophile substitutes it.

(i) **Reaction with hydrogen halides**. Alcohols react readily with hydrogen halides to give alkyl halides and water. The reaction is carried out either by passing the dry hydrogen halide gas into the alcohol or by heating the alcohol with the concentrated aqueous halogen acid. HBr may be obtained in the presence of alcohol by reaction between conc. H_2SO_4 and KBr, while HI may be obtained by reaction between H_3PO_4 and KI in presence of alcohol.

The reaction is an example of nucleophilic substitution reaction in which halide ion substitutes hydroxide ion. The least reactive of the hydrogen halides, HCl, requires the presence of zinc chloride for reaction with primary and secondary alcohols. The more reactive *tert*-butyl alcohol is converted into the corresponding chloride by simple shaking with HCl at room temperature.



Reactivity of HX : HI > HBr > HCl

Bond dissociation energy of HI is least and thus I^- will substitutes $\bar{O}H$ readily as compared to HBr and HCl.

Reactivity of ROH: tertiary > secondary > primary > CH_3

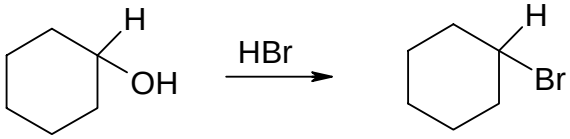
Examples:

$$CH_3CH_2OH + HCl \xrightarrow[\text{heat}]{ZnCl_2} CH_3CH_2Cl + H_2O$$

Ethyl chloride

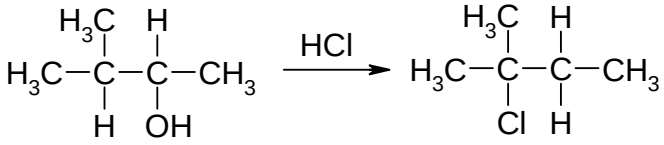
$$(CH_3)_3COH \xrightarrow[\text{room temp.}]{\text{Conc. HCl}} (CH_3)_3CCl$$

tert-Butyl alcohol — *tert*-Butyl chloride



Cyclohexanol — 1-Bromocyclohexane

The alkyl group in the halide does not always have the same structure as the alkyl group in the parent alcohol i.e., rearrangement of the alkyl group may take place. For example:



3-Methylbutan-2-ol — 2-Chloro-2-methylbutane

Mechanism:

(a) For all alcohols except CH_3OH and primary alcohols (S_N1, Unimolecular Nucleophilic Substitution takes place).

(i) $ROH + HX \rightleftharpoons RO^{\oplus}H_2 + X^-$

$RO^{\oplus}H_2 \rightleftharpoons [R^{\oplus}] + H_2O$

Carbonium ion

(ii) $[R^{\oplus}] + X^- \longrightarrow RX$

Alkyl halide

(b) In case of primary alcohols and CH_3OH (S_N2, Bimolecular Nucleophilic Substitution takes place)

$$X^- + RO^{\oplus}H_2 \longrightarrow [X\cdots R\cdots OH_2] \longrightarrow X{-}R + H_2O$$

If, however, an alcohol is heated with concentrated hydroiodic acid and red phosphorus, it is converted into a paraffin.

$$C_2H_5OH + 2HI \longrightarrow C_2H_6 + I_2 + H_2O$$

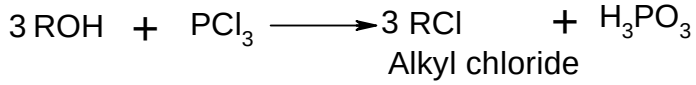
Ethane

(ii) **Reaction with phosphorus halides**. Phosphorus pentachloride gives alkyl chloride with alcohols.

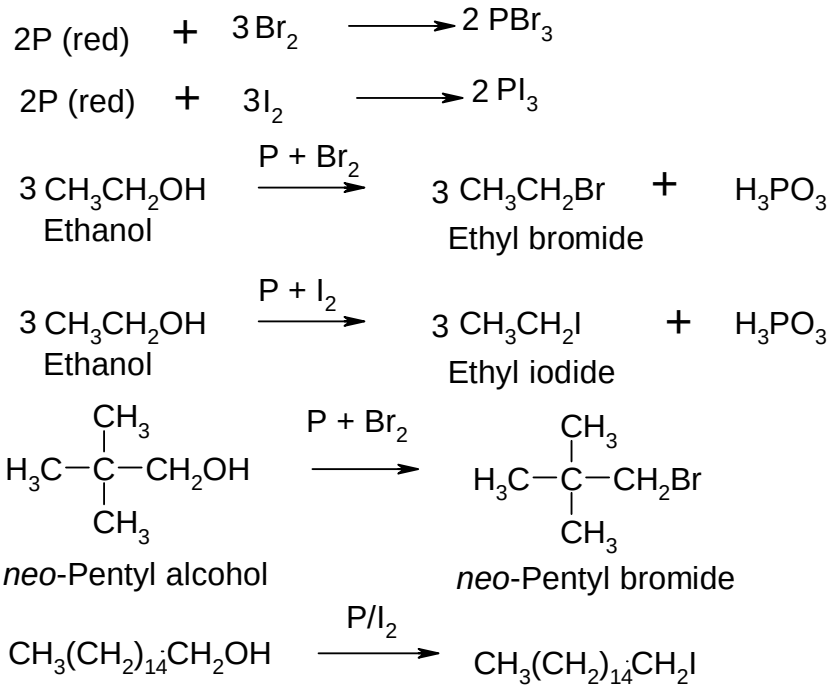
$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl\uparrow$$

Alkyl chloride

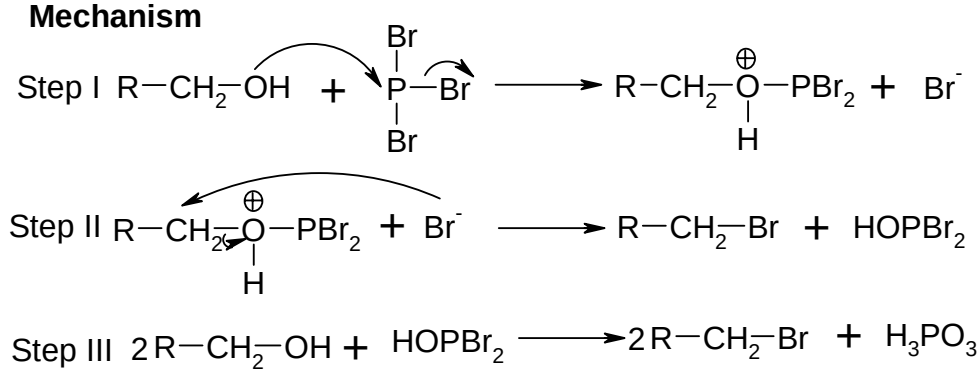
Phosphorus trichloride gives poor yields of alkyl chloride.



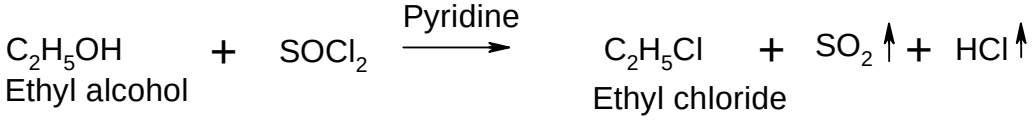
Phosphorus tribromide and phosphorus triiodide react with alcohols and give very good yields of alkyl halides. These phosphorus trihalides are usually prepared *in situ* by warming with bromine or iodine with red phosphorus



Mechanism

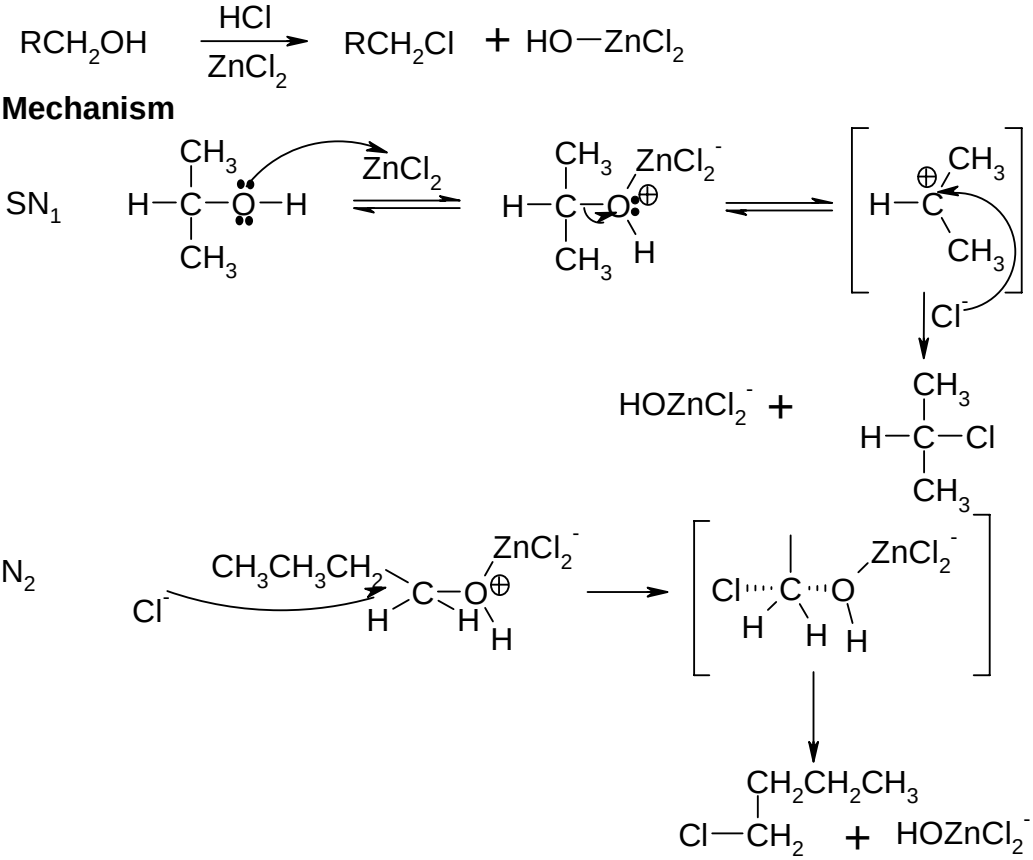


(iii) **Reaction with thionyl chloride**. Alcohols react with thionyl chloride to give alkyl chlorides.



The use of thionyl chloride is preferred over PCl_5 and PCl_3 for converting alcohols to alkyl halides because the side products in this case are gaseous SO_2 and HCl and there is no need to purify the product.

(iv) **Reaction with Lucas reagent**. The reagent composed of HCl and $ZnCl_2$ is called the Lucas reagent. Secondary and tertiary alcohols react with the Lucas reagent by the S_N1 mechanism while primary alcohols react by S_N2 mechanism.



(v) **Dehydration**. Alkenes are obtained.

Dehydration of all the three classes of alcohols may be done by passing over alumina at 150°-350°C. Primary alcohols are dehydrated by concentrated sulphuric acid at 170°C, and secondary and tertiary alcohols by boiling with dilute sulphuric acid.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[350^0C]{Al_2O_3} \underset{\text{Ethene}}{C_2H_4} + H_2O$$

In the case of dehydration of secondary and tertiary alcohols, hydrogen present on the adjacent carbon atom containing least number of hydrogen atoms is eliminated most easily. Thus:

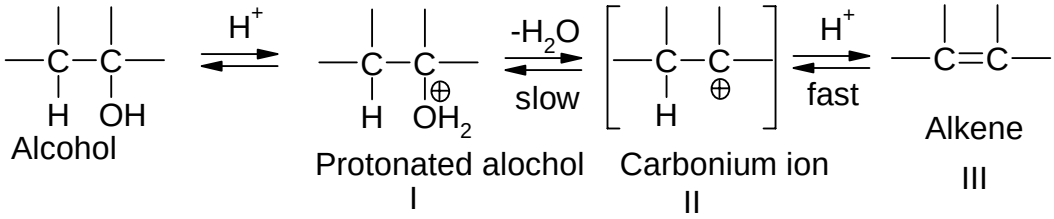
$$CH_3CH_2CH(OH)CH_3 \xrightarrow[H_2SO_4]{-H_2O} \begin{cases} CH_3CH_2CH{=}CH_2 \ \text{(I)} \\ CH_3CH{=}CHCH_3 \ \text{(II)} \end{cases}$$

The main product is but-2-ene (II).

Alcohols containing no α-hydrogen atom undergo dehydration and molecular rearrangement simultaneously, *e.g.*, *neo*-pentyl alcohol gives 2-methylbut-2-ene.

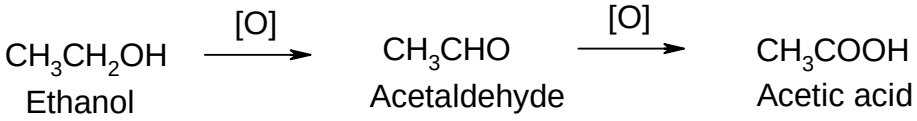
$$\underset{\textit{neo}\text{-Pentyl alcohol}}{(CH_3)_3C{-}CH_2OH} \xrightarrow{-H_2O} \underset{\text{2-Methylbut-2-ene}}{CH_3C(CH_3){=}CHCH_3}$$

Mechanism of dehydration. It has been already discussed in detail in the Alkene Chapter, however it may be remembered that dehydration involves (i) formation of protonated alcohol, RO^+H_2, (ii) its slow dissociation into a carbocation and (iii) fast expulsion of a hydrogen ion from the carbocation to form an alkene. This is an example of E_1 elimination.

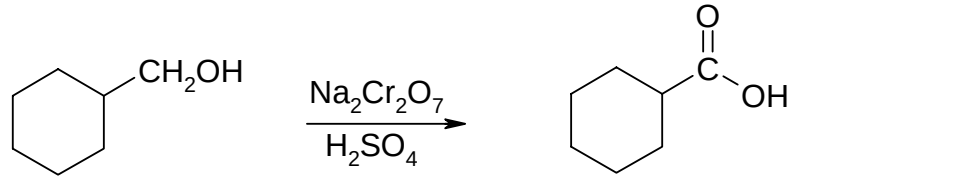


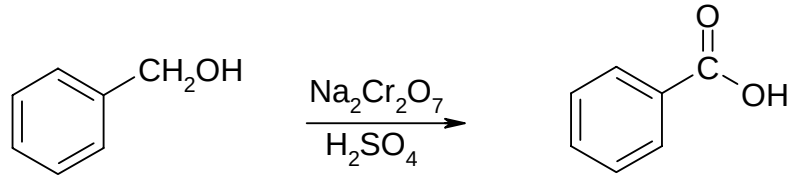
III. (i) **Oxidation of alcohols**. Oxidation of primary and secondary alcohols can be brought about by a variety of oxidizing agents. The product(s) differ depending upon the type of the alcohol and oxidizing agent used. Oxidation of 3° alcohol require severe conditions and results in mixture of products.

(a) A primary alcohol first gives an aldehyde and then an acid, both containing the same number of carbon atoms as the original alcohol.

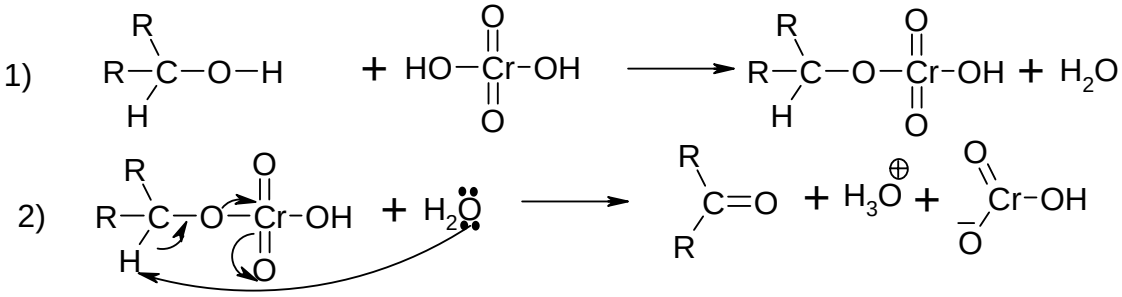


Chromic acid (H_2CrO_4 prepared by dissolving sodium dichromate in a mixture of sulfuric acid and water) oxidizes 1° alcohol directly to carboxylic acid.

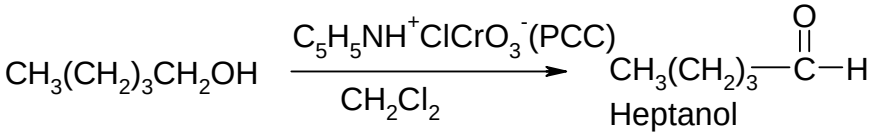




Mechanism

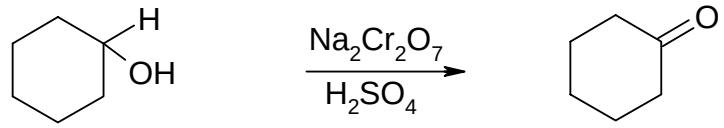


A better reagent for the oxidation of 1° alcohol to aldehyde is pyridinium chlorochromate (PCC), a complex of CrO_3 with pyridine and CH_2Cl_2.



Collins reagent is a complex of chromium trioxide pyridine and is the original version of PCC.

(b) Secondary alcohols are easily oxidized to ketones containing the same number of carbon atoms. The chromic acid reagent is often best for laboratory oxidation of secondary alcohols.

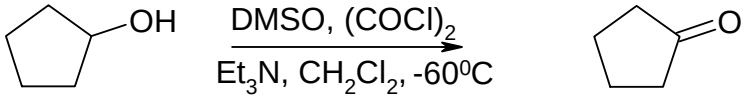


Cyclohexanol Cyclohexanone

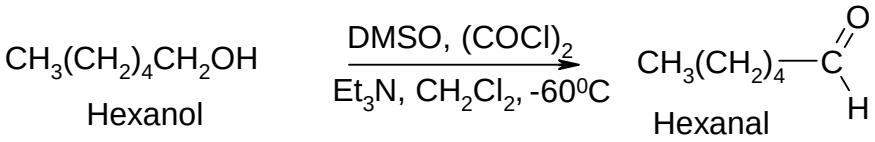
PCC can also be used for the oxidation of 2° alcohol to ketones.

(c) Tertiary alcohols are resistant to oxidation under moderate conditions. Since, they have no H atoms on the carbinol carbon atom, so oxidation must take place by breaking C-C bond. These oxidations require severe conditions and result in mixture of products.

(d) **Limitations of chromium reagents**: Chromium reagents are expensive and result in the formation of environmentally hazardous oxidation byproducts so other reagents are also recommended. (i) $KMnO_4$ and HNO_3 can be used in place of chromium reagents. Since they are strong enough so the reaction conditions have to be controlled, otherwise it would lead to the cleavage of C-C bond. (ii) The Swern oxidation uses DMSO and oxalyl chloride at low temperature, followed by a hindered base. This is an alternative to $KMNO_4$ and HNO_3 reagents. This oxidises 1° alcohols to aldehyde and 2° alcohols to ketones.



Cyclopentanol Cyclopentanone



Hexanol Hexanal

Breath Analyser Test. The oxidation of alcohols to carboxylic acids have been recently used as a breath analyzer test for detecting the level of ethanol in the breath (and therefore blood) of suspected alcohol intoxicated persons, especially drivers. The following reaction is involved,

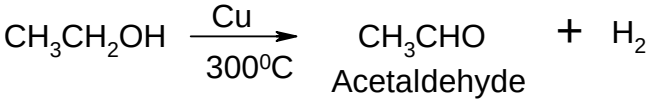
$$2\,K_2Cr_2O_7 + 8\,H_2SO_4 + 3\,CH_3CH_2OH \longrightarrow 2\,Cr_2(SO_4)_3 + 2\,K_2SO_4 + 3\,CH_3COOH + 11\,H_2O$$

Orange Green

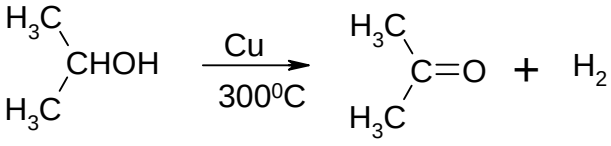
In the simplest version of this test, the culprit is asked to blow into a tube containing $K_2Cr_2O_7$ and H_2SO_4 supported on powdered silica gel for a duration of 10-20 seconds. Any alcohol present in the breath is oxidized to acetic acid, which results in change of colour from orange to green in the tube. But, if the test is positive, it is taken as justification by law or enforcement officers to administer a more accurate blood or urine screening. The test works because of the diffusion of blood alcohol through the lungs into the breath. If the green develops beyond the half way mark, a blood alcohol concentration greater than 0.08% is indicated, which is considered as a criminal offense in many countries.

(ii) **Action of reduced copper**. Primary, secondary and tertiary alcohols give different products when their vapours are passed over reduced copper at 300°C. Two atoms of hydrogen are eliminated producing a carbon-oxygen double bond. The process is known as catalytic dehydrogenation.

(a) A primary alcohol is dehydrogenated to an aldehyde

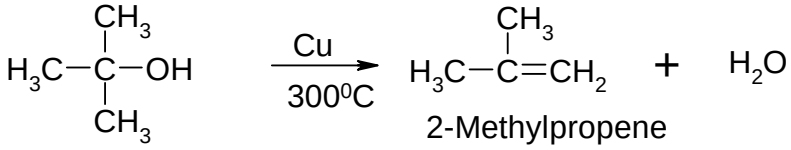


(b) A secondary alcohol is dehydrogenated to a ketone



iso-Propyl alcohol Acetone

(c) A tertiary alcohol is dehydrogenated to an olefin



tert-Butyl alcohol 2-Methylpropene

Distinction between Primary, Secondary and Tertiary Alcohols

The three classes of alcohols may be distinguished from one another by the following methods:

(i) **Oxidation test**. The mode of oxidation of three types of alcohols is characteristic of each type. Thus, the identification of the oxidation products of a given alcohol indicates whether it was primary, secondary or tertiary.

Primary alcohol	Secondary alcohol	Tertiary alcohol
RCH_2OH aq. $KMNO_4$ ↓ Oxidation RCHO Aldehyde ↓ Oxidation RCOOH	R_2CHOH ↓ Oxidation R_2CO Ketone ↓ Strong Oxidation $RCOOH + CO_2 + H_2O$	R_3COH ↓ Drastic Oxidation RCOOH or R_2CO
Acid containing same number of carbon atoms as the original alcohol.	Acid containing less number of carbon atoms than the original alcohol	Acid or ketone, each containing less carbon atoms than the original alcohol.

(iii) **Victor Meyer's method**. The test is carried out as follows:

(a) The alcohol is first treated with phosphorusiodide (or $P+I_2$) and converted into the corresponding iodide.

(b) The alkyl iodide is then treated with silver nitrite and converted into the corresponding nitrocompound.

(c) The nitroparaffin is finally treated with nitrous acid ($NaNO_2$+HCl) and then made alkaline. Primary alcohol gives red colour, secondary alcohol gives blue colour while the tertiary alcohol gives no colour.

Primary alcohol	Secondary alcohol	Tertiary alcohol

RCH_2OH ↓ HI $R-CH_2I$ ↓ $AgNO_2$ $R-CH_2NO_2$ ↓ HNO_2 $R-C(=NOH)-NO_2$ Nitrolic acid	R_2CHOH ↓ HI R_2CHI ↓ $AgNO_2$ R_2CHNO_2 ↓ HNO_2 $R_2C(NO)-NO_2$ Pseudonitrole	R_3COH ↓ HI R_3CI ↓ $AgNO_2$ R_3CNO_2 ↓ HONO No reaction
Gives red colour with KOH.	Gives blue colour with KOH.	No colour with KOH.

(iii) **Rate of esterification**. Alcohols form esters with inorganic acids and the rate of esterification is in the following order:

Tertiary > Secondary > Primary

With organic acids the rate of esterification is reversed.

The difference in the rates of esterification gives us a clue about the nature of alcohol.

(iv) **Lucas Test**. For this purpose, the unknown alcohol is treated with concentrated hydrochloric acid containing anhydrous zinc chloride (1:1) and the time of reaction is noted. The completion of the reaction is indicated by the separation of insoluble alkyl halide. Normally tertiary alcohols react immediately, secondary alcohols react within few minutes and the primary alcohols react slowly only on heating. Thus if the turbidity appears immediately, it is tertiary alcohol. If the turbidity appears in few minutes, it is secondary alcohol. If the turbidity appears on heating, it is primary alcohol.

$$RCH_2OH \xrightarrow[ZnCl_2]{\text{Conc. HCl}} RCH_2Cl + H_2O$$

$$R_2CHOH \xrightarrow[ZnCl_2]{\text{Conc. HCl}} R_2CHCl + H_2O$$

$$R_3COH \xrightarrow[ZnCl_2]{\text{Conc. HCl}} R_3CCl + H_2O$$

Individual Alcohols

Methyl Alcohol, Methanol (Carbinol), Ch_3oh

Occurrence. It occurs in nature in the form of methyl esters as

(i) Methyl salicylate in oil of winter green.

(ii) Methyl benzoate in oil of clove.

(iii) Methyl anthranilate in oil of jasmine.

Manufacture. Methyl alcohol is manufactured by the following methods:

(i) **From wood**. Methanol was originally produced by the destructive distillation of wood chips in the absence of air. This source led to the name **wood alcohol**.

The following products are obtained in destructive distillation of wood:

(a) **Wood gas**. It is a mixture of CO, H_2, CH_4, etc. and is used as a fuel for heating iron chambers.

(b) **Pyroligneous acid**. (Pyro = heat, ligneous = of wood). It is a brown aqueous distillate and is collected as the upper layer in the settling tank. It is composed of approximately:

Acetic acid	10%
Methyl alcohol	3%
Acetone	0.5%

(c) **Wood tar**. It is a thick black heavy liquid consisting mainly alkanes and phenols and is collected at the bottom of the settling tank.

It is used for the preservation of wood.

(d) **Wood charcoal**. It is left as a residue in the iron retorts and is used as a domestic fuel.

Recovery of methyl alcohol from pyroligneous acid.

Pyroligneous acid is treated for the recovery of methyl alcohol as under:

(a) **Removal of acetic acid**. Pyroligneous acid is separated from wood tar and treated with lime when acetic acid is retained as calcium acetate and the reaction mixture is distilled. Acetone and methyl alcohol distill over leaving calcium acetate in the still. Calcium acetate so obtained is distilled with concentrated H_2SO_4 when crude acetic acid distills over.

$$3\,CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + 2\,H_2O$$

Acetic acid — Calcium acetate

$$(CH_3COO)_2Ca + H_2SO_4 \longrightarrow CaSO_4 + 2\,CH_3COOH$$

Acetic acid

(b) **Removal of acetone**. The distillate from step (a) consists of methyl alcohol and acetone and is dried over lime and then subjected to fractional distillation. Acetone (b.p. 56°) distills over first and methyl alcohol (b.p. 64°) is obtained later and is collected. Crude methyl alcohol thus obtained is treated with anhydrous $CaCl_2$ when a solid crystalline compound of the composition, $CaCl_2.4CH_3OH$, is formed leaving behind acetone. The solid compound is separated and decomposed by warming with water to reproduce methyl alcohol. This is then distilled over quick lime to remove any moisture.

(ii) **From water Gas** (Patart process). This process has replaced the old process from wood and the product obtained is pure.

Water gas (a mixture of CO and H_2) obtained by passing steam over red hot coke is mixed with half of its volume of hydrogen. It is then subjected to a pressure of 200 atmospheres and passed over a catalyst (a mixture of oxides of Zn, Cr and Cu) at 350-400°C when methyl alcohol is obtained.

$$H_2O + C \xrightarrow{\text{Red hot}} CO + H_2$$

Steam — coke — Water gas

$$CO + H_2 + H_2 \xrightarrow[\text{Catalyst}]{350\text{-}400^0C} CH_3OH$$

(Water gas) — Methyl alcohol

(iii) **From methane**. Methane obtained from natural gas is mixed with oxygen in the ratio 9:1. The mixture is then passed through a copper tube at 200°C under a pressure of 100 atmospheres when methyl alcohol is obtained.

$$CH_4 + 1/2\ O_2 \xrightarrow[100\ atm.]{200^0C} CH_3OH$$

Methane — Methyl alcohol

Physical Properties.

(i) Methyl alcohol is colourless inflammable liquid, b.p. 64°C.
(ii) It has a sharp wine-like smell and has a burning taste.
(iii) It is miscible with water in all proportions and is lighter than water.
(iv) It is poisonous and if taken internally causes blindness and even death.
(v) It burns with a faintly luminous flame.

Chemical Properties. Chemically it gives all the general reactions of primary alcohols. It combines with $CaCl_2$ to form $CaCl_2.4CH_3OH$ and hence cannot be dried on anhydrous $CaCl_2$.

Uses. Methyl alcohol is used:
(i) as a solvent for fats, oils and varnishes.
(ii) as an antifreeze in engine radiators.
(iii) as a petrol substitute.
(iv) For denaturing ethyl alcohol.
(v) For the manufacture of formaldehyde.

Toxic effects of Methanol. Chronic exposure to methanol, either orally or by inhalation, causes headache, insomnia, gastrointestinal problems and blindness in humans due to edema of the retina and atrophy of the optic nerve head. It also causes hepatic and brain alterations in the animals.

Ethyl Alcohol, Ethanol
(Methyl carbinol), C_2H_5OH

Occurrence. It is commonly named as alcohol. It occurs naturally in the form of its esters with organic acids in many essential oils and fruits.

Since it is commercially obtained from starchy grains so it is also known as Grain alcohol.

Manufacture. Ethylene (from cracked petroleum) is absorbed in concentrated sulphuric acid (98%) at 75-80°C under pressure. Ethyl hydrogen sulphate is obtained, which is then diluted with water and heated. Ethyl alcohol is obtained due to hydrolysis which is purified by fractional distillation.

$$\underset{\text{Ethylene}}{C_2H_4} + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogensulphate}}{C_2H_5HSO_4}$$

$$C_2H_5HSO_4 + HOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4$$

(ii) **From acetylene**. Acetylene is first converted into acetaldehyde by water in the presence of sulphuric acid and mercury sulphate (Catalyst).

$$\underset{\text{Acetylene}}{HC\equiv CH} + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

Acetaldehyde is then catalytically reduced to ethyl alcohol.

$$CH_3CHO + H_2 \xrightarrow[140^0C]{Ni} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

(iii) **By alcoholic fermentation**. It is the conversion of certain sugars into alcohol by enzymes present in yeast. Alcohol is manufactured by this process from the following two materials.

(a) **Molasses**. It is the mother liquor left after the extraction of canesugar from cane juice. It is a dark coloured syrupy liquid and contains about 50 percent of fermentable sugar, mostly sucrose, glucose and fructose. Molasses form a very cheap and valuable source of industrial alcohol.

(b) **Starch**. It can be obtained from wheat, potatoes, barley, maize etc.

Manufacture from Molasses. The production of alcohol from molasses involves the following steps:

(i) **Dilution**. Molasses are diluted with water so that the concentration of sugar is brought down to 8-10 percent.

(ii) **Addition of sulphuric acid and ammonium salts**. The diluted molasses are acidified with dilute sulphuric acid which favours the growth of yeast cells but hinders the growth of undesirable bacteria. Suitable quantitites of ammonium sulphate and ammonium phosphate are added which act as food for the yeast.

(iii) **Fermentation**. Yeast is now added to the molasses solution and temperature is kept at 30°C for 2-3 days. During this fermentation process, air is bubbled through the liquor to keep the yeast cells alive and active. When the fermentation is over, the concentration of alcohol is 15-18 percent. The fermented liquor is technically called wash. The reaction takes place are as follows:

(a) $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(Yeast)}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

(b) $\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{(Yeast)}]{\text{Zymase}} 2\,\underset{\text{Alcohol}}{C_2H_5OH} + 2CO_2\uparrow$

Carbon dioxide evolved during the fermentation process is collected as a by-product.

(iv) **Distillation**. The wash is next subjected to distillation in a coffy still provided with fractionating columns.

Each fractionating column is fitted with shelves having baffle plates and tubes. Wash is allowed to fall near the top. While the wash travels down through the tubes, steam and alcohol vapours pass up through the baffle plates. At each shelf, alcohol vaporizes from the wash, while the steam condenses. The vapour of alcohol from the top of the column are led to the condenser, where they condense. The distillate is called raw spirit and contains 95 percent alcohol. The mass which remains behind the still is called spent wash and is used as cattle food.

(v) **Rectification**. The raw spirit is further refined by fractional distillation. The following fractions are collected.

(a) First running. It mainly consists of acetaldehyde (b.p. 21°C).

(b) Middle running or rectified spirit. It consists of 95% alcohol (b.p. 78.1°C).

(c) Last running or fused oil. It is a mixture of alcohols mostly containing amyl alcohol. The fraction is obtained between the range 125-140°C.

These days, distillation and rectification are done in a single operation.

Manufacture from Starch. The process employing potatoes as the raw material involves the following steps.

(i) **Liberation of Starch**. Potatoes are sliced and crushed. The crushed mass is then heated with steam under pressure at 140-150°C. The starch cells are broken and brought into a milky solution, known as Mash. The process is known as Mashing.

(ii) **Malting**. The enzyme diastase required to hydrolyse starch into maltose is obtained from germinated barley. For this purpose, barley is moistened with water and spread in dark rooms in layers of 5 inches thickness. It is allowed to germinate at 15°C for 2-4 days. The germination is stopped by heating the barley to 60°C. The germinated product is technically known as Malt.

(iii) **Saccharification**. To the mash obtained in step (i), malt obtained in step (ii) is added and temperature is kept at 50°C. Within half an hour, diastase present in the malt converts the starch into maltose. The resulting sweet is known as Wort.

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

Alternatively, starch may be directly converted into glucose on heating with dilute sulphuric acid. The excess of the acid is neutralized by lime.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \longrightarrow \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

(iv) **Fermentation**. To the solution of maltose (or glucose) obtained above, yeast is added and alcoholic fermentation allowed to proceed at about 30°C. the following reactions take place.

(a) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[(Yeast)]{Maltase} 2\,C_6H_{12}O_6 + C_6H_{12}O_6$
Maltose — Glucose — Fructose

(b) $C_6H_{12}O_6 \xrightarrow[(Yeast)]{Zymase} 2\,C_2H_5OH + 2\,CO_2\uparrow$
Ethanol

Thus maltase converts maltose into glucose while zymase converts glucose into alcohol. It is evident that if starch is hydrolysed by dilute sulphuric acid, glucose present will be directly converted into alcohol by zymase.

The fermented liquor or Wash obtained above contains about 6-10% of alcohol.

(v) **Distillation and Rectification**. The wash is then distilled and rectified in the unit as described above. The product is 95% alcohol known as rectified spirit.

By products of Alcohol Industry. The important by-product of alcohol industry are:

(i) Carbon dioxide. It is stored under pressure in iron cylinders and sold for use in aerated waters. Solid CO_2 is sold as dry ice for refrigeration purposes.

(ii) Acetaldehyde. During rectification, it is recovered from the first run.

(iii) Fused oil. This is obtained as the last run between 125-140°C. It is a mixture of alcohols and is used in the manufacture of amyl acetate, a valuable solvent.

(iv) Spent wash. It is a solid mass left after the distillation of wash and is used as cattle food.

(v) Argol. It is potassium hydrogen tartarate and is obtained as a brown residue during the fermentation of grape juice. It is used for the manufacture of tartaric acid.

Absolute Alcohol. Rectified spirit contains about 95 percent of alcohol. It is not possible to remove the remaining water completely by fractional distillation as a mixture of 95.6 percent alcohol with water forms a constant boiling mixture at 78.1°C, a temperature 0.2°C lower than the boiling point of pure alcohol (78.3°C).

Absolute alcohol (100 percent) or pure alcohol is obtained by repeatedly distilling rectified spirit over fresh lime. The last traces of moisture, about 0.3%, are removed by redistilling it over a calculated quantity of magnesium or calcium metal.

For commercial purposes, absolute alcohol is obtained by distilling rectified spirit with a small amount of benzene (Azeotropic distillation). A ternary mixture of water (7.5%), alcohol (18.5%) and benzene (74%) distills over at 64.9°C till all the water is removed. Then the temperature rises and the remaining benzene distills over as the binary mixture with alcohol at 68.3°C. Finally absolute alcohol distills over.

Power Alcohol. Industrial alcohol (Rectified spirit) mixed with petrol and benzene is used for generation of power. Alcohol thus obtained is known as power alcohol. In India, there is good scope of power alcohol on account of the shortage of petrol.

Denatured Alcohol or Methylated Spirit. Rectified spirit is mixed with poisonous substances like methyl alcohol, acetone or pyridine to make it unfit for drinking purposes. The product known as methylated spirit or denatured spirit is then sold in the market for industrial purposes like preparation of varnishes. Sometimes a colouring material is also added to the rectified spirit to give it a different appearance.

Physical Properties.

(i) Ethyl alcohol is a colourless liquid with a pleasant smell.

(ii) It boils at 78.3°C and has a specific gravity 0.789 at 20°C.

(iii) It is miscible with water in all proportions.

(iv) It is an excellent solvent for fats, resins and other organic substances. It also dissolves inorganic substances like NaOH, KOH and sulphur.

(v) It has a specific intoxicating effect on the system.

Chemical Properties. Chemically, ethyl alcohol gives all the general reactions of primary alcohols.

Uses. Ethyl alcohol is used:

(i) as a solvent for gums, varnishes, drugs, tinctures, oils perfumes, inks etc.
(ii) as a fuel for lamps and stoves.
(iii) in the manufacture of chloroform, iodoform, ether, acetic acid, ethylene, etc.
(iv) as a preservative in biological specimens.
(v) as a liquid for spirit levels and thermometers.
(vi) as an antifreeze for automobile radiators.
(vii) in sterilizing spirit and as power alcohol.

For the sake of convenience in transportation, it is converted into solid alcohol fuel by dispersing alcohol in a jelly of calcium acetate and a little stearic acid.

Propyl Alcohol C_3H_7OH. There are two possible propyl alcohols.

(i) *n*-Propyl alcohol or Propan-1-ol. $CH_3CH_2CH_2OH$.
(ii) *iso*-Propyl alcohol or Propan-2-ol. $CH_3CHOHCH_3$.

1. Propan-1-ol

1. Preparation. It is present in fusel oil and can be obtained from it by fractional distillation.

2. It can also be prepared by the hydrogenation of carbon monoxide.

$$3\,CO + 6\,H_2 \longrightarrow CH_3CH_2CH_2OH + 2\,H_2O$$

3. A more recent method is by the catalytic reaction of propargyl alcohol.

$$HC{\equiv}C{-}CH_2OH + 2\,H_2 \longrightarrow CH_3CH_2CH_2OH$$

Properties.

It is a colourless liquid b.p. 97.4°C, miscible with water ether and ethanol. On oxidation it gives propionic acid. It gives all the general reactions of alcohols. It is used as a solvent in organic synthesis.

2. *iso*-Propyl alcohol Propan-2-ol $CH_3CHOHCH_3$

Preparation

Propan-2-ol is prepared by the catalytic hydration of propylene. It is commonly used as rubbing alcohol because has less drying effect on the skin.

$$H_3C{-}CH{=}CH_2 + H_2O \xrightarrow[\text{Catalyst}]{\text{100-300 atm., } 300^0C} H_3C{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

It is a colourless liquid. b.p. 82°C. Soluble in water, alcohol and ether.

It is used as solvent and in the preparation of esters, and acetone. Under the name of Petrobol it is used as solvent in cosmetics and hair tonics.

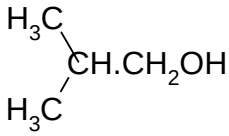
Both these alcohols are poisonous. They are more intoxicating than ethanol.

Butyl alcohol C_4H_9OH.

The following are the possible isomeric forms. All of these are known.

(1) *n*-Butyl alcohol $CH_3CH_2CH_2CH_2OH$

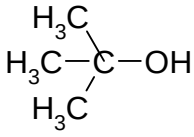
Butan-1-ol

(2) *iso*-Butyl alcohol 

2-methylpropan-1-ol

(3) *sec*-Butyl alcohol $CH_3CHOHCH_2CH_3$

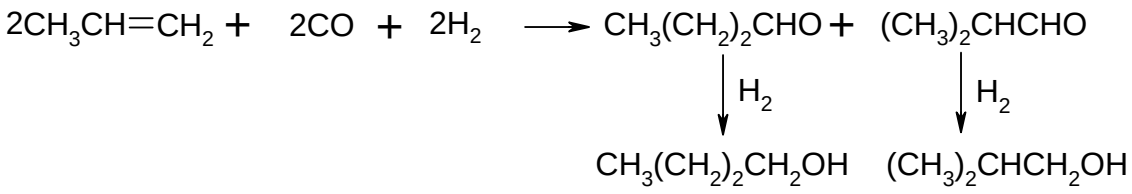
Butanol-2-ol

(4) *tert*-Butyl alcohol 

1,1-Dimethylethanol

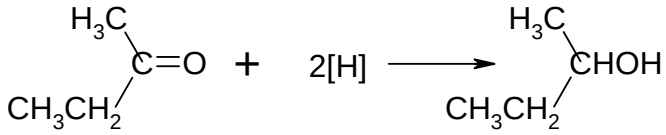
***n*-Butyl alcohol & *iso*-Butyl alcohol:**

n-Butanol and *iso*-butyl alcohol are industrially prepared from propene by the Oxoprocess. A mixture of propene, CO & H_2, under pressure at elevated temperature and in the presence of a catalyst forms isomeric aldehyde which are first separated and then reduced to give the corresponding alcohol.

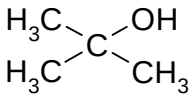


***Secondary* Butyl alcohol**. $CH_3CH_2CHOHCH_3$

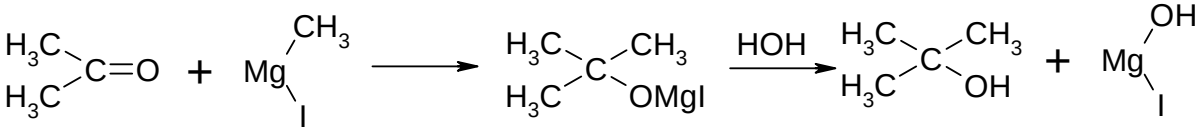
It is prepared by the reduction of methyl ethyl ketone.



***Tertiary* butyl alcohol**



It is prepared by the action of methyl magnesium iodide on acetone followed by hydrolysis.



It is a solid at ordinary temperature. m.p. 25°C and b.p. at 83°C.

It is mainly used as an alkylating agent in organic chemistry.

Conversion in alcohols.

(a) **Ascending series in alcohols**.

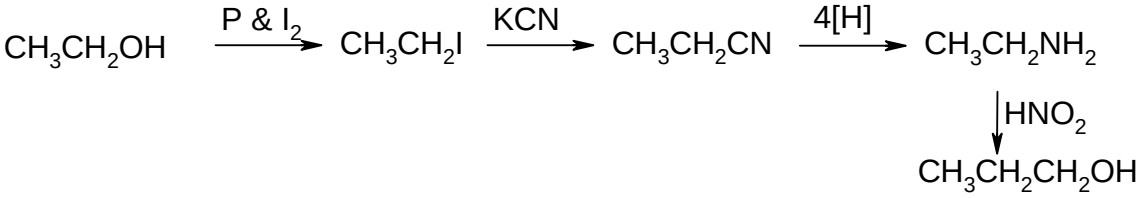
Following steps are followed to get a higher alcohol from a lower one.

(i) Convert –OH into –X by treatment with phosphorus halide.

(ii) Convert –X into –CN by treatment with KCN.

(iii) Reduce –CN to $-CH_2NH_2$ by treatment with sodium and ethanol.

(iv) Convert $-CH_2NH_2$ to $-CH_2OH$ with HNO_2



(b) **Descending series in alcohols**

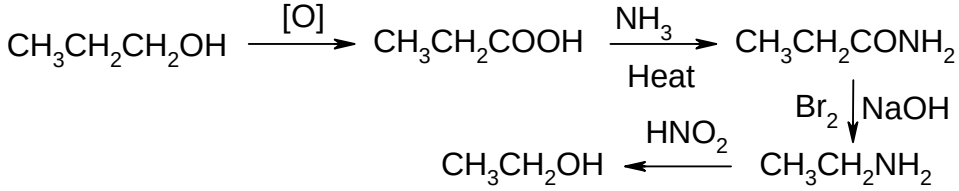
Following steps are followed to get lower alcohol from a higher one:

(i) Oxidise the $-CH_2OH$ to $-COOH$ by aqueous $KMnO_4$.

(ii) Convert the $-COOH$ to $CONH_2$ by heating the ammonium salt.

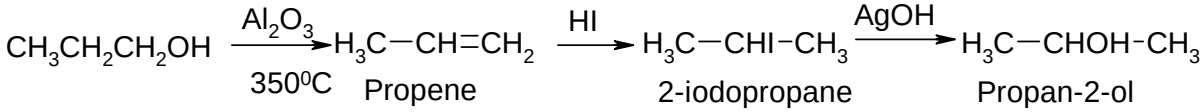
(iii) Convert the $-CONH_2$ to $-NH_2$ by Hoffmann Bromo-amide reaction (NaOH + Br_2)

(iv) Convert $-NH_2$ to $-OH$ by treatment with HNO_2.

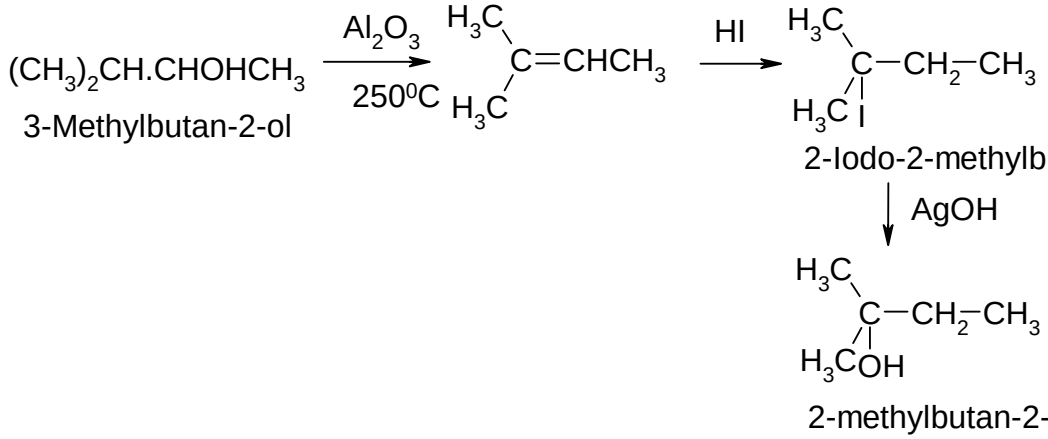


Conversion of a primary alcohol to a secondary or tertiary alcohol.

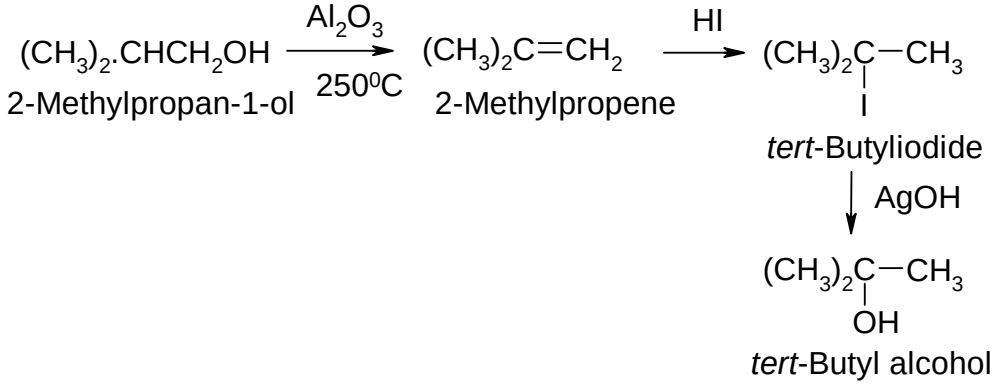
(i) Primary alcohol to secondary alcohol. A primary alcohol on dehydration with Al_2O_3 at 350°C yields an olefin which on treatment with HI yields an alkyl halide. This on hydrolysis with AgOH gives secondary alcohol.



(ii) Secondary alcohol into tertiary. It follows exactly the above scheme.



(iii) Primary into Tertiary Alcohol. It also follows exactly the same scheme.



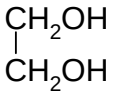
POLYHYDRIC ALOCHOLS

Dihydric and Trihydric alcohols.

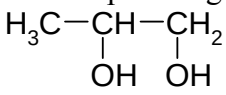
Dihydric alcohols (alkane diols) and trihydric alcohols (alkane triols) are derived by replacing two or three hydrogen atoms from different carbon atoms in alkanes. Thus the general formula of di- and tri-hydric alcohols are:

Alkanes	Dihydric alcohols	Trihydric alcohols
C_nH_{2n+2}	$C_nH_{2n}(OH)_2$	$C_nH_{2n-1}(OH)_3$

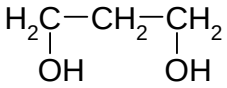
Dihydric alcohols are sweet in taste and therefore are also called *glycols*, an equivalent of Greek word meaning *sweet*. *Glycols* or diols are alcohols containing two hydroxyl groups. The glycols in which the two –OH groups are attached to adjacent carbon atoms are known as 1,2-*glycols*. Some important glycols are:



Ethylene glycol
(Ethan-1,2-diol)

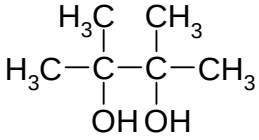


Propylene glycol
(Propan-1,2-diol)

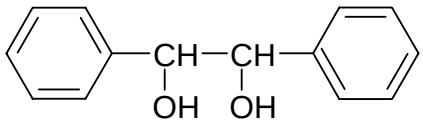


Trimethylene glycol
(Propan-1,3-diol)

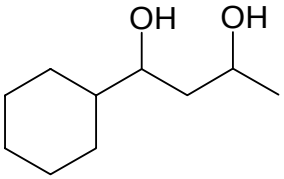
Glycols have both common names and I.U.P.A.C names



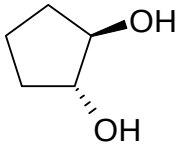
Pinacol
2,3-Dimethylbutan-2,3-diol



Hydrobenzoin
1,2-Diphenylethan-1,2-diol



1-Cyclohexylbutan-1,3-diol



trans Cyclopentan-1,2-diol

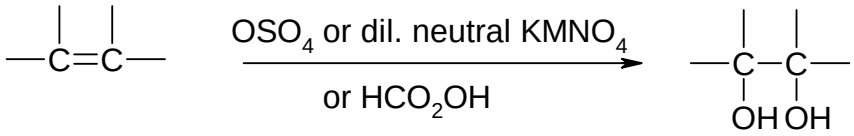
Preparation of Glycols.

Glycols are usually obtained by one of the following methods.

(1) **Hydroxylation of alkenes**. Glycols are often prepared by hydroxylation of carbon-carbon double bonds, either directly or *via* the epoxide.

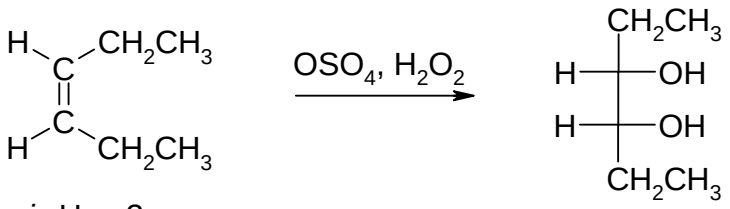
Direct hydroxylation of alkenes. Numerous oxidizing agents can cause hydroxylation, three of the most commonly used are OsO_4, cold, dilute neutral $KMnO_4$ and per acids (RCO_2OH), *e.g.*, peroxyformic acid (HCO_2OH)

Glycols, being dihydroxy alcohols, their formation amounts to addition of two hydroxyl groups to the double bond.



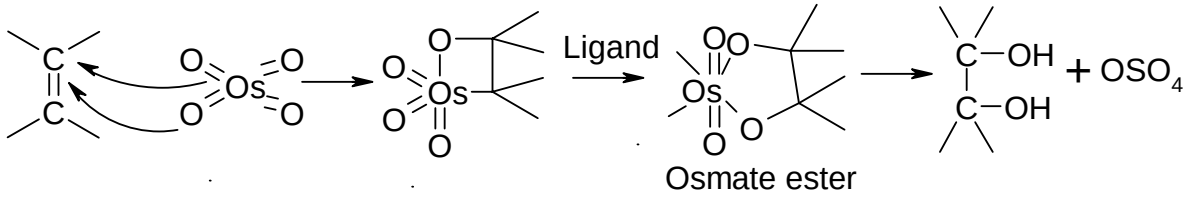
A Glycol

(a) **Hydroxylation of alkene with OsO_4**. OsO_4 reacts with alkene in a concerted step to form a cyclic osmate ester. Hydrogen peroxide hydrolyses the osmate ester and reoxidises osmium to osmium tetroxide. This continues to hydroxylate more molecules of the alkene. Reaction is accelerated by tertiary bases, especially pyridine.



cis Hex-3-ene *meso* Hexan-3,4-diol

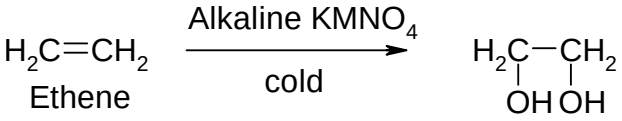
Mechanism:



Osmate ester

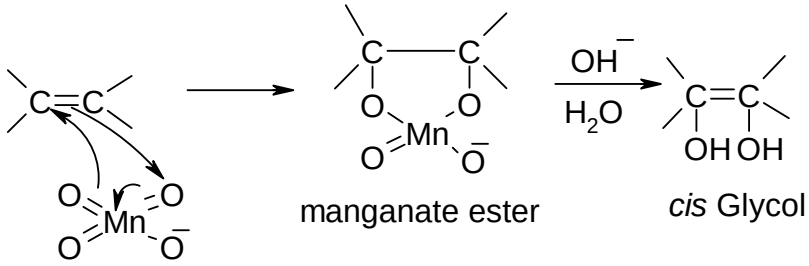
Because the two C-O bonds are formed simultaneously with the same osmate ester, the O atoms add to the same face of the alkene resulting in *syn* addition.

(b) **Direct hydroxylation of alkenes with neutral $KMnO_4$**. OsO_4 is highly toxic, expensive and volatile and therefore a cold dilute solution of $KMNO_4$ can be used in its place. Hydroxylation with permanganate is carried out by stirring together the alkene and the dilute aqueous permanganate solution at room temperature, when the alkene is oxidized to glycol.



Ethene Ethan-1,2-diol (*Ethylene glycol*)

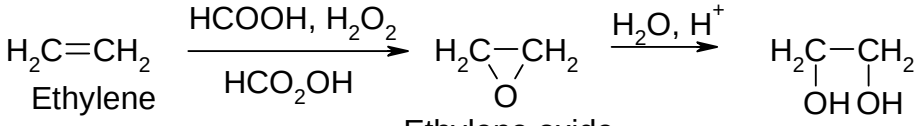
The mechanism of hydroxylation with permanganate is also believed to proceed *via* a cyclic intermediate which accounts for *cis*-hydroxylation.



manganate ester *cis* Glycol

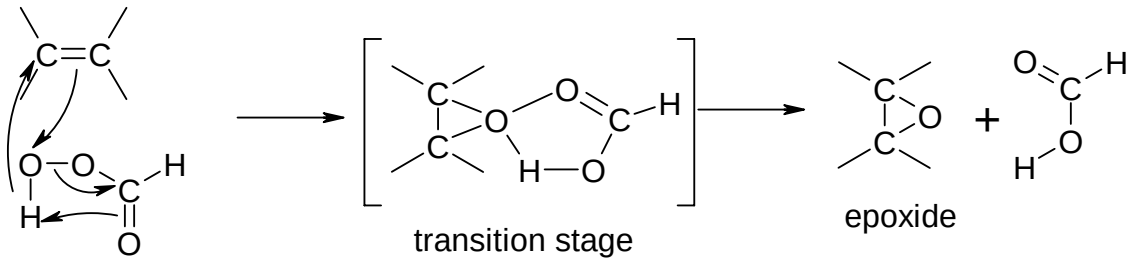
Higher temperature and higher concentration of acid or alkali are avoided, since under these vigorous conditions, cleavage of the double bond occurs.

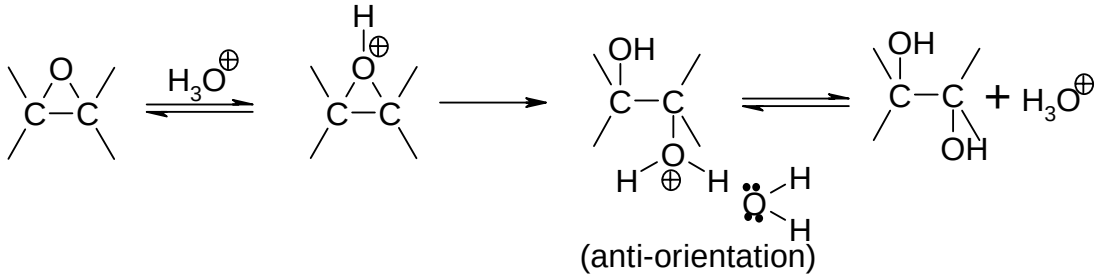
(c) **Hydroxylation of alkenes *via* epoxide with per acids**. Hydroxylation with peroxyformic acid is carried out by allowing alkene to stand with a mixture of hydrogen peroxide and formic acid, for few hours, and then heating the product with water to hydrolyse the intermediate epoxide.



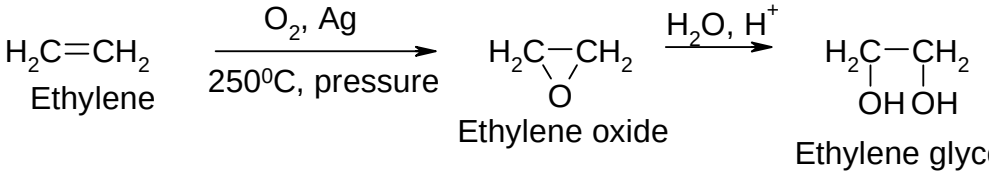
Ethylene Ethylene oxide Ethylene glycol

Alkene is first converted to an epoxide by the peroxy acid and then epoxide is opened by water. This reaction provides anti-hydroxylation. Epoxide is formed from one face of the alkene and then attacked from the rear face to give the anti-hydroxylated product.

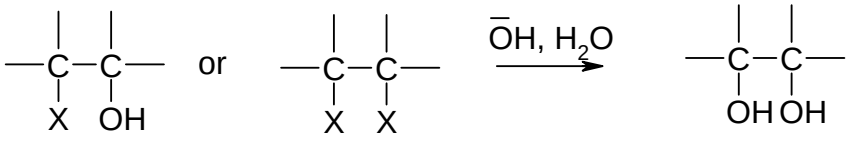




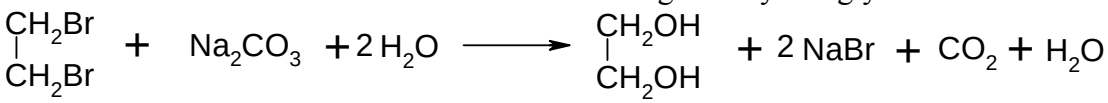
(d) **Hydroxylation *via* epoxide by catalytic oxidation (with silver catalyst)**. When ethylene and oxygen are passed over heated silver oxide, ethylene oxide is formed which on boiling with dilute mineral acid gets hydrolysed to ethylene glycol.



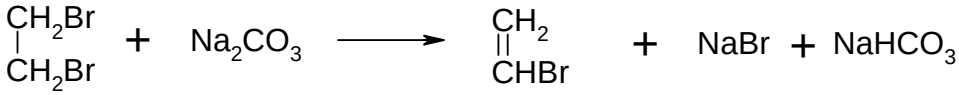
(2) **Hydrolysis of halides**. Halohydrins or dihalides are hydrolysed to diols.



(a) **Hydrolysis of dihalogen derivatives of alkanes**. Ethylene dichloride or dibromide is heated with sodium carbonate solution to give ethylene glycol.

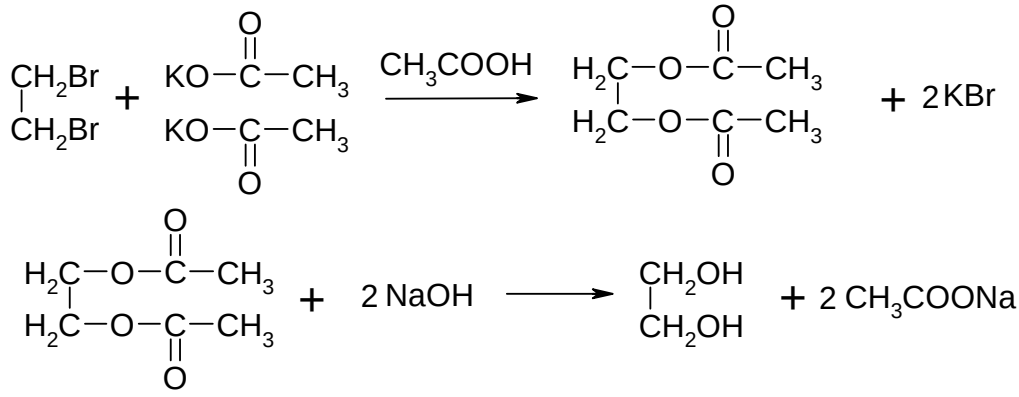


The yield of glycol is only 50% due to the formation of some vinyl bromide in this reaction.

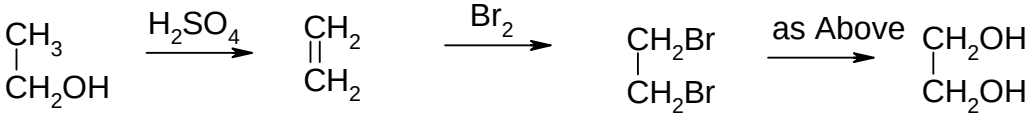


The use of sodium hydroxide also results in the formation of vinyl bromide as a by-product. Weak bases are used in these hydrolysis reactions to avoid the dihalides to undergo dehydrohalogenation.

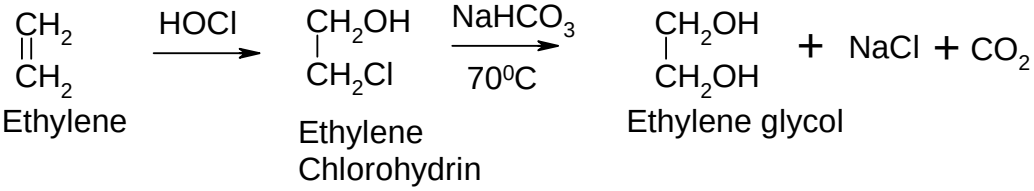
The best result is obtained by using potassium acetate and glacial acetic acid and then hydrolyzing the diacetate with HCl in methyl alcohol solution or sodium hydroxide:



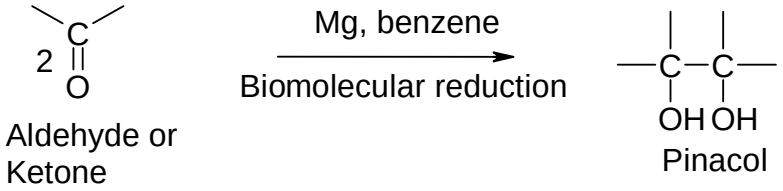
The yield of glycol in this case is about 84%. This method can also be used to convert a monohydric alcohol into a dihydric alcohol.



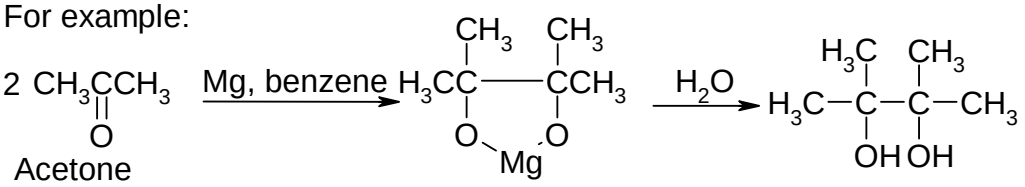
(b) **Hydrolysis of ethylene chlorohydrin**. Ethyl alcohol obtained by cracking petroleum is passed through hypochlorous acid at 0°C. The chlorohydrin thus formed is hydrolysed with hot aqueous $NaHCO_3$ solution at 70°C or by heating with Na_2CO_3 at 100°C or by boiling with lime.

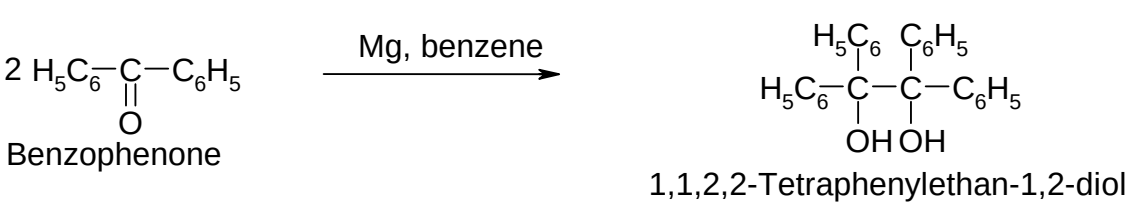


(3) **Bimolecular reduction of carbonyl compounds**. **Formation of pinacols**. Symmetrical glycols can often be obtained by bimolecular reduction of aldehydes and ketones with magnesium in benzene. This type of reduction brings about formation of a bond between two carbonyl carbons. Such glycols are known as Pinacols.



For example:





obtained from the boiling point of ethylene glycol. Its boiling point, 197°C, (mol. wt. = 62) is much higher than the boiling point, 97°C, of propan-1-ol (mol. wt. = 60).

The lower glycols are miscible with water. Those containing as many as seven carbon atoms show appreciable solubility in water. Ethylene glycol is hygroscopic and miscible with water and alcohol in all proportions but insoluble in ether.

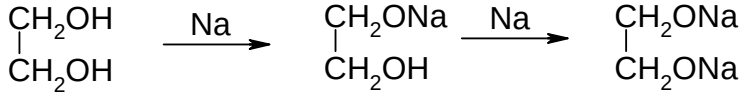
Ethylene glycol owes its use as antifreeze (under the name Prestone) to its high boiling point, low freezing point and higher solubility in water.

Chemical Properties

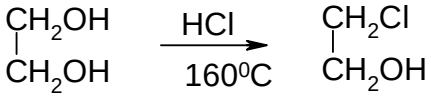
Glycols undergo the same reactions as monohydroxy alcohols like ester formation, halide formation, etc. the glycols undergo oxidation with cleavage of carbon and carbon bond which alcohols do not undergo.

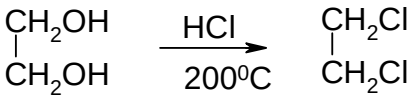
Ethylene glycol has two primary alcohol groups in its molecule and, therefore, it shows properties of a primary alcohol in a two fold degree.

1. **Reaction with sodium metal**. With metallic solution it reacts forming first monosodium and then disodium derivatives.

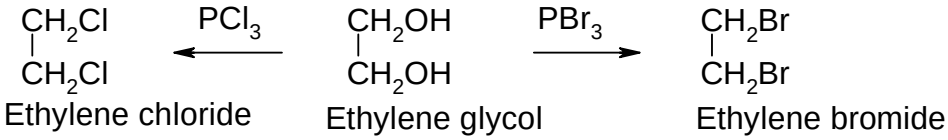


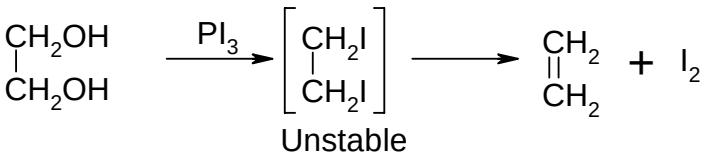
2. **Reaction with HCl**. With HCl it gives ethylene chlorohydrin at 160°C and ethylene chloride at 200°C.



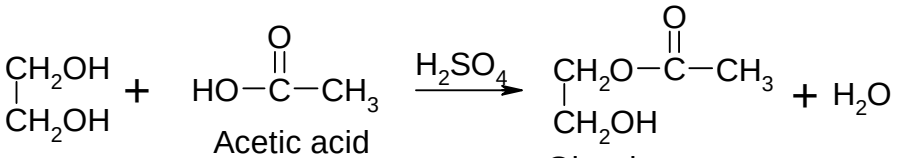


3. **Reaction with PX_3**. With PBr_3, ethylene dibromide is formed while with PI_3, ethylene diiodide is first formed which, being unstable, decomposes to give ethylene and iodine.



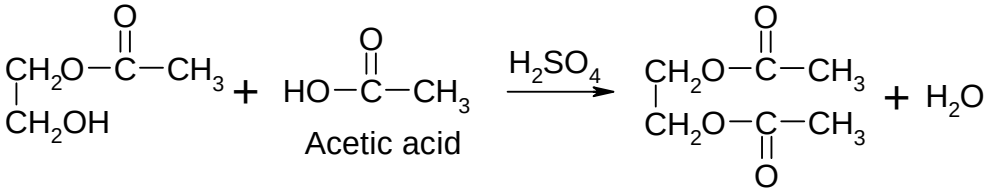


4. **Reaction with organic acids**. Glycol reacts with acids to form mono and diesters. With acetic acid, for example, glycol monoacetate is first formed and then the diacetate.



Acetic acid

Glycol monoacetate

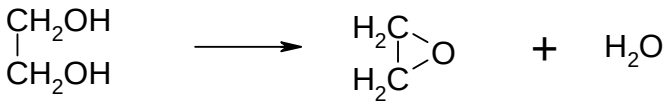


Acetic acid

Glycol diacetate

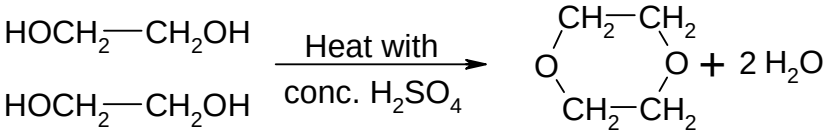
5. **Dehydration**. Glycol gives different products under different experimental conditions.

(i) **Action of heat**. When glycol is heated alone at 500°C, it forms ethylene oxide, *e.g.*,

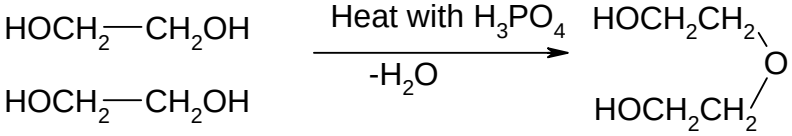


Ethylene oxide

(ii) **With Conc. H_2SO_4**. It gives dioxane (an industrial solvent) when distilled with small amount of sulphuric acid.

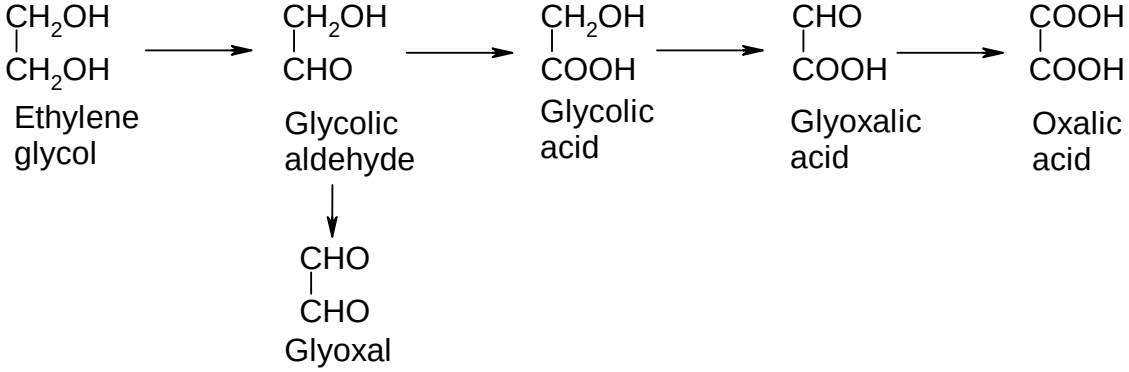


(iii) **With phosphoric acid**. It is quite interesting that a dehydrating agent like phosphoric acid gives polyethylene glycols. These are condensation polymers having both alcohol and ether as functional groups. There are excellent solvents for gums, resins, etc.



Di-(-hydroxymethyl)ether

6. **Oxidation**. It is possible to oxidize each of the CH_2OH groups first to the CHO and then to the COOH group. Thus, the theoretical oxidation sequence of ethylene glycol would be:



Ethylene glycol

Glycolic aldehyde

Glycolic acid

Glyoxalic acid

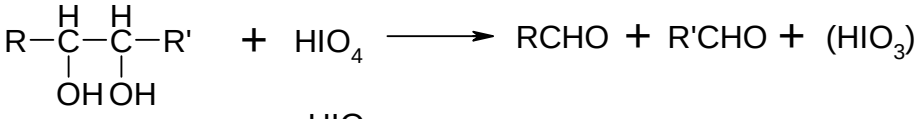
Oxalic acid

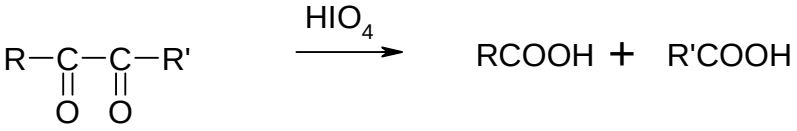
Glyoxal

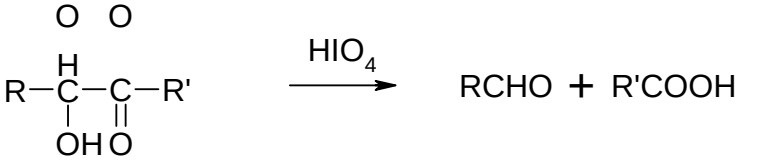
By proper selection of oxidizing agents and careful regulation of temperature, some of the products have been prepared in adequate quantities. Thus, oxidation of glycol with hydrogen peroxide in the presence of a ferrous salt (catalyst) produces glycolic aldehyde. The latter, when oxidized with bromine water, gives glycolic acid. Nitric acid, in cold, oxidizes

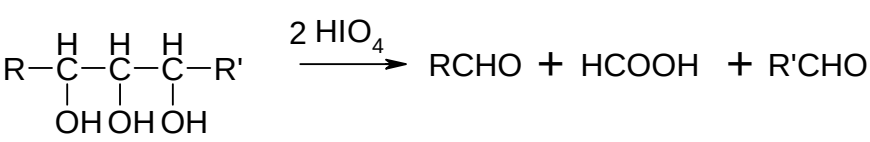
glycol to glycolic acid; at higher temperatures, oxalic acid is produced. With $KMnO_4$ or $K_2Cr_2O_7$ the bond breaks between the two hydroxylated carbon atoms to give carboxylic acid.

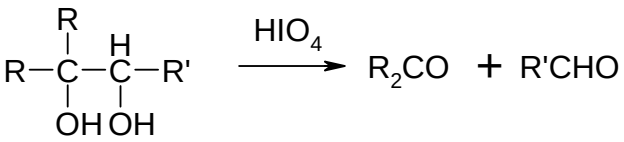
7. **Oxidation with periodic acid, HIO_4. (Periodic acid oxidation) (*Malaprade reaction*)**. Compounds containing two or more –OH or >C=O groups attached to adjacent carbon atoms on oxidation with periodic acid undergo cleavage of carbon bonds. For example:

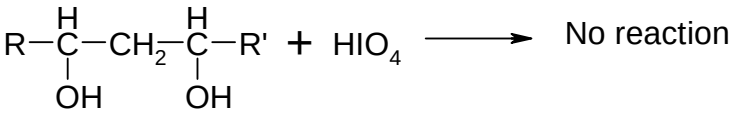
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

Oxidation by HIO_4 resulting in cleavage in carbon-carbon bond is helpful in determining the structure of 1,2-glycols. Oxidation by HIO_4 is qualitatively established by the formation of a white ppt. of $AgIO_3$ on adding silver nitrate solution to the reaction mixture. As this oxidation is almost quantitative, valuable information is obtained from the quantity of periodic acid used and from the nature and the amount of the products formed.

Let us study the oxidative cleavage of glycol with molecular formula $C_4H_8(OH)_2$. Its three isomers butan-1,2-diol, butan-1,3-diol or butan-2,3-diol can be distinguished as under:

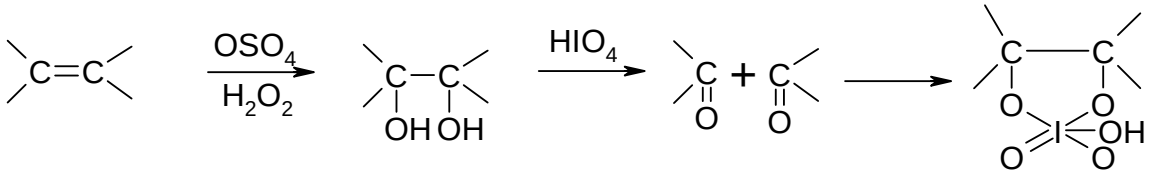
(i) $CH_3CH_2CHOHCH_2OH$ (Butan-1,2-diol) $\xrightarrow{HIO_4}$ HCHO (Formaldehyde) + CH_3CH_2CHO (Propionaldehyde)

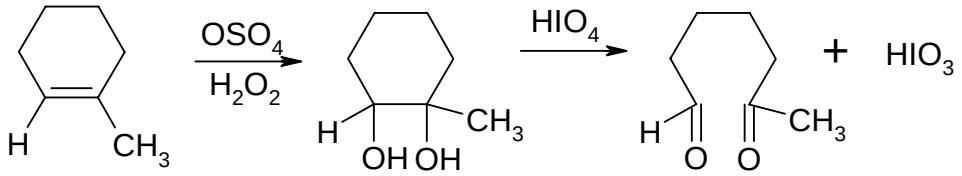
(ii) $CH_3CHOHCHOHCH_3$ (Butan-2,3-diol) $\xrightarrow{HIO_4}$ 2 CH_3CHO (Acetaldehyde)

(ii) $CH_3CHOHCH_2CH_2OH$ (Butan-1,3-diol) $\xrightarrow{HIO_4}$ No reaction

Thus their structure is elucidated from product analysis.

Mechanism: Periodic acid cleavage of a glycol probably involves a cyclic periodate intermediate.



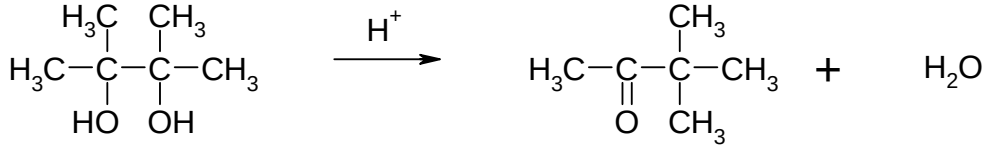


alkene *cis*-glycol

8. **Oxidation with Lead tetracetate, $Pb(OAc)_4$**

Oxidation of glycol with lead tetraacatate yields corresponding aldehydes as with periodic acid.

9. **Pinacol Rearrangement**. Pinacol (2,3-dimethylbutan-2,3-diol) on treatment with mineral acids gets dehydrated to form methyl *tert*-butyl ketone, known as pinacolone. The dehydration is accompanied by rearrangement of the carbon skeleton.

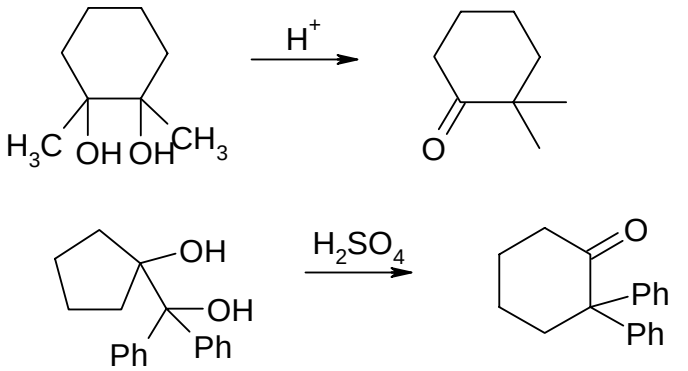


2,3-Dimethylbutan-2,3-diol

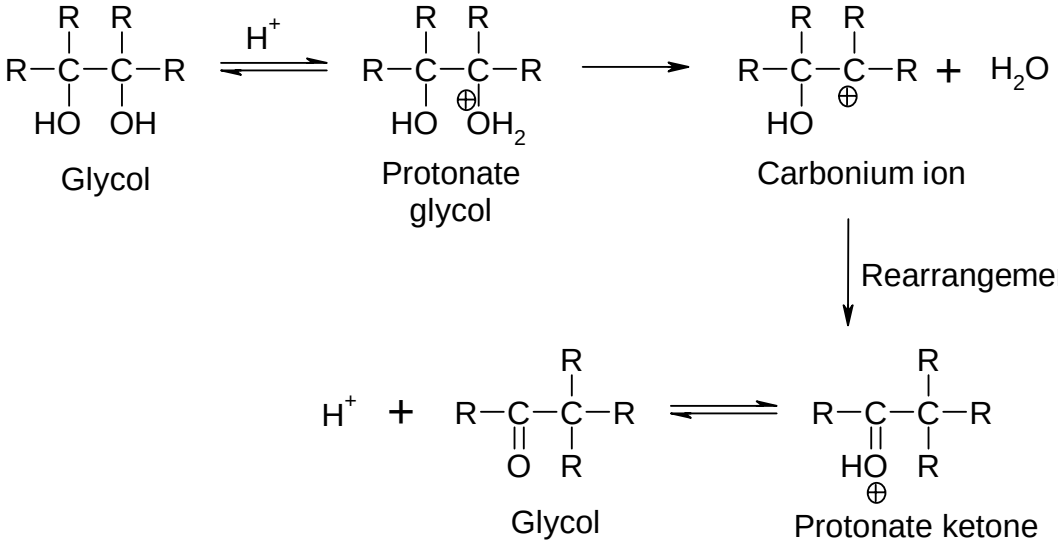
tert-Butyl methyl ketone
3,3-Dimethylbutan-2-one

Other glycols undergoes analogous reactions, which are named as pinacol-pinacolone rearrangements.

Some examples of pinacol-pinacolone reactions are :

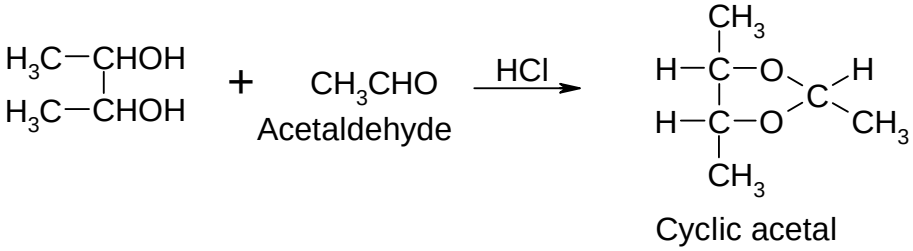


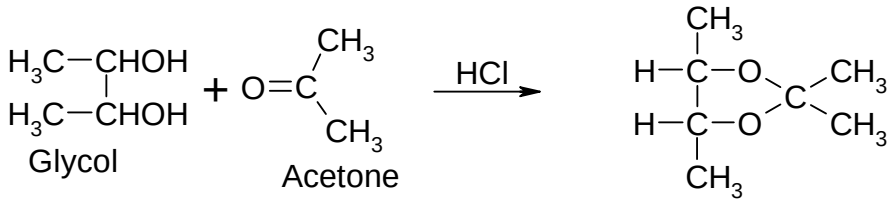
Mechanism. The glycol first gets protonated, loses water to form a carbonium ion and then the rearrangement of the carbonium ion takes place by 1,2-shift to yield the protonated ketone.



As in most 1,2-shifts to electron-deficient atoms, the migrating group is at no time completely free. It does not break away from the carbon it is leaving until it has attached itself to electron-deficient carbon. The mechanism is concerted.

9. **Formation of cyclic compounds**. An important class of cyclic acetals or ketals also called dioxanes is obtained when α-glycols react with aldehydes or ketones in presence of *p*-toluenesulphonic acid.





Glycerol (1,2,3-Propantriol)

General

Glycerol is commonly known as glycerine. It occurs in nature in oils and fats, which are mixtures of esters of glycerol (glycerides) with higher fatty acids and unsaturated acids.

Manufacture

Glycerol is obtained in large quantities as a by-product in the manufacture of soap.

Glycerol from petroleum by synthetic method. Large quantities of glycerol are now synthesised from propylene obtained from petroleum.

$$CH_3CH{=}CH_2 \xrightarrow[\text{at } 500^0C]{\text{Chlorination}} ClCH_2CH{=}CH_2 \xrightarrow[38^0C]{\text{Hypochlorous acid(HOCl)}}$$

Propylene — Allyl chloride

$$ClCH_2CHClCH_2OH \xrightarrow{NaOH} HOCH_2CHOHCH_2OH$$

1,2-Dichloro-3-hydroxypropane — Glycerol

Complete synthesis

The synthesis of glycerol is of great theoretical importance, because glycerol is present in plants and animals, and also because this synthesis constitutes a step in the synthesis of simple sugars. Starting with carbon and hydrogen, we may obtain acetylene and then acetaldehyde and acetic acid. Glycerol can be synthesised through the following series of reactions from acetic acid.

$$2\,CH_3COOH \xrightarrow[\triangle]{\text{Distil Ca salt}} CH_3COCH_3 \xrightarrow{\text{Reduce}} CH_3CHOHCH_3$$

Acetic acid — Acetone — *iso*-Propyl alcohol

$$CH_3CHOHCH_3 \xrightarrow{H_2SO_4} H_3C{-}CH{=}CH_2$$

Propene

$$H_3C{-}CH{=}CH_2 \xrightarrow[400\text{-}500^0C]{Cl_2} ClH_2CHCH{=}CH_2 \xrightarrow[12\text{ atm. }150^0C]{Na_2CO_3} HOH_2C{-}CH{=}CH_2$$

Allyl chloride — Allyl alcohol

$$HOH_2C{-}CH{=}CH_2 \xrightarrow{HOCl} HOCH_2.CHCl.CH_2OH \xrightarrow{\text{NaOH soln.}} HOH_2C{-}CHOH{-}CH_2OH$$

2-Chloropropan-1,3-diol — Glycerol

Physical properties

(i) Glycerol is a colourless syrupy liquid which, when pure, freezes to a crystalline solid (m.p. 17°C) and boils at 290°C. If however, impurities are present, it can be distilled only under reduced pressure without decomposition.

(ii) It has sweet taste and is soluble in alcohol and water but is insoluble in ether.

Chemical Properties

(1) **Action of sodium metal**. Sodium metal reacts with primary alcoholic groups to form mono-sodium and di-sodium glycerollate.

$$\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix} \xrightarrow{Na} \begin{matrix}CH_2ONa\\|\\CHOH\\|\\CH_2OH\end{matrix} \xrightarrow{Na} \begin{matrix}CH_2ONa\\|\\CHOH\\|\\CH_2ONa\end{matrix}$$

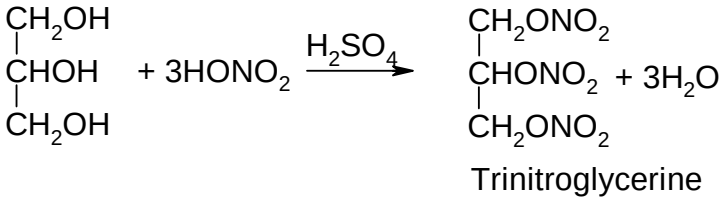
(2) **With PCl_3**. Glycerol reacts with PCl_5 to give a trichloro derivative.

$$\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix} + 3PCl_5 \longrightarrow \begin{matrix}CH_2Cl\\|\\CHCl\\|\\CH_2Cl\end{matrix} + 3POCl_3 + 3HCl$$

1,2,3-Trichloropropane

(3) **Action with acids.**

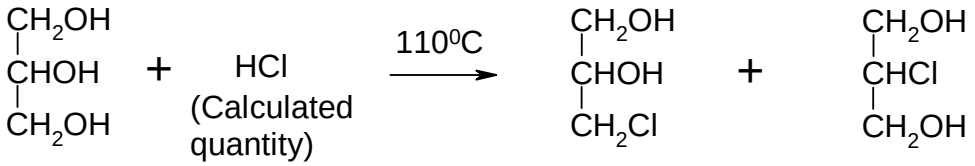
(a) **With nitric acid**. With cold mixture of Conc. HNO_3 and H_2SO_4, it gives trinitroglycerine.



Trinitroglycerine

In fact it is glycerol trinitrate and is known as *Noble's oil*. It is a colourless, poisonous oily liquid. It is highly explosive and used in the formation of dynamite.

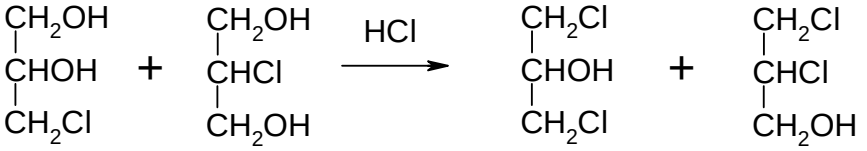
(b) **Action of HCl gas**. When HCl gas is passed into glycerol, heated to 110°C, a mixture of two monochloro derivatives is obtained.



1-Chloro-2,3-dihydroxy propane

2-Chloro-1,3-di hydroxypropane

On passing more HCl gas, keeping the same temperature, a mixture of two dichloro derivatives (1,3dichloropropan-2-ol and 2,3-dichloropropanol) is obtained, provided the quantity of HCl is 25% more than the calculated quantity.



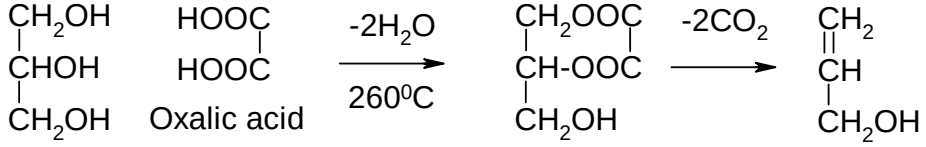
1,3-Dichloropropan-2-ol

2,3-Dichloro-propanol

Similar results are obtained with HBr.

(c) **Action of oxalic acid**.It gives allyl alcohol at 260°C and formic acid at 120°C.

(a)

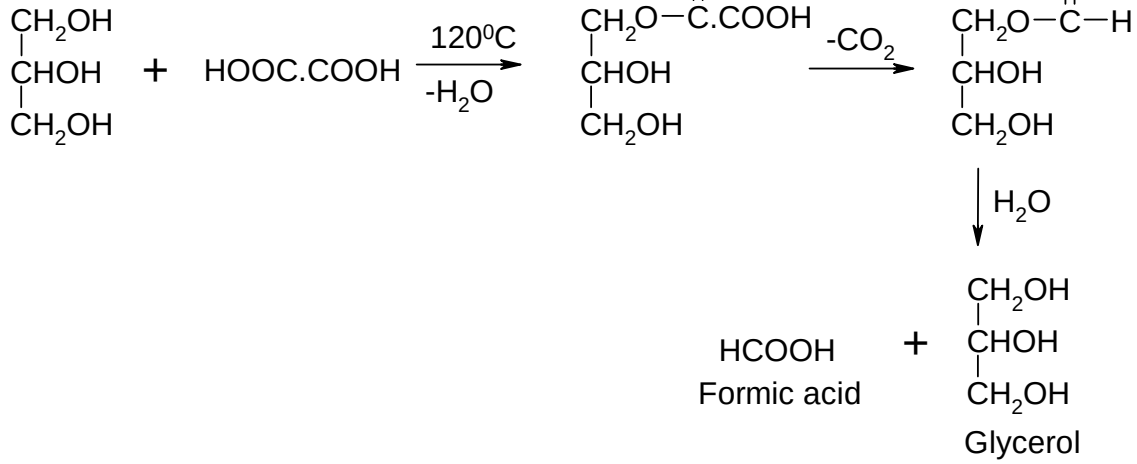


Glycerol

Oxalic acid

Allyl alcohol

(b)

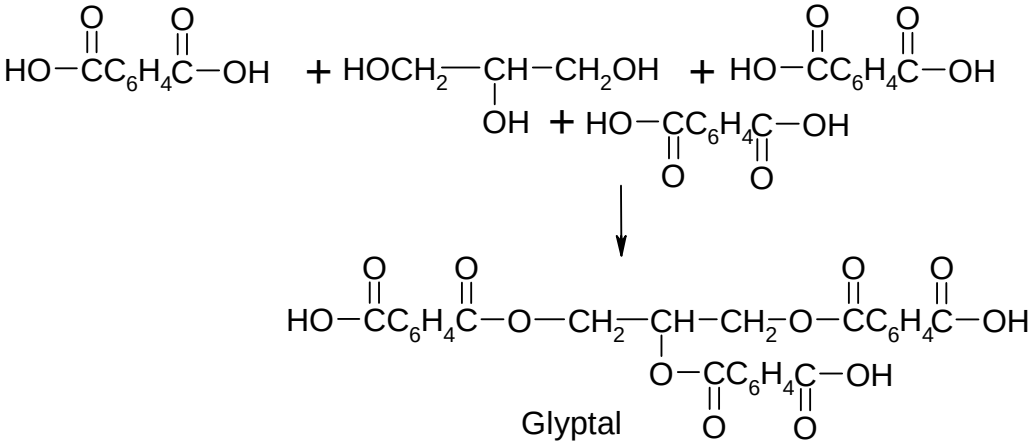


Formic acid

Glycerol

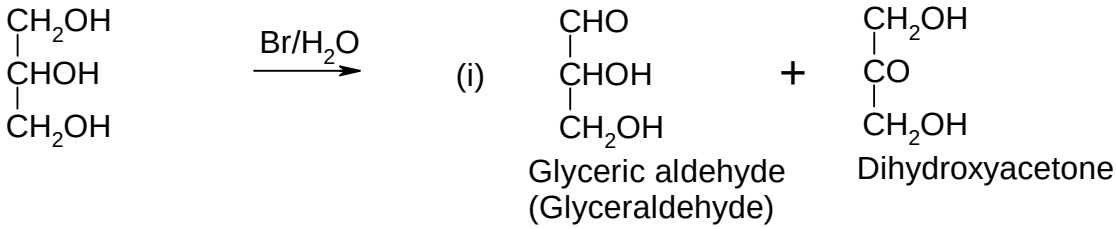
Thus it is a continuous process to get formic acid from oxalic acid.

(d) **With phthalic acid**. Glyptals or alkyl resins are formed which are useful for the manufacture of paints and lacquers.

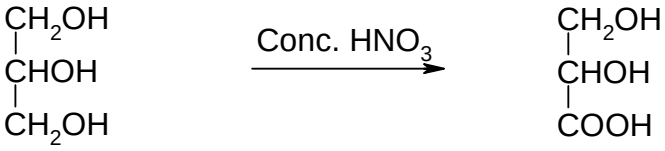


(4) **Oxidation**. It gives different oxidation products depending on the nature of the oxidizing agent used. Thus,

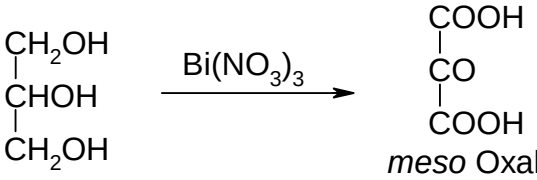
(a) Bromine water gives glyceric aldehyde and dihydroxyacetone.



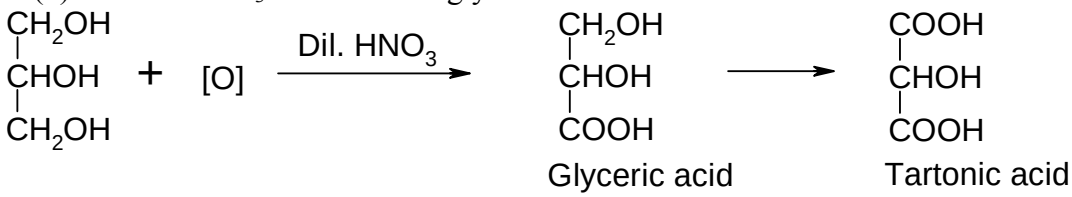
(b) Conc. HNO_3 gives glyceric acid.



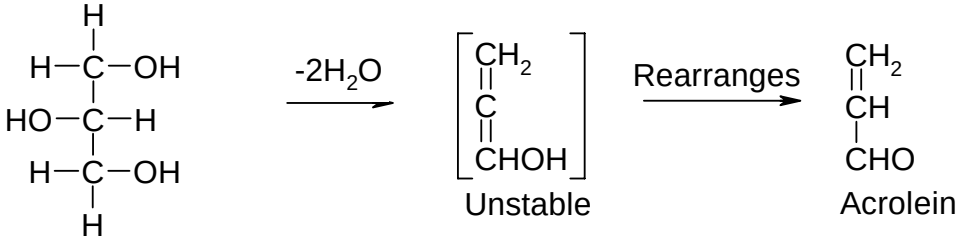
(c) Bismuth nitrate gives meso-oxalic acid,



(d) Dil. HNO_3 oxidizes it to glyceric acid and then tartonic acid.



(5) On heating with $KHSO_4$ it loses two water molecules and acrolein is formed.

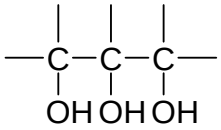


Structure of Glycerol.

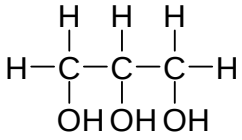
(i) From analytical data, it is known that the molecular formula of glycerol is $C_3H_8O_3$.

(ii) Since on acetylation it forms a triacetyl derivative, it shows the presence of three hydroxyl groups.

(iii) Since two hydroxyl groups cannot be attached to the same carbon atom in a stable compound, the three hydroxyl groups must be attached, one each, to the three carbon atoms. Thus:



Complete structure of glycerol is as under.



This structure is confirmed by its synthesis from elements given earlier.

Uses

(i) The chief use of glycerol is in the manufacture of nitroglycerine which is highly explosive.

(ii) On account of its non-drying character, glycerol is used in making non-drying stamp colours, shoe blacking, for filling gas meters and for preserving fruits. It is also used in the manufacture of toilet soaps and cosmetics preparations.

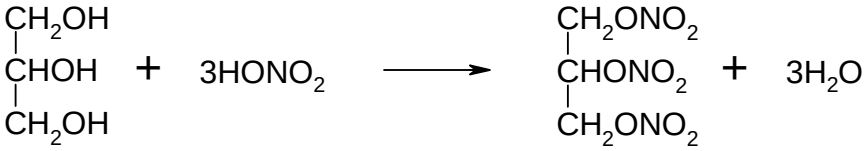
(iii) On account of its high viscosity, glycerol is used as lubricant for watches and clocks.

(iv) As a sweetening agent in confectionary and beverages.

(v) In the preparation of formic acid and allyl alcohol.

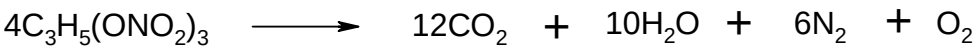
(vi) As an antifreeze in automobile radiators.

Nitroglycerine. It is manufactured by adding glycerol gradually to a cold mixture of fuming nitric acid and concentrated sulphuric acid.



Nitroglycerine

Nitroglycerine is a poisonous colourless, oily liquid, and is insoluble in water. When ignited, it usually burns quietly. When heated rapidly, struck, or detonated, it explodes violently. The decomposition, which accompanies explosion, gives gaseous products occupying about 11,000 times the volume of nitroglycerine.



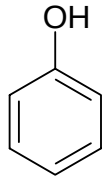
It is used in the manufacture of dynamite, by absorbing it in wood pulp and adding solid ammonium nitrate. Nitroglycerine is mixed with gun-cotton (cellulose nitrate) to make blasting gelatin or gelignite. A mixture of nitroglycerine, gun-cotton, and Vaseline is cordite (the smokeless powder). Another use of nitroglycerine is in the treatment of angina pectorosis.

Phenols

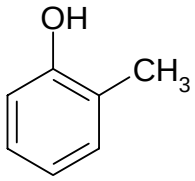
Aromatic compounds that contain one or more hydroxyl groups (-OH) directly attached to the benzene ring are known as aromatic hydroxyl compounds. Phenol is the simplest among the aromatic hydroxyl compounds.

Nomenclature. There are three types of phenols,

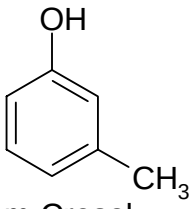
(i) **Monohydric phenols.** If only one hydroxyl group is present in the benzene nucleus, the compounds are known as monohydric phenols. e.g.,



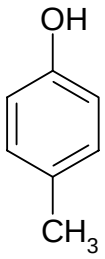
Phenol



o-Cresol

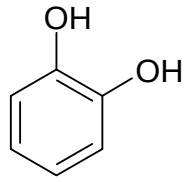


m-Cresol

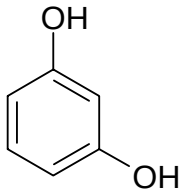


p-Cresol

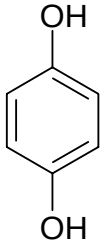
(ii) **Dihydric phenols.** If two hydroxyl groups are present on the benzene nucleus, the compounds are known as dihydric phenols. e.g.,



o-Dihydroxybenzene
(catechol)

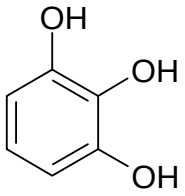


m-Dihydroxybenzene
(resorcinol)

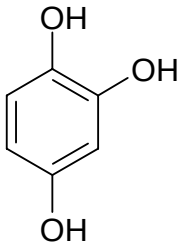


p-Dihydroxybenzene
(quinol)

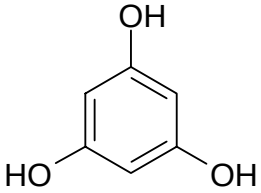
(iii) **Trihydric phenols.** If three hydroxyl groups are present on the benzene nucleus, the compounds are known as trihydric phenols. e.g.,



Pyrogallol

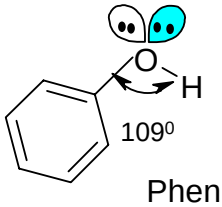


Hydroxyquinol



Phloroglucinol

Structure. The structure of a phenol resembles that of an alcohol having sp^3 hybridized oxygen atom.

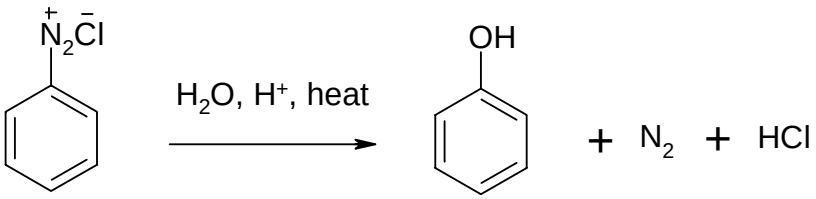


Phenol

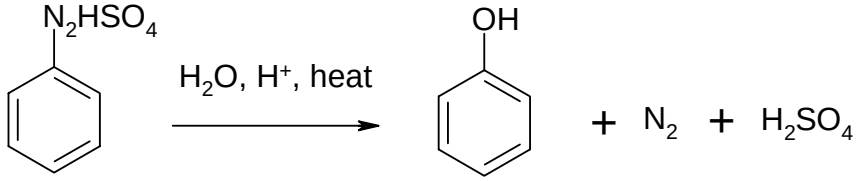
Preparation of Phenol.

(i) **By the hydrolysis of benzene diazonium chloride.** The most convenient method of preparation of phenol involves the hydrolysis of diazonium salts. The diazonium salt may be prepared by the reaction of an aromatic primary amine with nitrous acid at a low temperature. Hydrolysis of the diazonium salt with water and acid gives phenol.

Thus if an aqueous solution of benzene diazonium chloride is added slowly to a large volume of boiling dilute H_2SO_4, phenol is obtained.



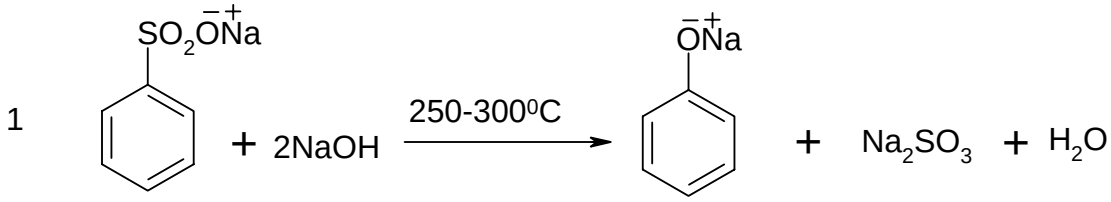
Benzene duazonium hydrogen sulfate gives better results due to the absence of side reactions.



Benzene diazonium hydrogen sulfate

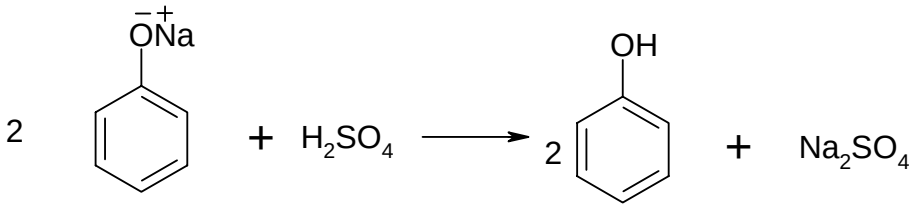
Phenol (64%)

(ii) **By fusing sodium benzene sulfonate with sodium hydroxide.** Sodium benzene sulfonate is mixed with an excess of caustic soda, and heated to 250-300 °C. Sodium phenoxide thus obtained is treated with sulphuric aid to get phenol.

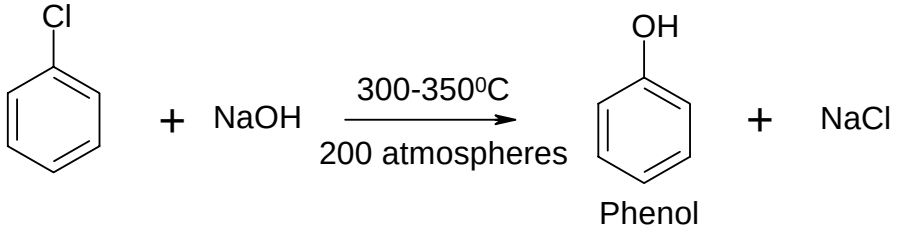


Sodium benzene sulfonate

Sodium phenoxide



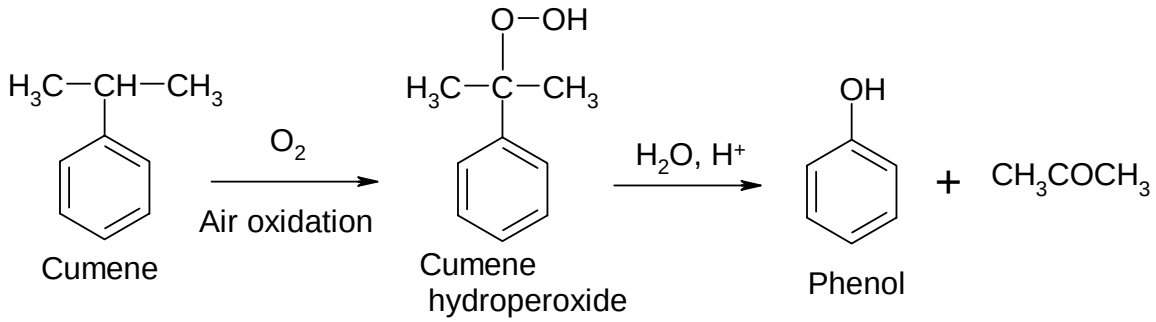
(iii) **By heating chlorobenzene with caustic soda under pressure (Dows Process).** A mixture of chlorobenzene and 10% solution of caustic soda or sodium carbonate is heated to 300-350 °C under 200 atmospheres pressure in presence of about 10% diphenyl ether.



Phenol

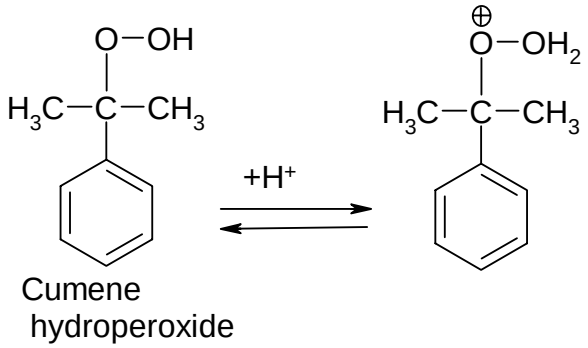
It is one of the chief commercial methods for the preparation of phenol.

(iv) **From cumene hydroperoxide.** In recent years a new method for the synthesis of phenol from cumene or isopropyl benzene has been developed . This has the potentiability of becoming the principal source of phenol.

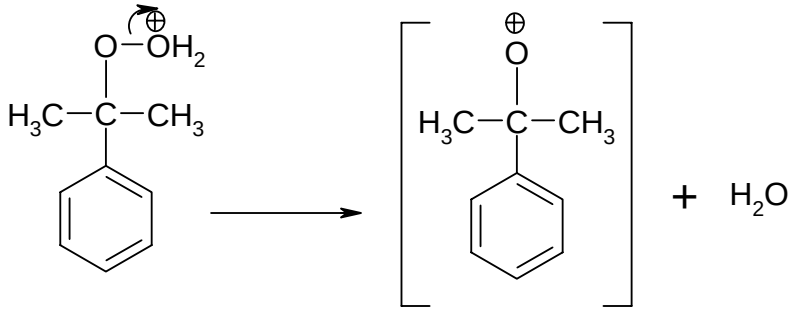


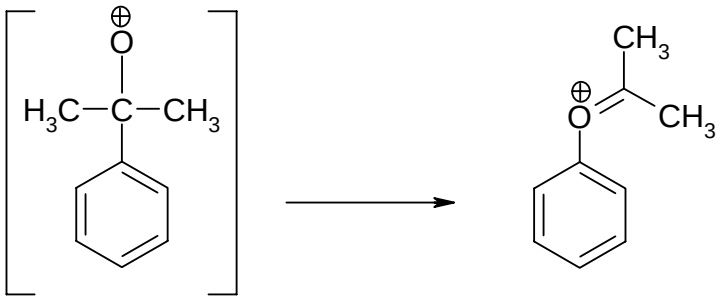
The rearrangement involved in the transformation of cumene hydroperoxide into phenol is 1, 2 shift to an electron-deficient oxygen atom as the phenyl group is joined to carbon in the peroxide and to oxygen in the phenol.

(a) **Protonation of hydroperoxide.** Acid converts peroxide into protonated peroxide.

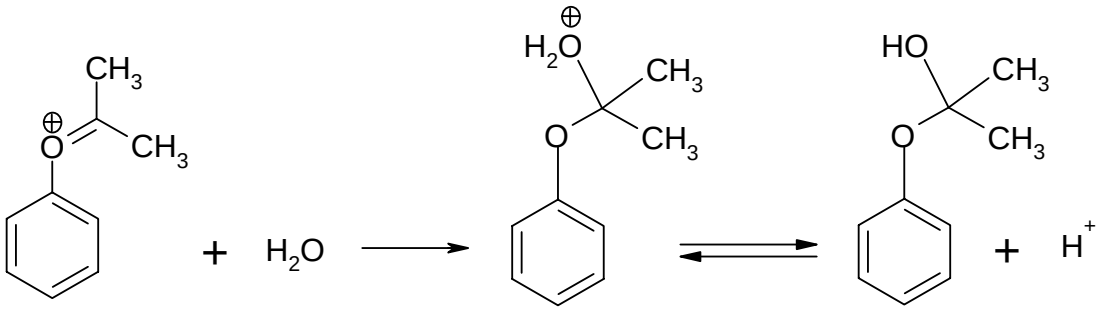


(b) **Elimination of water and migration of phenyl group.** Protonated peroxide loses a molecule of water to form an intermediate in which oxygen bears only six electrons. Simultaneously 1, 2 shift of the phenyl group from carbon to electron-deficient oxygen takes place yielding carbonium ion.

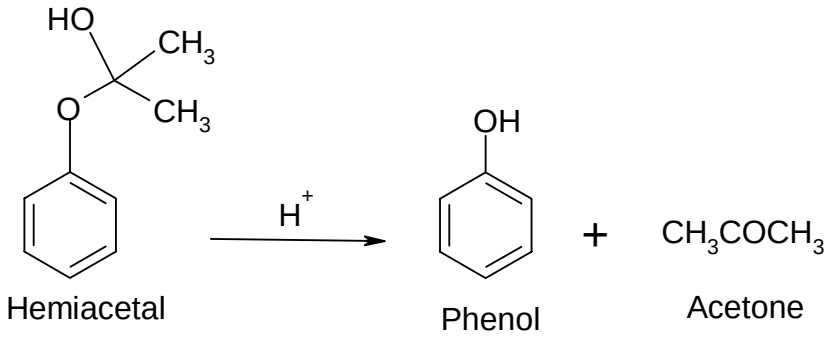




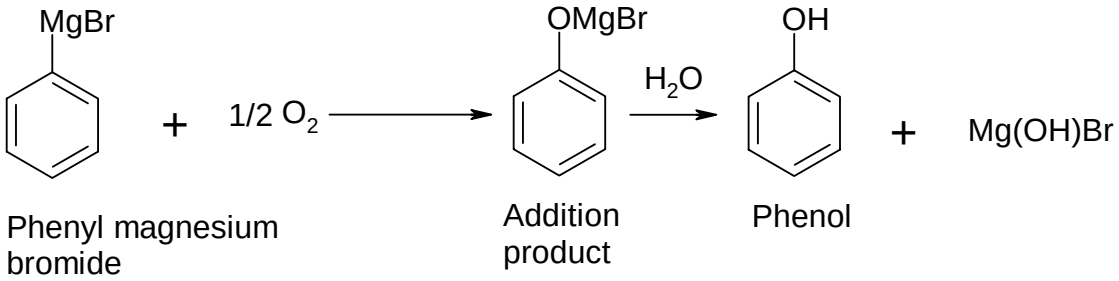
(c) **Acceptance of water molecule**. The carbonium ion reacts with water to give hydroxy compound (hemiacetal)



(d) **Decomposition of hemiacetal**. The hemiacetal breaks down to give phenol and acetone.



(v) **From Grignard's reagent.** By treating with oxygen and followed by hydrolysis of the addition product.



Physical Properties.

(i) Phenol forms colourless , hygroscopic needle-shaped crystals which turns pink on exposure to air or light.
(ii) The phenol melts at 43 °C and boils at 183 °C.
(iii) Phenol is somewhat soluble in water (9 gram per 100 gram).
(iv) It has a characteristic odour and is poisonous in nature.
(v) It has a corrosive action on skin and causes blisters.

Chemical properties.

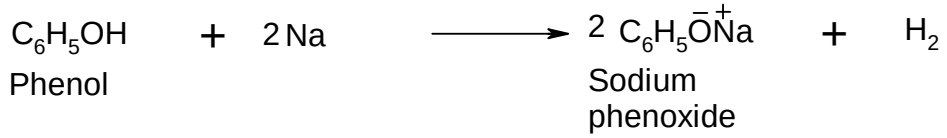
The reactions of phenol may be divided into three classes.

I Reactions of the phenolic hydroxyl group (-OH)
II Reactions of the benzene nucleus.
III Special reactions.

I Reactions of the hydroxyl group.

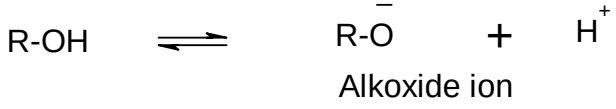
(i) **Acidic behaviour and salt formation.** Phenol behaves as a weak acid and reacts with caustic alkalies to form salts, e.g.,

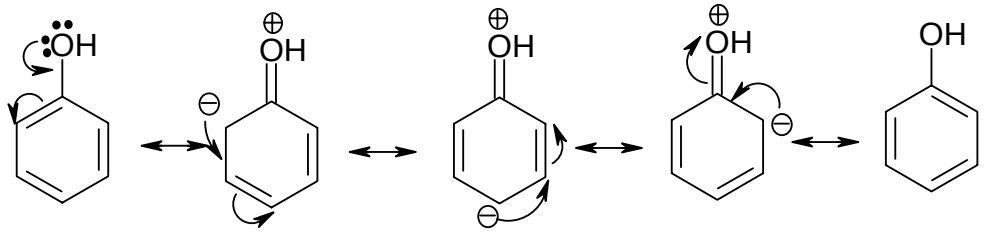
With sodium metal also, it reacts to form sodium phenoxide.



Phenol does not decompose a carbonate or a bicarbonate showing that it is a weaker acid than even carbonic acid.

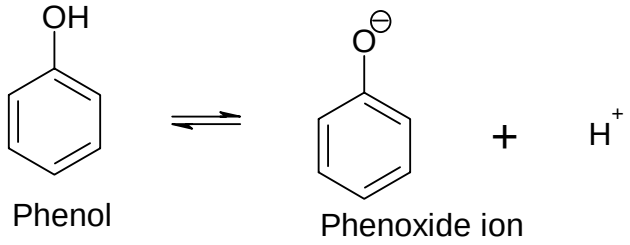
Phenol is stronger acid than alcohols, one possible explanation is that the former exists as a resonance hybrid whereas the latter do not.



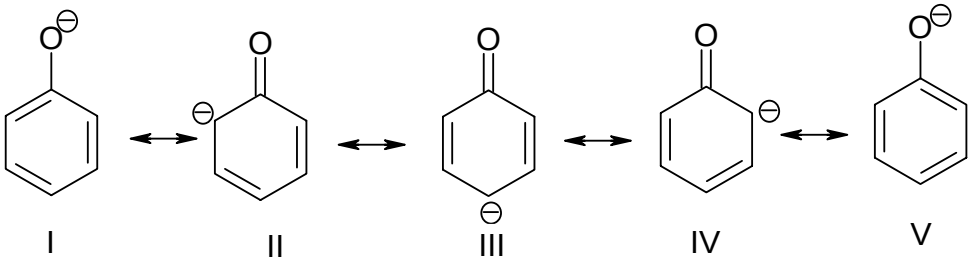


Thus in phenol, the oxygen atom acquires a positive charge and so attracts the electron pair of the O-H bond, thereby facilitating the release of a proton. Since resonance is impossible in alcohols, the hydrogen atom is more firmly linked to the oxygen atom and alcohols are, therefore neutral.

Thus phenol dissociates to liberate a proton H^+ and phenoxide ion,



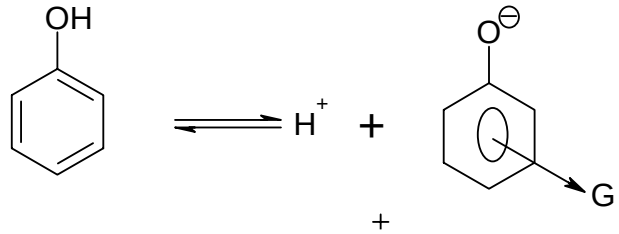
Phenoxide ion also shows resonance forms. **I-V**



The phenoxide ion is more stabilized by resonance than is the unionized molecule because of delocalization of the negative charge only. In the unionized molecule, unlike charges are spread out which increases its energy and decreases stability in comparison to phenoxide ion. Thus equilibrium of the reaction from phenol to phenoxide will prefer to proceed in forward direction .

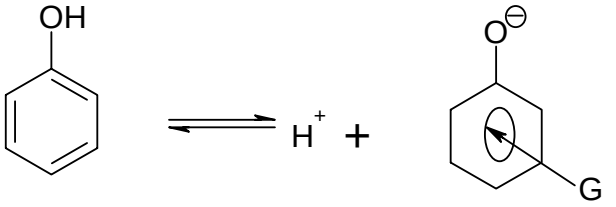
Effect of substituent on acidic behaviour

The acid strength of phenol is effected appreciably by the substituents. Groups like nitro, chloro, cyano etc., increase the acidic behaviour whereas groups like alkyl decrease it. This is the reason why nitrophenol is a stronger acid as compare to cresols. The electron-withdrawing groups result in a greater stabilization of the phenoxide ion. The electron-releasing groups, infact destabilize the phenoxide ion by intensifying the negative charge. This is shown as under:-



G withdraws electrons: stabilizes ion, increases acidity.

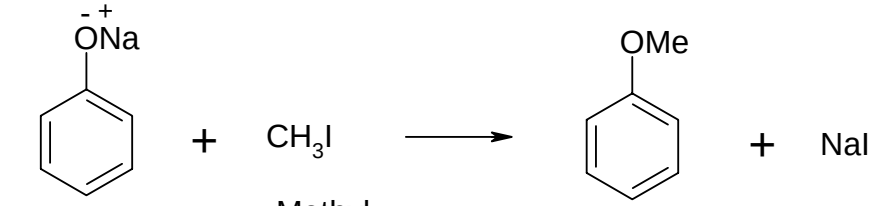
[G = $-NO_2$, -X, $\overset{+}{N}R_3$, -CHO, -COR, -COOR, -CN]



G releases electrons: destabilizes ion, decreases acidity.

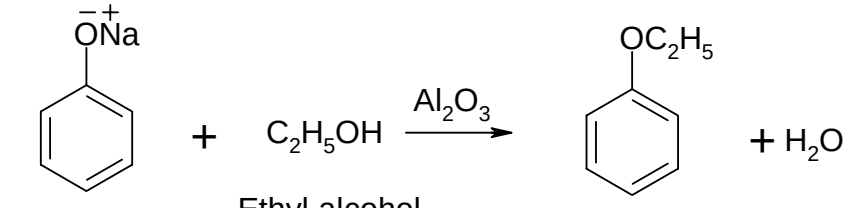
[G = $-CH_3$, $-C_2H_5$]

(ii) **Alkylation.** Sodium phenoxide when treated with alkyl halides forms phenolic ethers. For methyl ether, methyl sulfate $(CH_3)_2SO_4$, may be used.



Sodium phenoxide | Methyl Iodide | Phenyl methyl ether or anisole

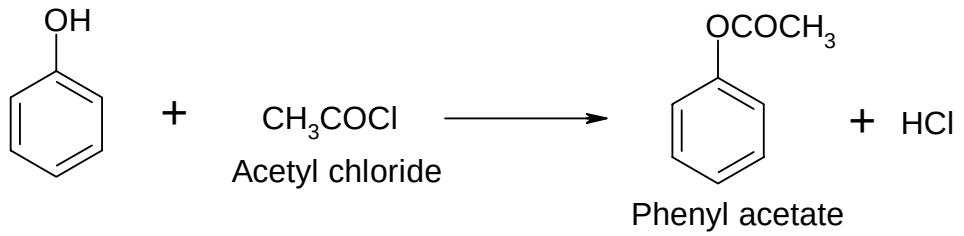
This method resembles Williamson's synthesis for preparing ether. Mixed ether can also be obtained by passing the mixed vapours of phenol and some alcohol over heated alumina or thoria.

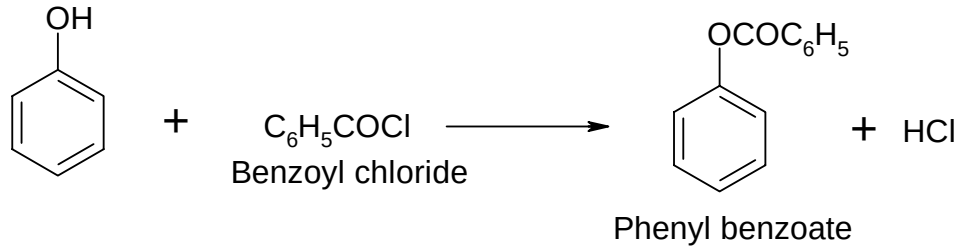


Sodium phenoxide | Ethyl alcohol | Phenyl ethyl ether or phenetole

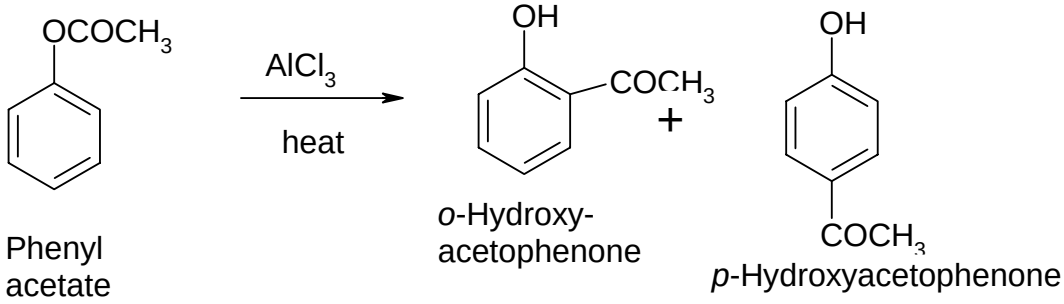
(iii) **Acylation.** Phenol reacts with acid chlorides and acid anhydrides to form corresponding ethers. The hydrogen atom of the hydroxyl group is replaced by the corresponding acyl group (RCO-).

The reaction with benzoyl chloride is called **Schotten Baumann's reaction.**





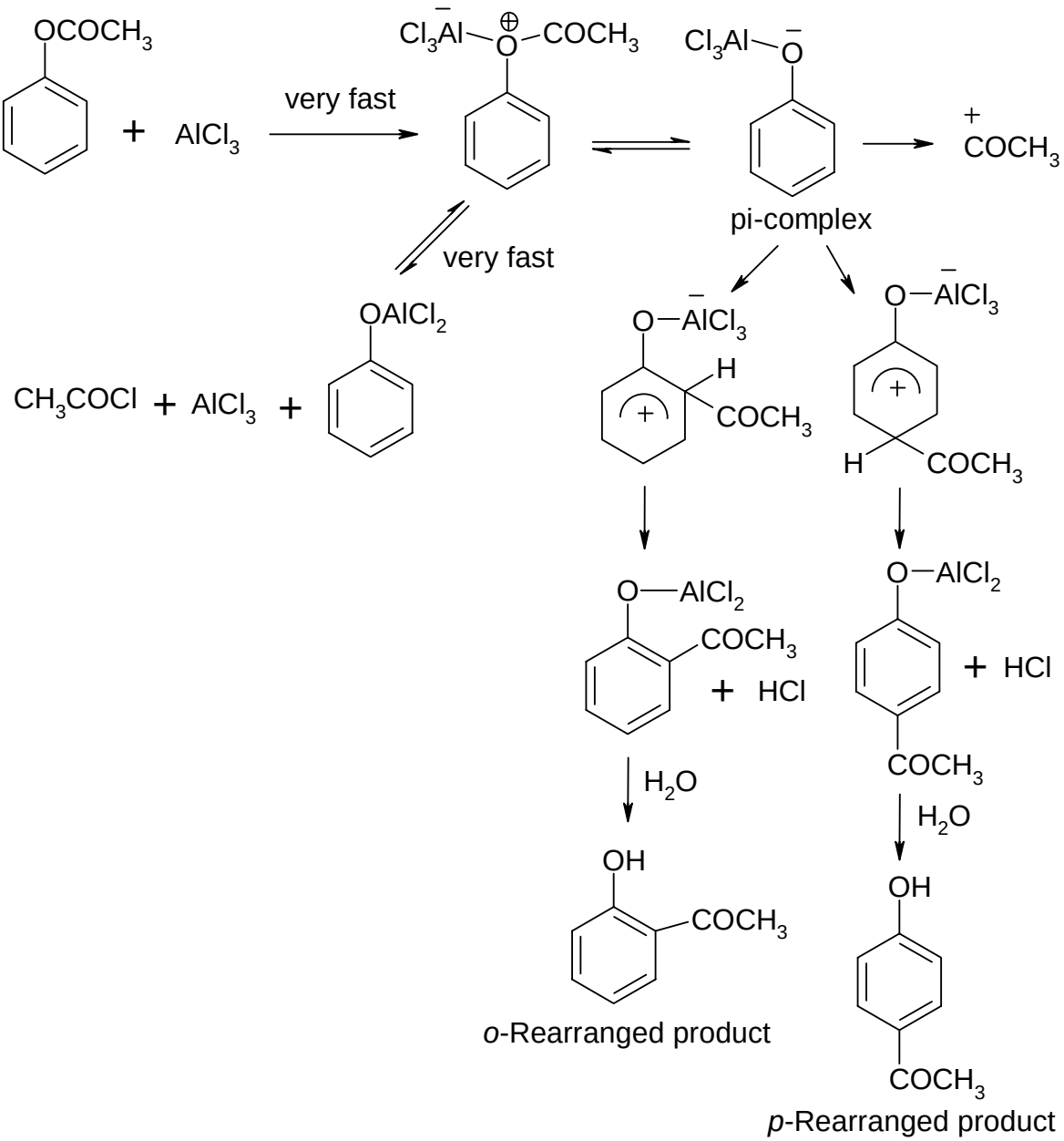
When esters of phenol are heated with anhydrous $AlCl_3$, the acyl group migrates from the phenolic oxygen to an *ortho*- or *para*- position on the ring, thus yielding a ketone. This reaction of conversion of phenolic esters to acylated phenols in presence of a lewis acid or a catalyst is known as **Fries rearrangement**, *e.g.*,



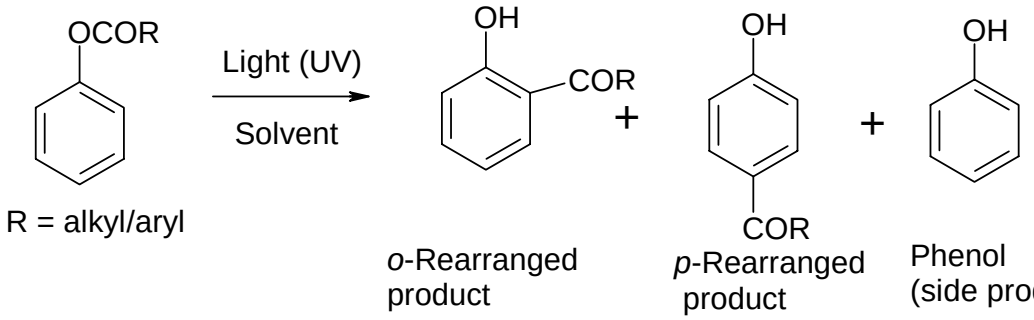
The *ortho*/*para* ratio is largely dependent on the reaction temperature, solvents used and on the catalyst concentration. Low temperature (60 °C or less) favours *p*-isomer whereas high temperature (above 160 °C) favours *o*-isomer. The *para*-product is appeared to be kinetically controlled, whereas the *ortho*-product is thermodynamically controlled. Perhaps, owing to steric hindrance, the *ortho*-isomer can't be formed at a low temperatures

Mechanism of Fries rearrangement:

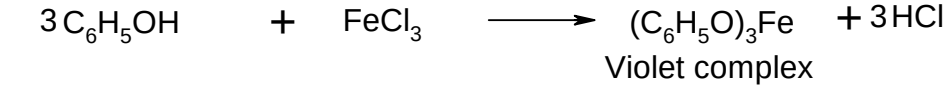
The mechanism of Fries rearrangement is a matter of much controversy .Several mechanisms has been proposed but the exact mechanism is still not completely worked out. The most common mechanism was given by Ogata and Tabuchi. They suggest an intramolecular migration of acetyl group to both *ortho*- and *para*- positions, involving a normal –complex intermediate. The representation is given below:



The classical Fries rearrangement was reported to have a photochemical analogue.
This analogue rearrangement reaction catalysed by light is called Photo-Fries rearrangement.
For example:



(iv) **Action with ferric chloride.** With neutral ferric chloride, it gives a violet colour.

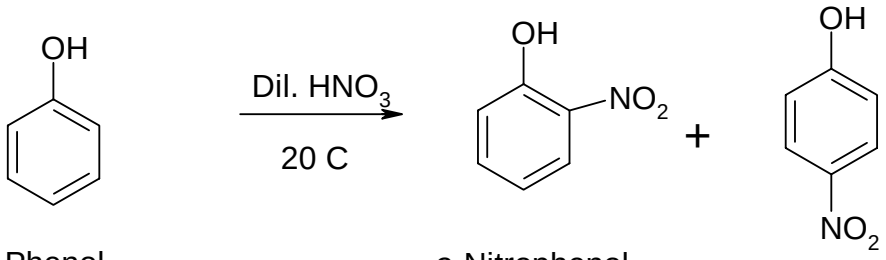


II Reactions of the benzene nucleus.

The –OH group present on benzene ring, being electron-donating not only makes electrophilic substitution easier but it also directs the new group at the *ortho*- or *para*-positions due to +Resonance effect . Thus it undergoes nitration, sulfonation and halogenation giving *ortho*- and *para*- derivatives.

(i) **Nitration**

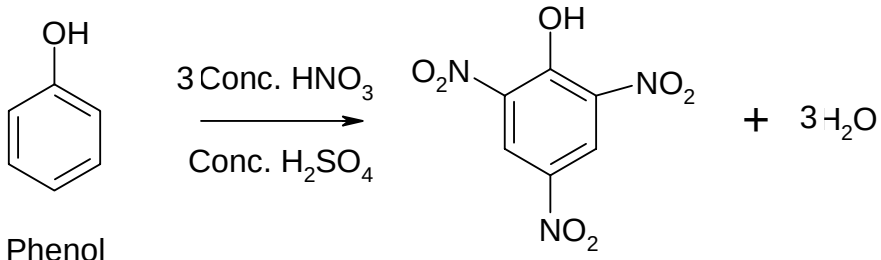
(a) With dilute nitric acid, it gives a mixture of *ortho*- and *para*-nitrophenol



Phenol *o*-Nitrophenol *p*-Nitrophenol

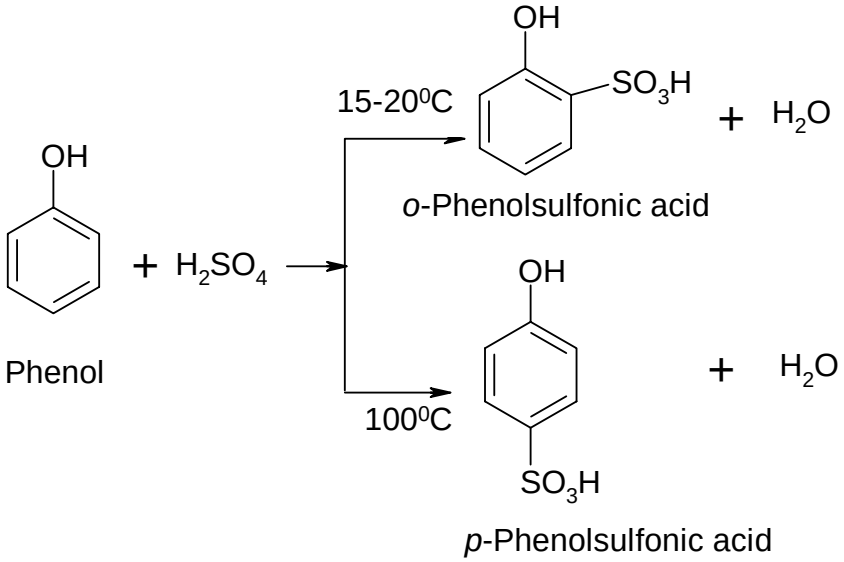
The mixture of *p*-nitrophenol and *o*-nitrophenol can be separated by steam distillation due to difference in their boiling points. *p*-Nitrophenol is less steam volatile due to intermolecular hydrogen bonding, while *o*-nitrophenol is more volatile due to intramolecular hydrogen bonding.

(b) With concentrated nitric acid, it forms 2,4,6-trinitrophenol, commonly known as picric acid.



Phenol 2,4,6-Trinitrophenol or picric acid

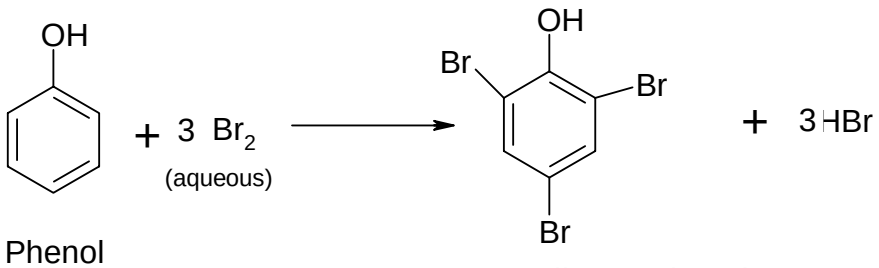
(ii) **Sulfonation.** Sulfonation of phenol occurs readily to yield chiefly the *ortho*-isomer or the para-isomer depending upon temperature:



o-Phenolsulfonic acid

Phenol *p*-Phenolsulfonic acid

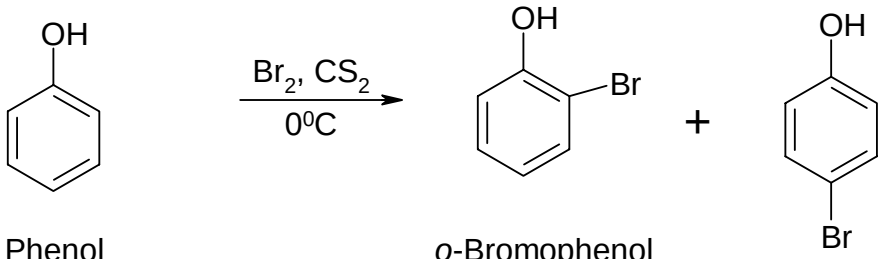
(iii) **Halogenation.** With aqueous solution of bromine, it readily forms tribromophenol.



Phenol

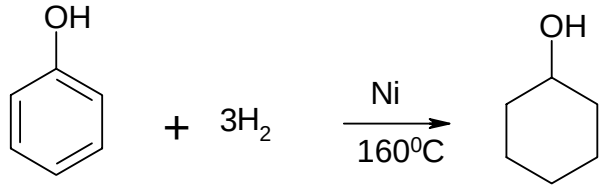
2,4,6-Tribromophenol
(white precipitate)

If halogenation is carried out in a solvent of low polarity, such as chloroform, CCl_4 or CS_2 , reaction can be limited to mono halogenation.



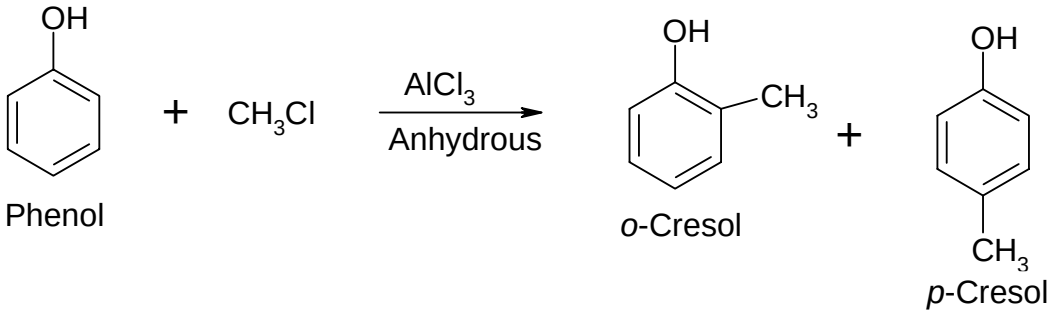
Phenol *o*-Bromophenol *p*-Bromophenol

(iv) **Hydrogenation.** When reduced by hydrogen at 160 °C in the presence of finely divided nickel (catalyst), it forms cyclohexanol.



Phenol Cyclohexanol

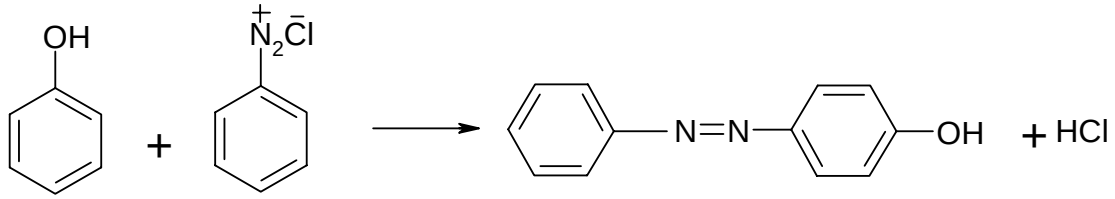
(v) **Friedel Craft's Alkylation.** Phenol gives this reaction forming *ortho*-and *para*-derivatives. The yields are poor and the main product is the *para* derivative.



Phenol *o*-Cresol *p*-Cresol

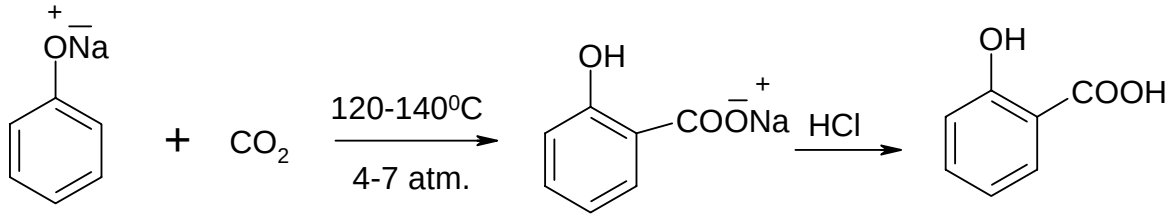
III Special reactions

(i) **Coupling reactions.** Phenol couples with benzene diazonium chloride in mildly alkaline solutions forming an azodye**.**



Phenol Benzene diazonium chloride *p*-Hydroxyazobenzene

(ii) **Kolbe's reaction (carbonation).** When sodium salt of phenol is heated with carbondioxide at 120-140 °C under pressure (6-7 atmospheres) sodium salicylate is produced. This on further treatment with HCl yields salicylic acid.

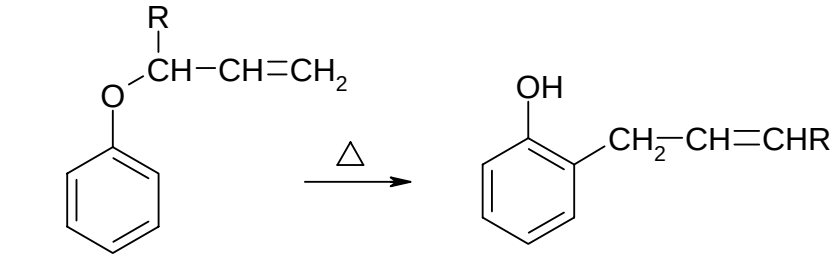


Sodium phenoxide Sodium salicylate Salicylic acid

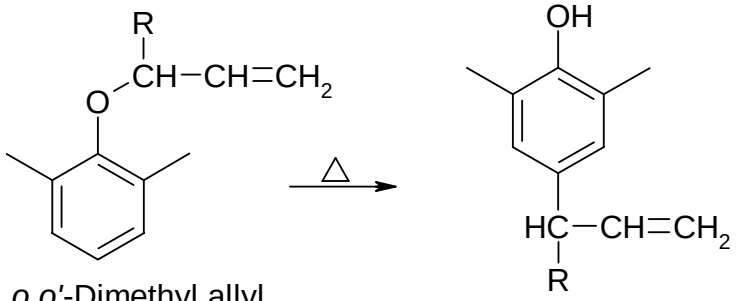
A small amount of *p*-isomer is also obtained. If potassium salt is used, the *o*-isomer is the main product.

(iv) **Claisen rearrangement**

The Claisen rearrangement is an example of pericyclic reactions, and belongs to the category of [3.3]-sigmatropic rearrangement. It involves intramolecular thermal conversion of allyl aryl ethers to allylphenols. The allyl group migrates from the ethereal oxygen to the ring carbon *ortho* to it. When both the *ortho*-positions are blocked, migration occurs at the respective *para*-position.

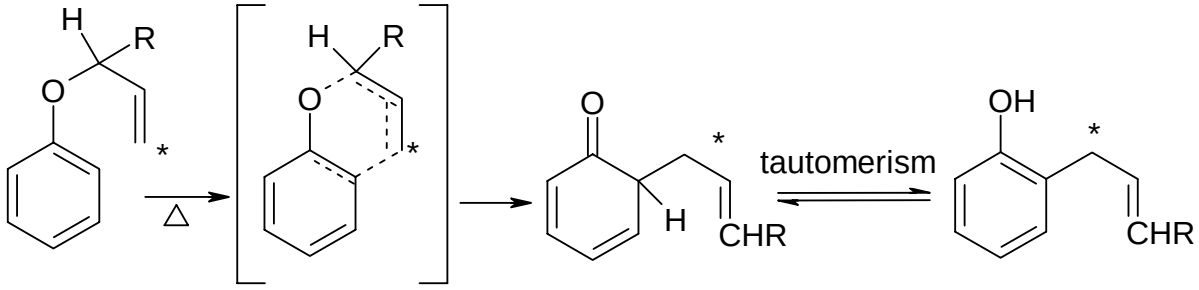


Allyl phenyl ether *o*-Migrated product



o,o'-Dimethyl allyl phenyl ether *p*-Migrated product

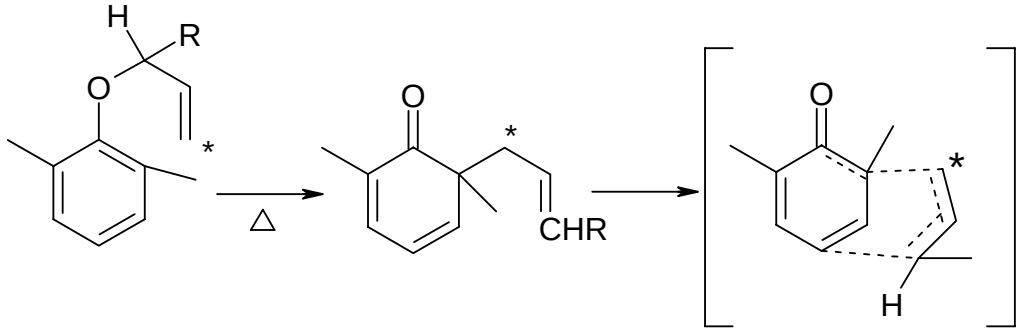
During ortho-migration the allyl group always undergoes an allylic shift- the carbon alpha to the ethereal oxygen atom in the substrate becomes gamma to the ring in the product. However in *para*- migration, the allylic group is found exactly as it was in the starting ether.



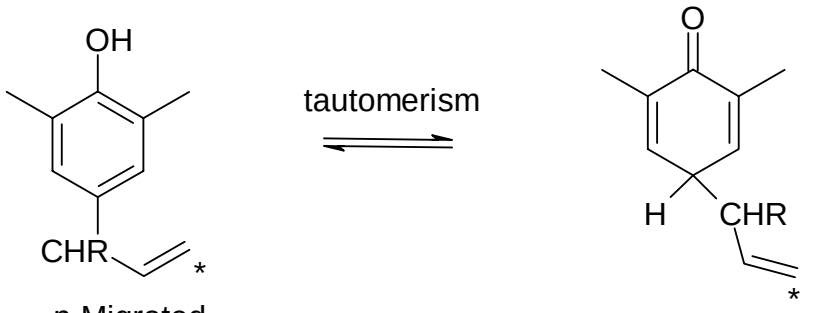
Six membered cyclic transition state

The Claisen rearrangement follows the first order kinetics. The rearrangement is strictly intramolecular and the mechanism is a concerted pericyclic [3,3]-sigmatropic shift.

The reaction proceeds through a cyclic six-membered transition state in which the rupture of the oxygen-allyl bond is synchronous with the formation of a carbon-carbon bond at an *ortho*-position.



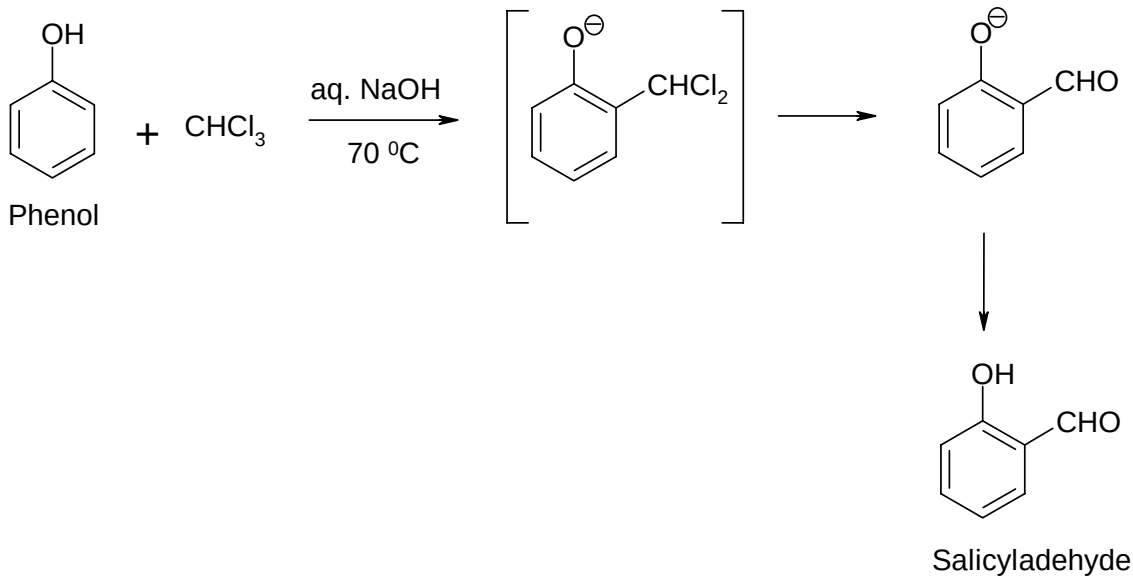
Six membered cyclic transition state



p-Migrated product

(iii) **Reimer and Tiemann's reaction**

(a) When heated with chloroform and caustic alkali, phenol gives o-hydroxybenzaldehyde (salicylaldehyde).

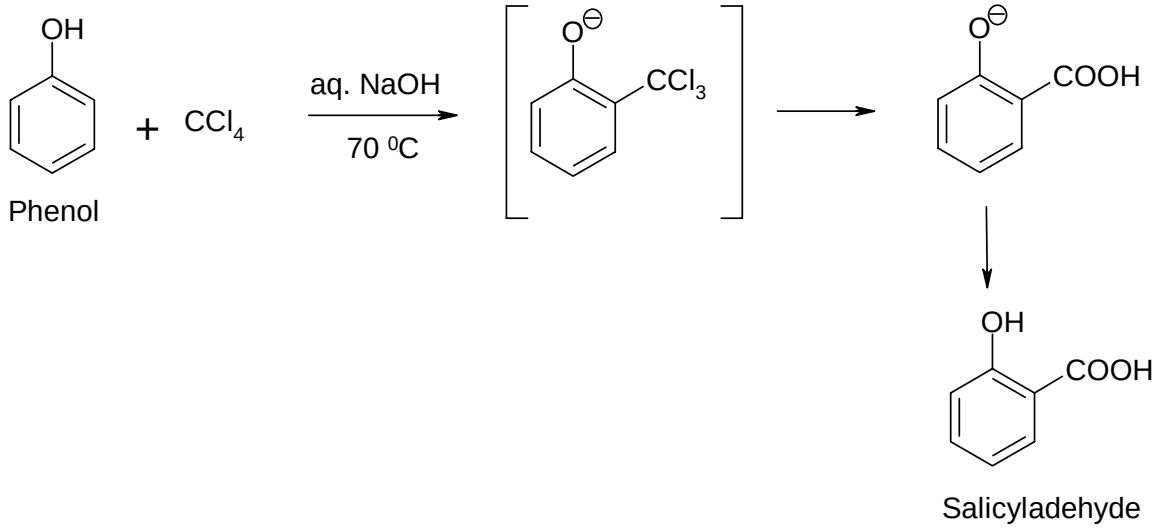


Phenol

Salicyladehyde

A substituted benzal chloride is initially formed which gets hydrolysed by the alkaline reaction medium.

(b) When heated with carbontetrachloride and caustic alkali, phenol gives *o*-hydroxybenzoic acid (salicylic acid)

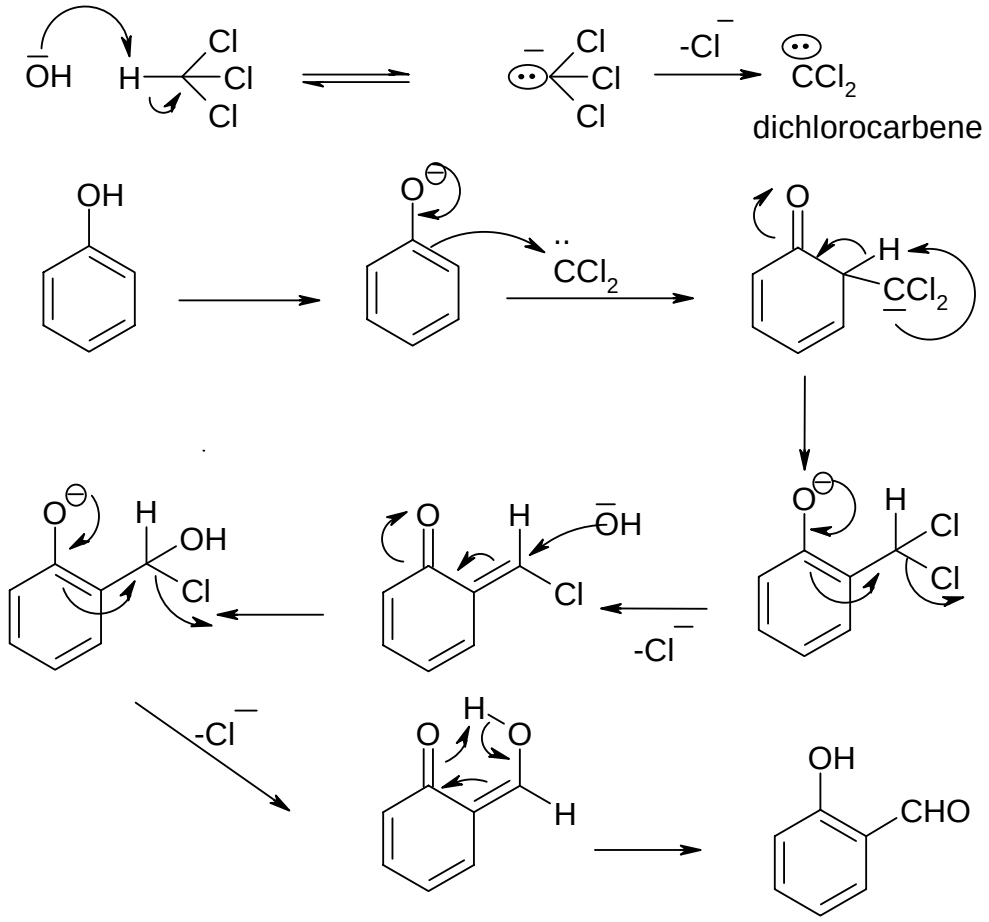


Phenol

Salicyladehyde

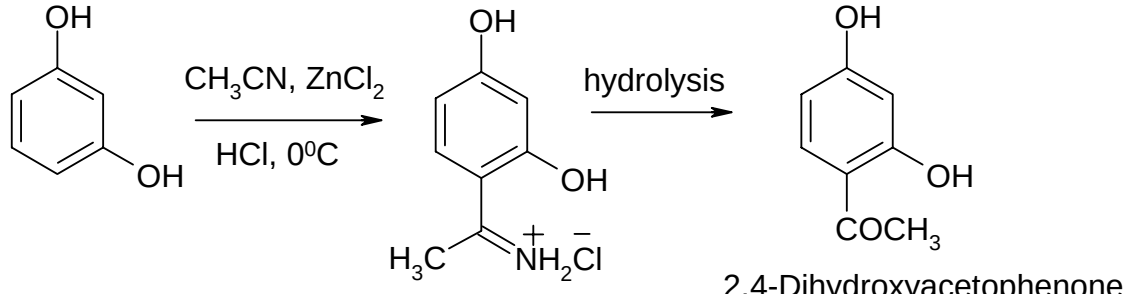
Mechanism of Reimer Tiemman Reaction:

The reaction involves the formation of an electron deficient reactive species dichlorocarbene by the action of alkali on chloroform, which is attack by the electron rich *ortho*-position of the phenoxide ring to form *ortho*-dichloromethylphenolate, which on hydrolysis yields the final product.

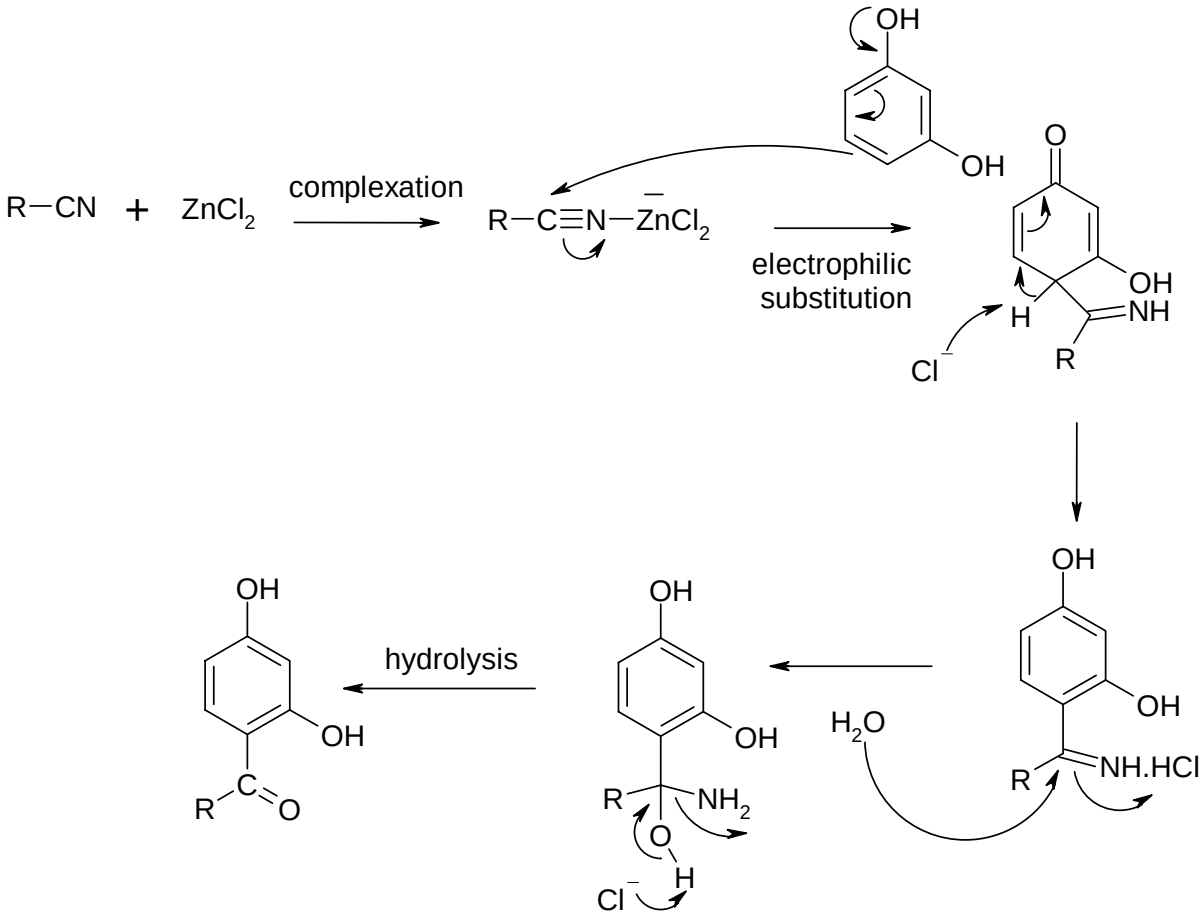


(v) **Houben-Hoesch reaction**

Friedel-Crafts type acylation using nitriles and HCl in presence of lewis acid is called Houben-Hoesch or Hoesch reaction. The reaction is usually applicable to phenols, phenolic ethers and some reactive heterocyclic compounds like pyyrole .



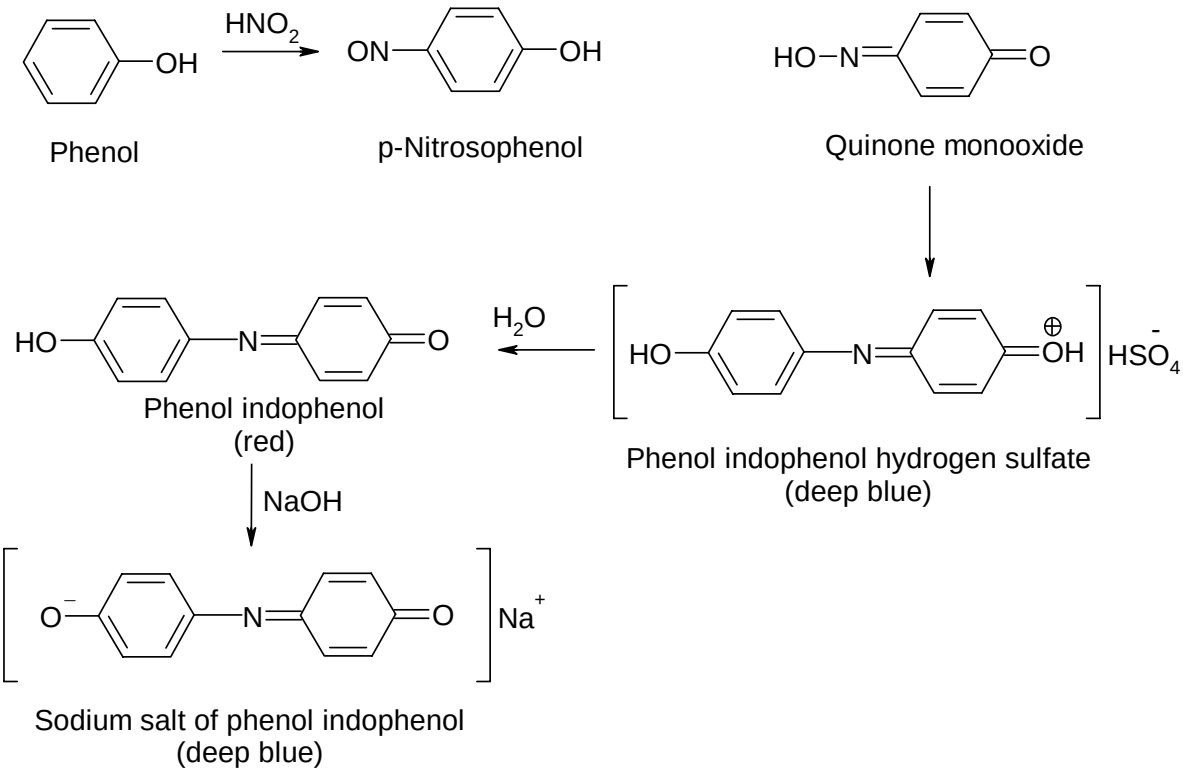
The reaction is not successful towards monohydric phenols due to the formation of imino-ether hydrochloride. The reaction is very successful with polyhydroxy phenols specially, the m-polyhydroxy phenols.



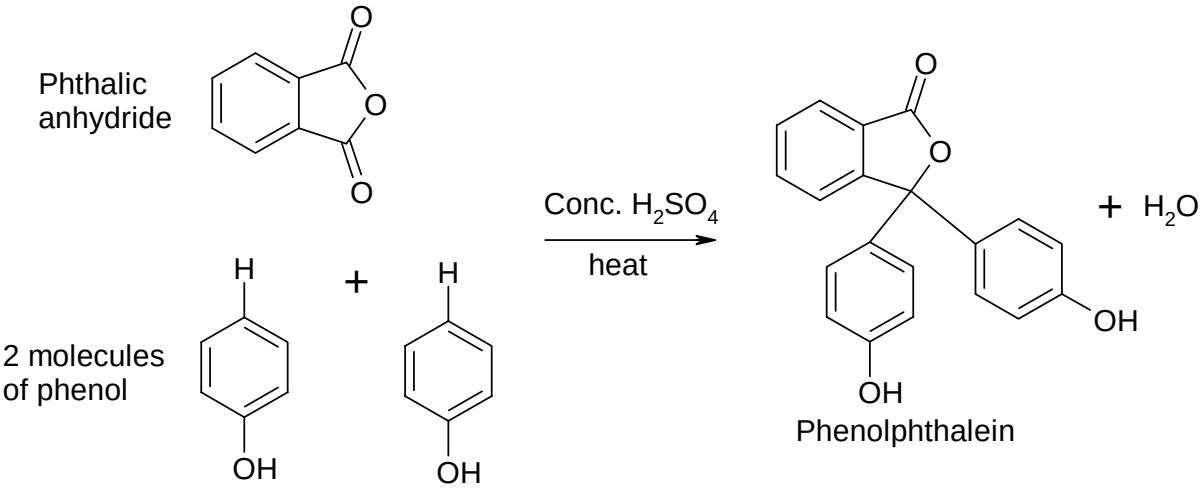
When hydrogen cyanide is used,aromatic aldehyde may be obtained and the reaction is called **Gatterman reaction.**

Thus Gattermann reaction is a special case of the Hoesch reaction.

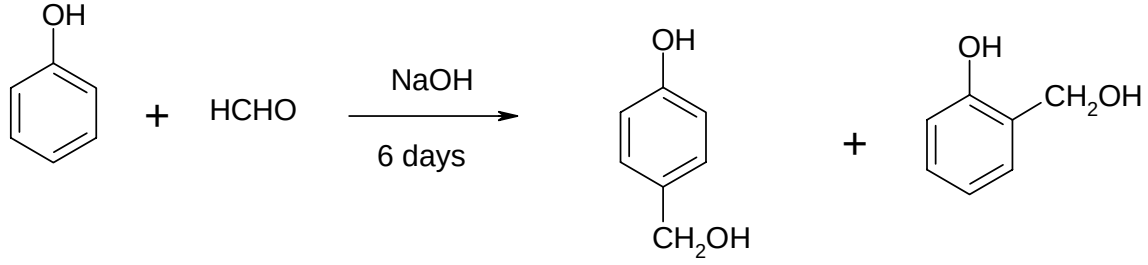
(iv) **Libermann's nitroso reaction** On warming phenol with concentrated sulfuric acid and sodium nitrite (or a nitrosoamine), a greenish blue colour is obtained. This on dilution with water changes to red but again turns green on addition of alkali.



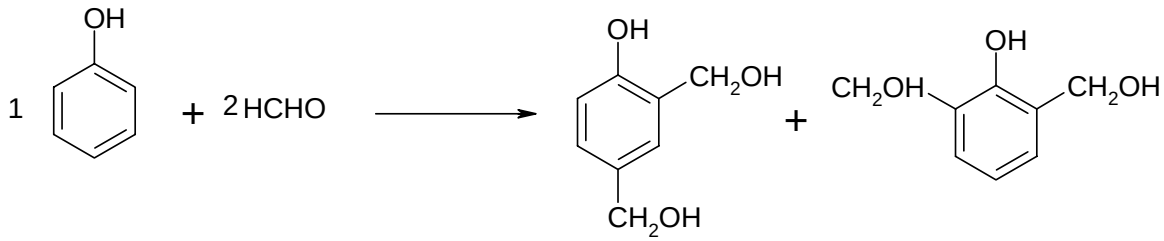
(v) **Condensation with phthalic anhydride.** When phenol is heated with phthalic anhydride in the presence of a little concentrated sulfuric acid, condensation takes place forming phenolphthalein.



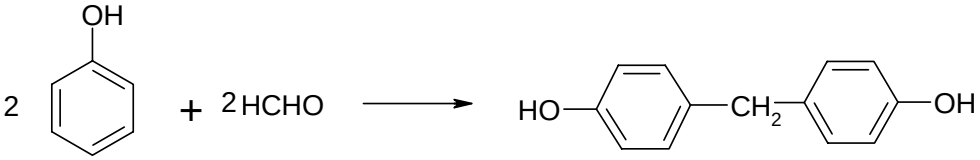
(vi) **Condensation with formaldehyde.** Phenol readily condenses with formaldehyde (formalin 40% aqueous solution) at low temperature and in the presence of dilute acid or alkali. The main product is *p*-hydroxybenzyl alcohol and a small amount of *o*-isomer (**Lederer Manasse reaction**)



With larger quatities of HCHO, bis-hydroxymethyl phenol and *p,p'*-dihydroxydiphenylmethane are obtained.

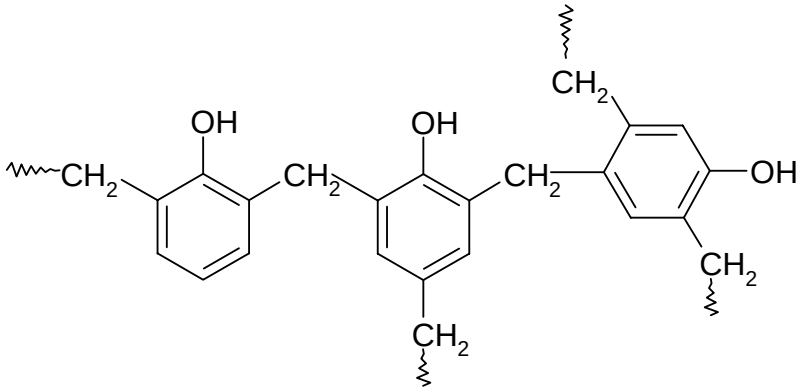


bis-Hydroxymethylphenol

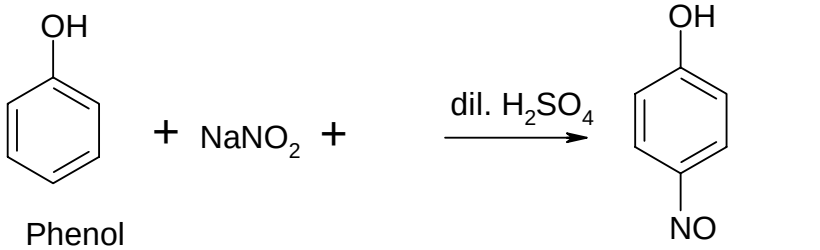


p,p'-Dihydroxydiphenymethane

Phenol and excess of HCHO slowly forms a three-dimensional polymer in the presence of dilute NaOH and this forms the basis of phenol-formaldehyde resin. One possibility is:



(vi) **Nitrosation**. When phenol is treated with $NaNO_2$ and dilute H_2SO_4 below 10 °C, nitroso group is introduced at the *para* position to the hydroxyl group.



Phenol

p-Nitrosophenol

Uses

(i) As a powerful antiseptic in soaps, lotions etc.
(ii) In the manufacture of bakelite plastics.
(iii) As a preservative for silk.
(iv) In the manufacture of picric acid.
(v) In the manufacture of drugs like salol, aspirin, salicylic acid, etc.

Ethers

Structure. Ethers are a class of compounds having the general formula:

(i) $R-O-R$ (ii) $R-O-R'$

Where R, R′ stand for alkyl groups like methyl, ethyl etc.

Ethers can be considered as substituted derivatives of water in which both hydrogen atoms are replaced by alkyl groups.

$H-O-H$ $R-O-R'$

Ethers can also be considered as anhydrides of alcohols or alkoxy derivatives of alkanes.

$$\begin{matrix} R-OH \\ R'-OH \end{matrix} \xrightarrow{-H_2O} R-O-R'$$

If the two groups attached to the oxygen atom are the same as in case (i) above, the ether is called a simple or symmetrical ether. In case the attached groups are different as in case (ii) above, the ether is called mixed or unsymmetrical ether.

Nomenclature. (i) Common system. Ethers are generally named by adding the word 'ether' after the names of alkyl groups linked to the oxygen atom. For naming simple ether, the name of alkyl group only is mentioned. In case of unsymmetrical aliphatic ethers, the two alkyls are named in the order of increasing number of carbon atoms.

	Examples are:	Common name
(i)	$H_3C-O-CH_3$	Dimethyl ether or methyl ether
(ii)	$H_5C_2-O-C_2H_5$	Diethyl ether or ethyl ether
(iii)	$H_3C-O-C_2H_5$	Methyl ethyl ether

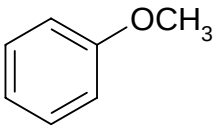
(ii) I.U.P.A.C. system. According to I.U.P.A.C. system, the aliphatic ethers are considered to be derivatives of alkanes in which a hydrogen atom has been replaced by an alkoxy group (-OR). In case of mixed ethers, the higher alkyl group determines the name of the parent hydrocarbon while the lower one forms the alkoxy group.

Examples:

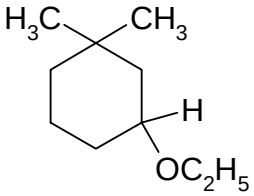
$H_3C-O-CH_3$ Methoxymethane

$H_5C_2-O-CH_3$ Methoxyethane

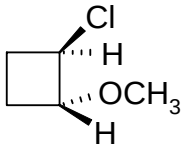
$H_3C-O-C_3H_7$ Methoxypropane



Methoxybenzene

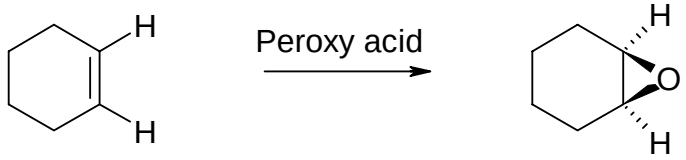


3-Ethoxy-1,1-dimethylcyclohexane



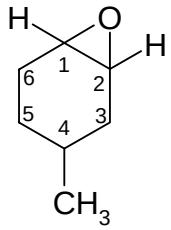
trans 1-chloro-2-methoxycyclobutane

Nomenclature of cyclic ethers. Epoxides (oxiranes) are cyclic three-membered ethers, usually formed by peroxyoxidase oxidation of the corresponding alkenes. The common name of an epoxide is formed by adding "oxide" to the name of the alkene that is oxidized, *e.g.*,



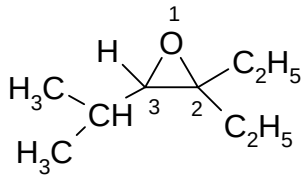
Cyclohexene oxide

One systematic method for naming epoxide is to name the rest of the molecule and use the term "epoxy" as a substitutent giving the number of the two carbon atoms bonded to the epoxide oxygen.



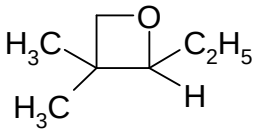
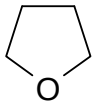
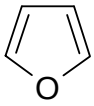
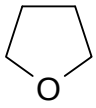
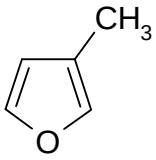
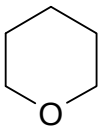
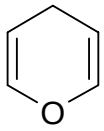
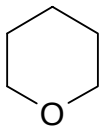
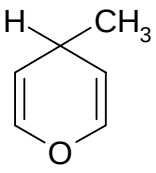
4-Methyl-1,2-epoxycyclohexene

Another system of naming is Oxirane system. Numbering starts with the heteroatom and going in the direction to give the lowest substituent number, *e.g.*,



2,2-Diethyl-3-*iso*-propyloxirane

Table I includes other cyclic ether having 4-6 numbered ring system.

S. No.	Ring size	Common name of the class	General structure	Example and name
1	4	Oxetane		 2-Ethyl-3,3-dimethyloxetane
2	5	Oxolane (aliphatic) Furan (aromatic)	 	 Oxolane  3-Methylfuran
3	6	Oxanol (aliphatic) Pyran (aromatic)	 	 Oxane  4-methylpyran

Isomerism in Ethers. Aliphatic ether show two types of isomerism:

(i) **Functional isomerism with alcohols**. Ethers are isomeric with alcohols as:

Ethers	Alcohols
$H_3C-O-CH_3$	CH_3CH_2OH
Methyl ether	Ethanol
$H_5C_2-O-C_2H_5$	$CH_3CH_2CH_2CH_2OH$
Ethyl ether	Butan-1-ol

(ii) **Metamerism**. This type of isomerism arises due to difference in the distribution of carbon atoms in the form of alkyl groups about the oxygen atom.

For example, the formula $C_4H_{10}O$ represents of following isomeric ethers:

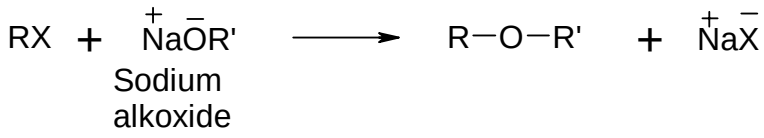
$H_3C-O-C_3H_7$ Methyl propyl ether

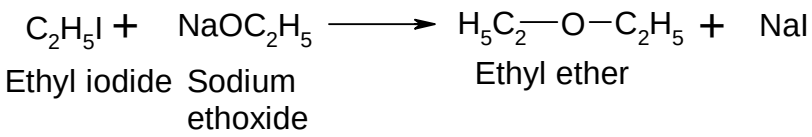
$H_5C_2-O-C_2H_5$ Ethyl ether

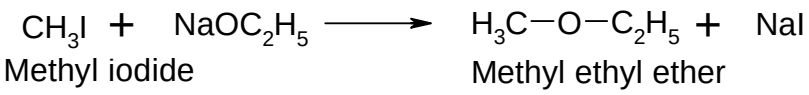
Methods of Preparation. Ethers can be prepared by the following general methods. Diethyl ether is the most important member of the series and commonly named as 'ether'.

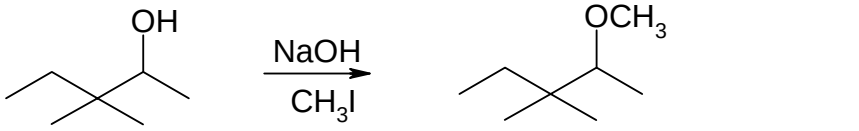
(1) **From alkyl halides** (Williamson's synthesis).

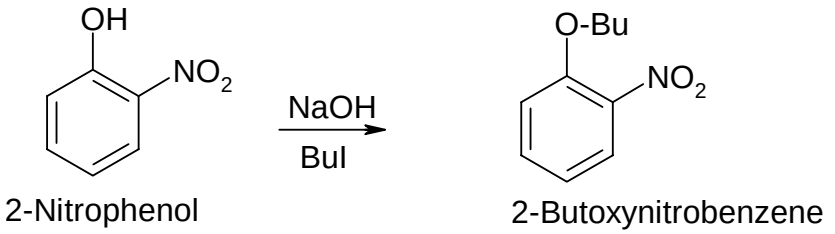
(a) For aliphatic ethers, the suitable alkyl halide is heated with sodium or potassium alkoxide.



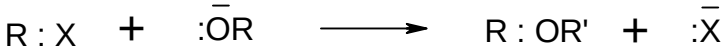




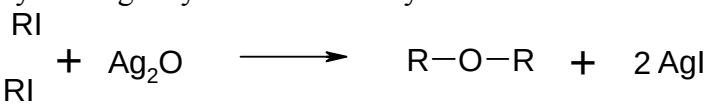


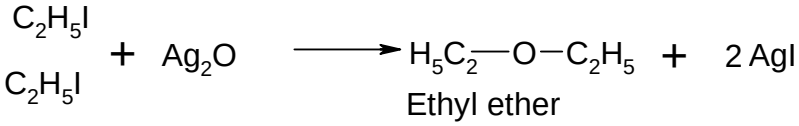


Mechanism. The Williamson's synthesis involves nucleophilic substitution of halide ion by alkoxy ion.

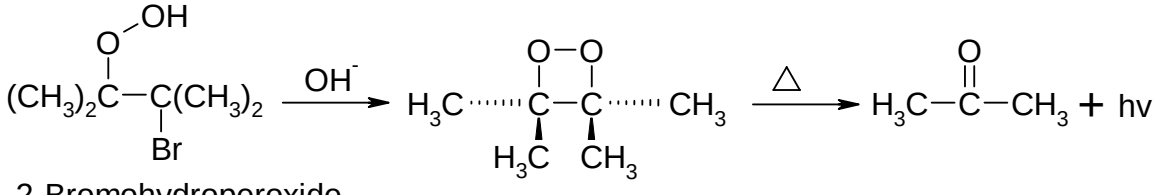


(b) By heating alkyl halides with dry silver oxide.



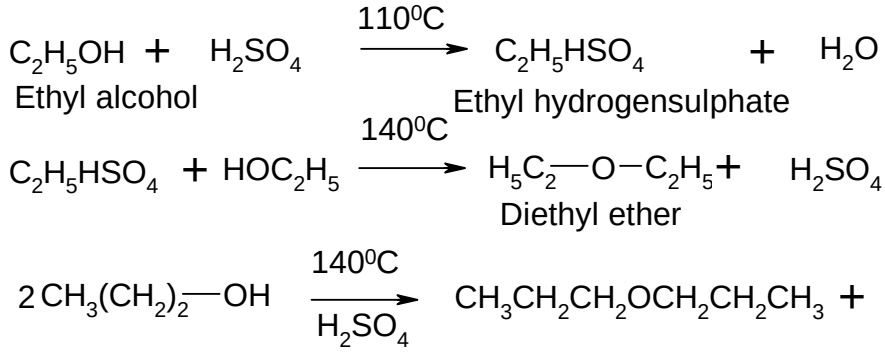


A recent application of Williamson's synthesis is an intramolecular Williamson type reaction in which a 2-bromohydroperoxide cyclizes to give 1,2-dioxocyclobutane (1,2-dioxetane). This compound decomposes to the corresponding carbonyl compounds with emission of light (Chemiluminescence). These dioxacyclobutanes are responsible for the bioluminescence of certain species like firefly, glowwarm in nature.

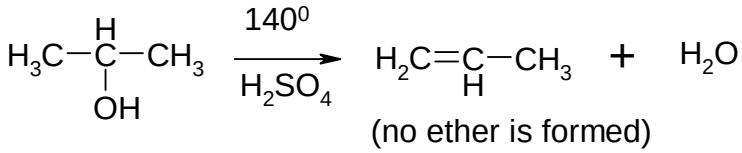


(2) **From monohydric alcohols**.

(a) By dehydration of alcohol by heating with concentrated sulphuric acid at 140°C. This method is of industrial importance.



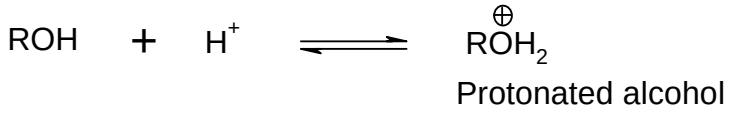
If the alcohol is hindered or tempers high, elimination occurs.

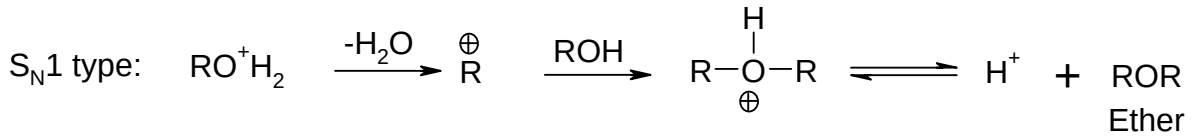


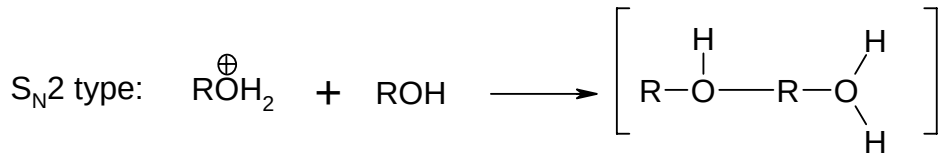
Alcohol is continuously added to keep its concentration in excess.

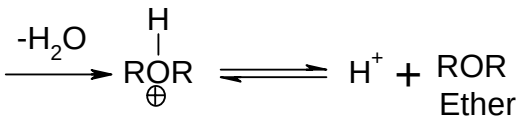
Mechanism.

It is also an example of nucleophilic substitution with the protonated alcohol as substrate and a second molecule of alcohol as nucleophile. For secondary and tertiary alcohols, the reaction is of S_N1 type since the protonated alcohol loses water before attack by the second molecule of alcohol. For primary alcohols, the reaction is of S_N2 type.



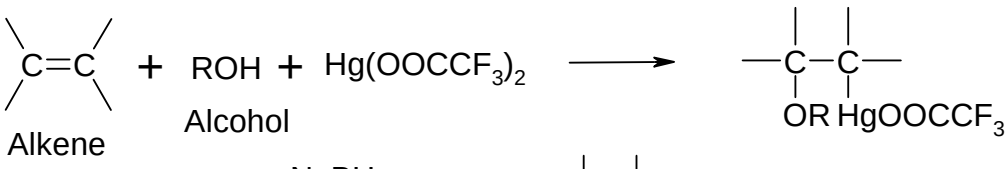


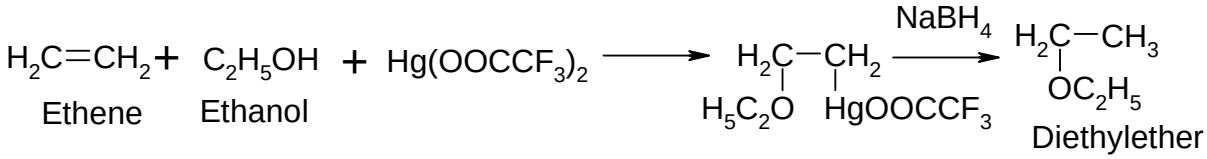




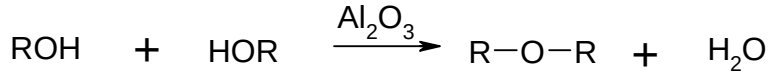
(b) **Alkoxymercuration-demercuration method**.

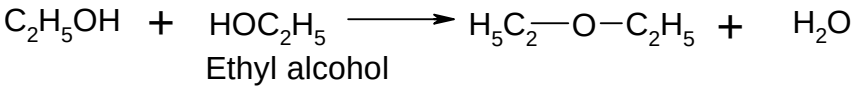
Alkenes react with mercuric trifluoroacetate in the presence of an alcohol to give alkoxymercurial compounds which on reduction yield ethers.





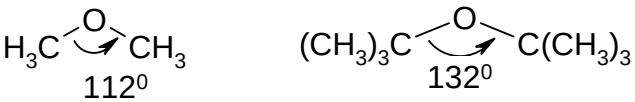
(c) By catalytic dehydration. Vapours of primary alcohols are passed over alumina (Al_2O_3) at 240-260°C.



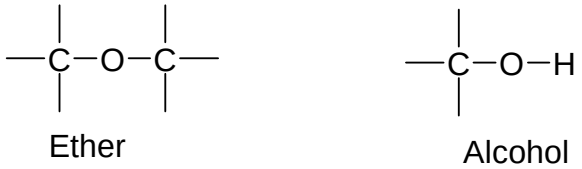


Physical Properties.

(i) The two C-O bond in ethers are at an angle of about 110-132° (not linear) depending upon the alkyl substitution, hence the dipole moments of two C-O bonds donot cancel each other. Consequently, ethers possess a small net dipole moment (*e.g.*, 1.18D for diethyl ether).



This weak polarity does not appreciably effect the boiling point of ethers, which are about the same as those of the corresponding alkanes (of comparable molecular weight) and much lower than those of isomeric alcohols, *e.g.*, methyl *n*-pentyl ether (100°C), *n*-heptane (98°C) and *n*-hexyl alcohol (157°C). The hydrogen bonding that holds alcohol molecule strongly together is not possible in ethers since they contain the hydrogen bonded only to carbon and not to oxygen as in alcohols:

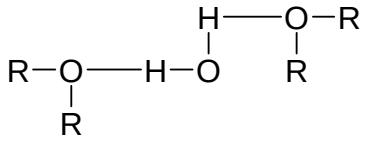


(ii) All common ethers are colourless, volatile and pleasant smelling liquids. Only dimethyl ether is gas at ordinary temperature.

(iii) They are highly inflammable.

(iv) They are lighter than water.

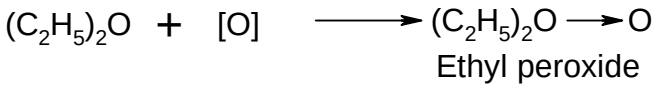
(v) They are only slightly soluble in water but are freely soluble in organic solvents like alcohol, chloroform, etc. The slight solubility of lower ethers in water is due to hydrogen bonding between water and ether molecules.



Chemical Properties.

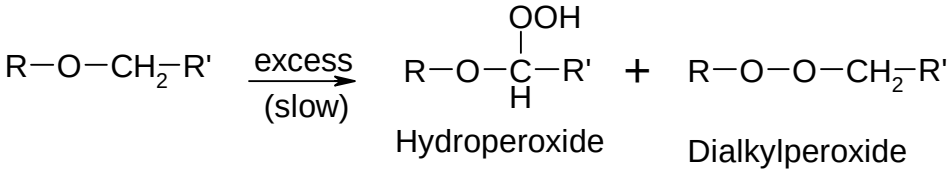
A. **Addition reactions**.

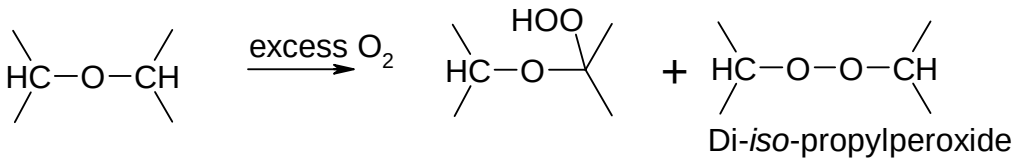
(i) **Formation of peroxide**. Ethers are chemically inert. Aliphatic ethers are not effected by oxidizing agent like $KMnO_4$ and $K_2Cr_2O_7$ but on prolonged contact with air or ozone they form peroxides. These peroxides are unstable and explode. Hence care should be taken to free ethers from peroxides before distillation.



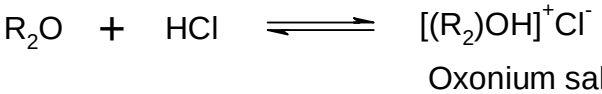
The presence of peroxide can be tested by shaking it with an aqueous solution of ferrous ammonium sulphate and potassium thiocyanate, when a red colour is obtained. To remove peroxide, the ether sample should be washed with a solution of ferrous ions and distilled with conc. H_2SO_4.

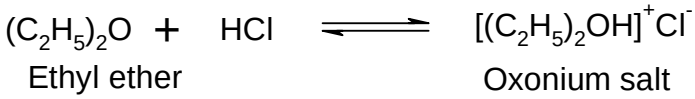
When ethers are stored in the presence of atmospheric oxygen, they slowly oxidize to produce hydroperoxides and dialkyl peroxides, both are explosive. Such a spontaneous oxidation by atmospheric O_2 is called an auto-oxidation.





(ii) **Formation of oxonium compounds**. Ethers are neutral to litmus but possess basic properties as they are capable of combining with strong mineral acids forming oxonium salt. Thus:

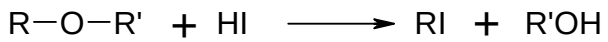


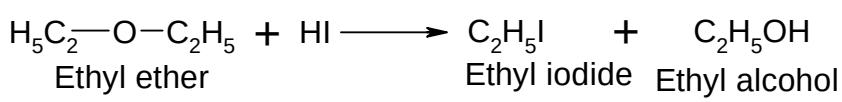


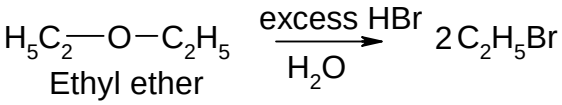
B. **Fission reactions**.

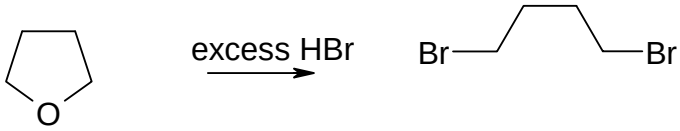
(i) **Cleavage by acids (Halogen acids)**.

The ether linkage gets broken only under vigorous conditions such as concentrated acids like HI or HBr at high temperature. In the first stage of cleavage, a molecule of an alcohol and an alkyl halide is formed. Under more drastic conditions, a second molecule of alkyl halide is formed.



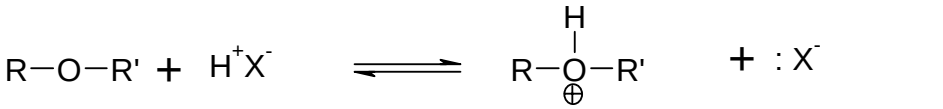


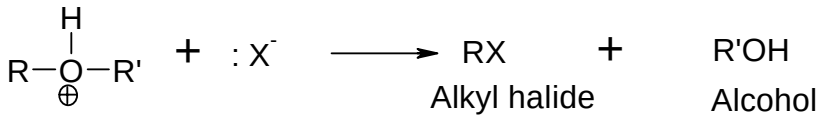




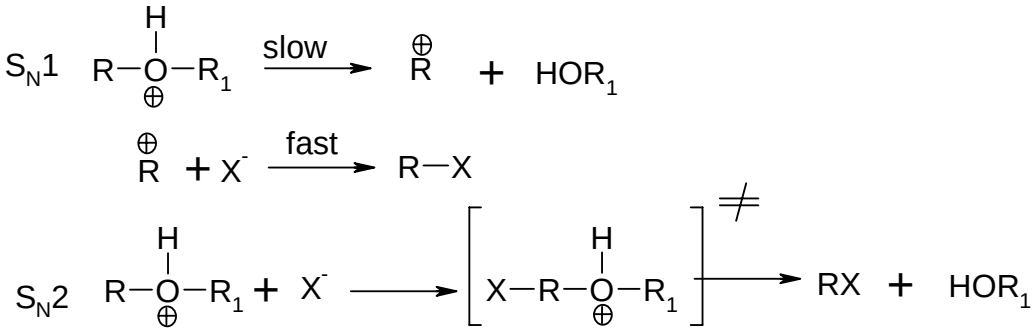
HBr gives similar reaction. The method provides a good method for establishing the structure of a given ether.

Mechanism. The initial reaction between an ether and an acid is the formation of the protonated ether. Cleavage involves nucleophilic attack by halide ion on the protonated ether, with displacement of the weakly basic alcohol molecule.

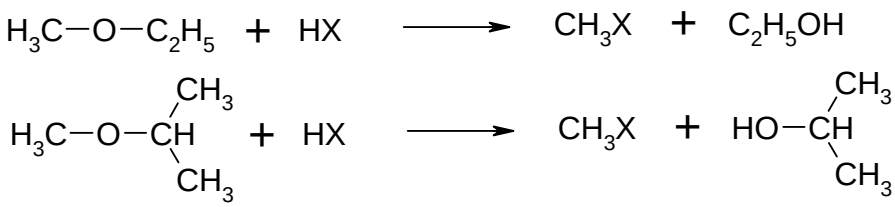




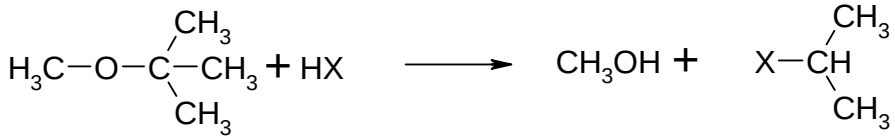
Reaction of the protonated ether with halide ion, similar to that of a protonated alcohol, can proceed by either S_N1 or S_N2 mechanism depending upon conditions and the structure of the ether. A primary alkyl group gives S_N2 displacement while a tertiary alkyl group gives S_N1 displacement.



The attack of halide ion is preferred on the smaller alkyl group, for *e.g.*,



However, the situation become reversed in the following example:



(ii) With conc. H_2SO_4. On heating a mixture of ether and conc. H_2SO_4, cleavage takes place to form alcohol and alkyl hydrogen sulphate.

$$R-O-R + H_2SO_4 \longrightarrow \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl hydrogensulphate}}{ROSO_3H}$$

$$\underset{\text{Ethyl ether}}{H_5C_2-O-C_2H_5} + HOSO_3H \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Ethyl hydrogensulphate}}{C_2H_5HSO_4}$$

(iii) With dilute sulphuric acid under pressure and high temperature. When ethers are heated with dilute H_2SO_4 under pressure, cleavage takes place and ethers are hydrolysed to corresponding alcohols.

$$R-O-R + H-O-H \xrightarrow{\text{dil. } H_2SO_4} 2\ ROH$$

$$\underset{\text{Ethyl ether}}{H_5C_2-O-C_2H_5} + \underset{\text{Steam}}{HOH} \xrightarrow{\text{dil. } H_2SO_4} \underset{\text{Ethyl alcohol}}{2\,C_2H_5OH}$$

(iv) Halogenation. Halogens react with ethers to give substitution products and the extent of halogenation is dependent on the conditions of reaction.

$$H_3C-CH_2-O-CH_2-CH_3 \xrightarrow[\text{dark}]{Cl_2} H_3C-\underset{\displaystyle Cl}{\underset{|}{CH}}-OCH_2CH_3$$

-Chloroethyl ether

$$\xrightarrow[\text{dark}]{Cl_2} H_3C-\underset{\displaystyle Cl}{\underset{|}{CH}}-O-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

-Dichloroethyl ether

$$CH_3CH_2-O-CH_2-CH_3 \xrightarrow[\text{light}]{\text{Excess } Cl_2} Cl_3C\overset{\displaystyle Cl}{\overset{|}{C}}-O-\overset{\displaystyle Cl}{\overset{|}{C}}CCl_3$$

Decachloroethyl ether

(v) **Action with phosphorus pentachloride**. Ethers react with PCl_5 in hot, while in cold there is no action.

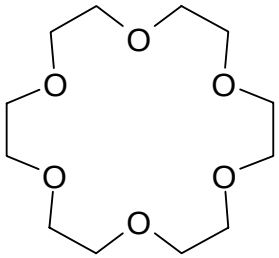
$$\underset{\text{Ether}}{C_2H_5OC_2H_5} + PCl_5 \xrightarrow{\text{heat}} \underset{\text{Ethyl chloride}}{2\,C_2H_5Cl} + POCl_3$$

(vi) Ethers react with CO at 125-180°C and at a pressure of 500 atmospheres, in the pressure of BF_3 plus a little water.

$$R_2O + CO \xrightarrow{\text{water}} RCO_2R$$

Crown ethers. The oxygen in ethers, as in alcohol is basic, i.e., its lone pair of electrons can coordinate to electron deficient metals, such as magnesium in Grignard reagents. Cyclic polyethers that contain multiple functional groups based on the 1,2-ethanediol unit are called crown ethers, so named because the molecules adopt a crownlike conformation in the crystalline state. For example, polyether 18-crown-6, where the number 18 refers to the total number of atoms in the ring, and 6 to the number of oxygens. The most striking feature of these crown ethers is their solvation power, in which several oxygen atoms may surround metal ions. The structure of crown ether enables them to function as strong cation binders, including cations found in ordinary salts. In this way, crown ethers can render the salts soluble in organic solvents. For example, potassium permanganate, a deep-violet

solid, completely insoluble in benzene, is ready dissolved in benzene in presence of 18-crown-6. The resultant solution allows oxidations in organic solvents. Dissolution is possible by effective solvation of the metal ion by six crown oxygens. The size of "cavity" in the crown ether can be tailored to allow the selective binding of only certain cations.



18-crown-6

Uses.

Ethers generally find use as solvents. Ethyl ether, in addition, was earlier used as anaesthetic agent but now a days ethers like ethrane and isoflurane have replaced it. For use in Grignard's reagent the ether must be free of traces of water and alcohol. Thus absolute ether is obtained by distilling ether with conc. H_2SO_4 and storing it over sodium metal. The anaesthetic ether is obtained by treating the industrial producer repeatedly with solutions of sodium bisulphate, sodium carbonate, washing with water and drying over sodium hydroxide.

Host-Guest Chemistry

Host-Guest chemistry describes complexes that are composed of two or more molecules or ions held together in unique structural relationships by hydrogen bonding or by ion pairing or by Van der Waals forces other than those of full covalent bonds.

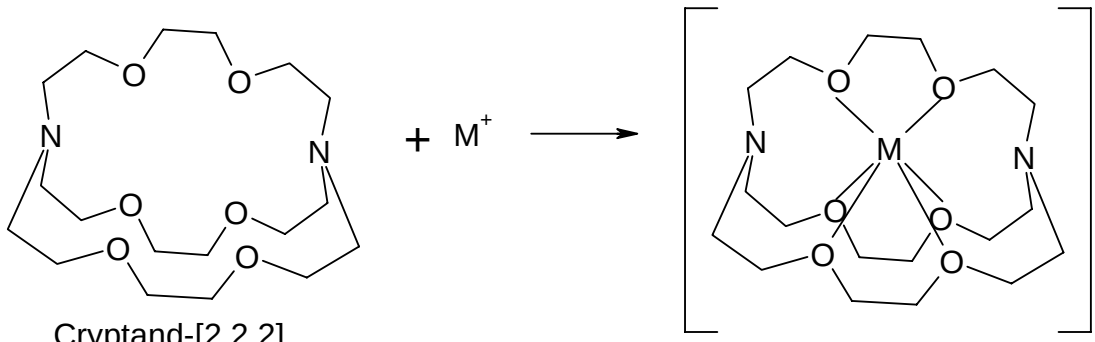
The host component is defined as an organic molecule or ion whose binding sites converge in the complex and the guest component is defined as any molecule or ion whose binding sites diverge in the complex. For example, in immunology, the host is the antibody while the guest is the antigen.

Host-guest chemistry is observed in:

- Cryptands
- Inclusion compounds
- Clathrates
- Intercalation compounds

Cryptands. Cryptands are a family of synthetic bi- and polycyclic multidentate ligands for a variety of cations The term cryptand implies that this ligand binds substrates in a crypt, interring the guest as in a burial. These molecules are three dimensional analogues of crown ethers but are more selective, and complex the guest ions more strongly. The resulting complexes are lipophilic.

The most common and most important cryptand is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$; IUPAC name of which is 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane. This compound is termed cryptand-[2.2.2], where the numbers indicate the number of ether oxygen atoms (and hence binding sites) in each of the three bridges between the amine nitrogen "caps". Many cryptands are commercially available under the trade name "Kryptofix."



Cryptand-[2.2.2]

A cryptate complex

The three-dimensional interior cavity of a cryptand provides a binding site - or hook - for "guest" ions. The complex between the cationic guest and the cryptand is called a cryptate. Cryptands form complexes with many "hard cations" including NH_4^+, lanthanides, alkali metals, and alkaline earth metals. In contrast to typical crown ethers, cryptands bind the guest ions using both nitrogen and oxygen donors. Their three-dimensional encapsulation mode confers some size-selectivity, enabling discrimination among alkali metal cations (e.g. Na^+ vs. K^+).

Cryptands are more expensive and more difficult to prepare but offer much better selectivity and strength of binding than other complexants for alkali metals, such as crown ethers. They are able to extract otherwise insoluble salts into organic solvents. Cryptands increase the reactivity of anions in salts since they effectively break up as ion-pairs. They can also be used as phase transfer catalysts by transferring ions from one phase to another. Cryptands enable the synthesis of the alkalides and electrides.

Inclusion Compound. In host-guest chemistry an inclusion compound is a complex in which one chemical compound *the host* forms a cavity when molecules of a second compound *i.e.*, *the guest* are located. The definition of inclusion compounds is very broad, it extends to channels formed between molecules in a crystal lattice in which guest molecules can fit. If the spaces in the host lattice are enclosed on all sides so that the guest species is 'trapped' as in a cage, such compounds are known as clathrates. In molecular encapsulation a guest molecule is actually trapped inside another molecule. For example, inclusion complexes are formed between cyclodextrins and ferrocene.

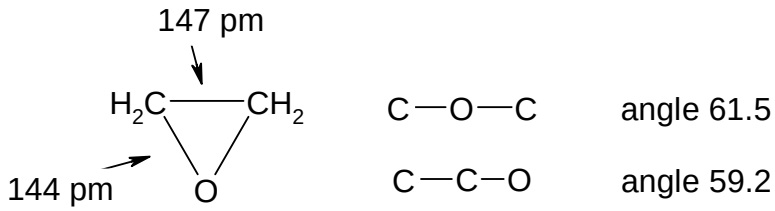
Clathrates. A clathrate or clathrate compound or cage compound is a chemical substance consisting of a lattice of one type of molecule, trapping and containing a second type of molecule. (The word comes from the Greek *klethra*, meaning "bars".) For example, a clathrate hydrate involves a special type of gas hydrate that consists of water molecules enclosing a trapped gas. Prospectors believe that compounds on the sea bed have trapped large amounts of methane in similar configurations. A clathrate therefore is a material which is a weak composite, with molecules of suitable size captured in spaces which are left by the other compounds. Clathrate complex used to refer only to the inclusion complex of hydroquinone, but recently it has been adopted for many complexes which consist of a host molecule (forming the basic frame) and a guest molecule (set in the host molecule by interaction). The clathrate complexes are various and include, for example, strong interaction *via* chemical bonds between host molecules and guest molecules, or guest molecules set in the geometrical space of host molecules by weak intermolecular force.

Intercalation Compounds. Intercalation is a term used in host-guest chemistry for the reversible inclusion of a molecule (or group) between two other molecules (or groups). The host molecules usually comprise some form of periodic network. Intercalation is found in DNA intercalation and in graphite intercalation compounds.

A large class of molecules intercalates into DNA - in the space between two adjacent base pairs. These molecules are mostly polycyclic, aromatic, and planar, and therefore often make good nucleic acid stains. Intensively studied DNA intercalators include ethidium, proflavin, daunomycin, doxorubicin, and thalidomide. DNA intercalators are used in chemotherapeutic treatment of concern, to inhibit DNA

Epoxides

Epoxides like cyclopropanes have significant angle strain. They tend to undergo reactions that open three-membered ring by cleaving one of the carbon-oxygen bonds.They have large dipole moments (1.7-1.8 D). Incorporating an oxygen atom into a three-membered ring requires its bond angle to be seriously distorted from the normal tetrahedral value. In ethylene oxide, the bond angle is 61.5.



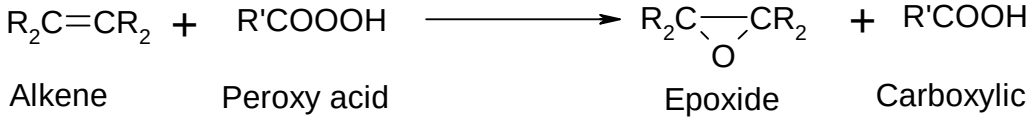
Methods of preparation. There are two main methods for the preparation of epoxides:

(i) Epoxidation of alkenes by reaction with peroxy acids.

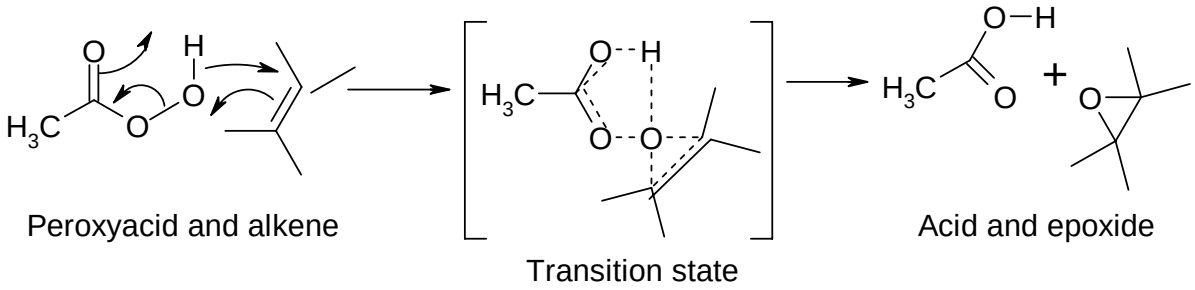
(ii) Base-promoted ring closure of vicinal halohydrins.

(i) **Epoxidation of alkenes**

The reaction of an alkene with an peroxyacid is called epoxidation.

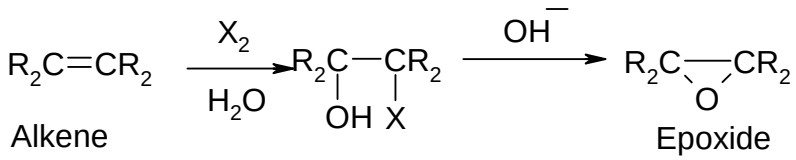


Epoxidation is a stereospecific *syn* addition. A commonly used peroxy acid is peroxyacetic acid (CH_3COOH). Substituents that are *cis* to each other in the alkene remain *cis* in the epoxide, while the substituents that are *trans* in the alkene remain *trans* in the epoxide. The mechanism of alkene epoxidation is believed to be a concerted process involving a single bimolecular elementary step.



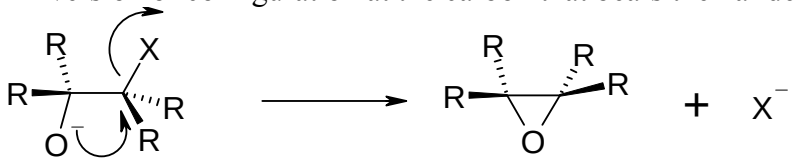
(ii) **Base-promoted ring closure of vicinal halohydrins.**

Halohydrins are readily converted to epoxides on treatment with base. Halohydrins are themselves prepared from alkenes.



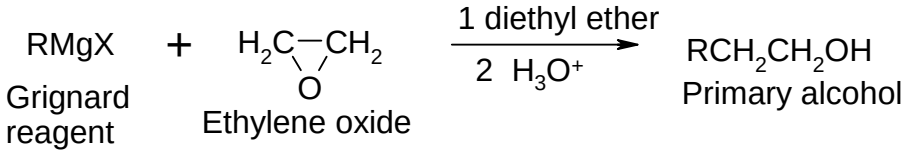
Reaction with base brings the alcohol function of the halohydrin into equilibrium with its corresponding alkoxide. The next step is the attack of the alkoxide oxygen on the carbon that bears the halide leaving group, giving an epoxide. Overall, the stereochemistry of this method is the same as that observed in the peroxyacid oxidation of alkenes. Substituents that are *cis* to each other in the alkene remain *cis* in the epoxide because formation of halohydrin

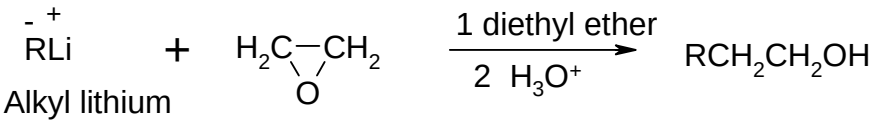
involves *anti* addition, and the ensuing the intramolecular nucleophilic substitution reaction takes place with inversion of configuration at the carbon that bears the halide bearing group.

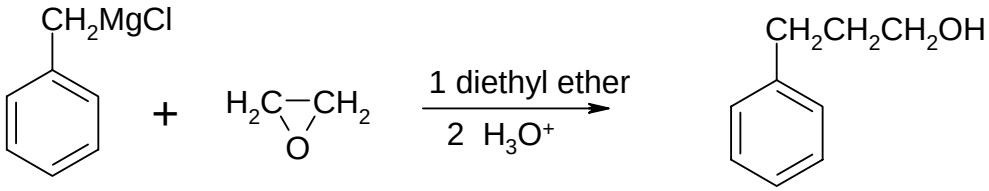


Reactions of epoxides

The most striking chemical property of epoxides is their greater reactivity towards nucleophilic reagents as compared to simple ethers. Epoxide reacts rapidly with nucleophiles under conditions in which other ethers are inert. This enhanced reactivity results from large angle strain of epoxides. Reactions that open the ring relieve this strain.







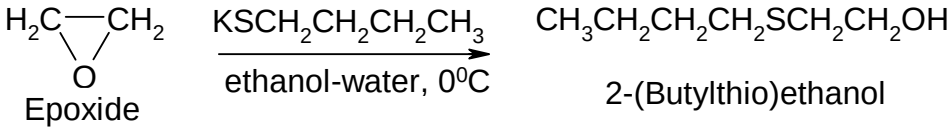
Nucleophiles other than Grignard reagents also open epoxide rings.These reactions are carried out in two ways.

(i) Anionic nucleophiles in neutral or basic solution

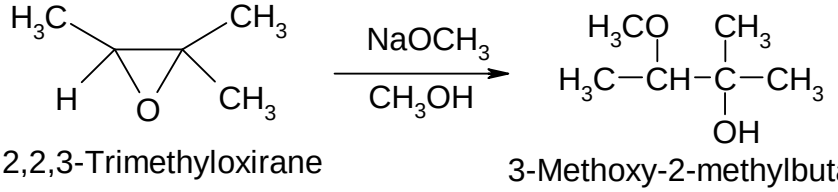
(ii) Acid catalyzed ring opening

(i) **Anionic nucleophiles in neutral or basic solution**

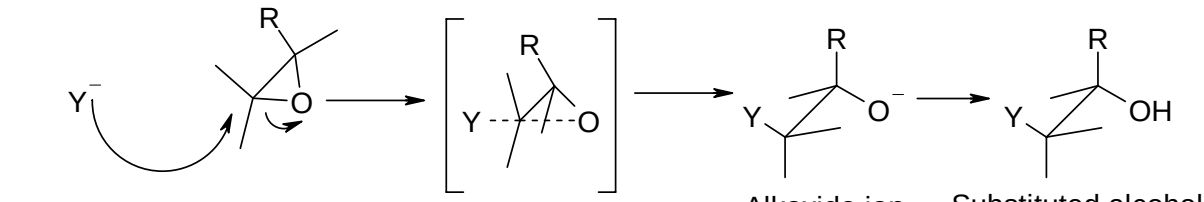
Nucleophilic ring opening of epoxides has many of the features as of S_N2 reaction. Inversion of configuration is observed at the carbon at which substitution occurs.



Unsymmetrical epoxides are attacked at the less substituted, less sterically hindered carbon of the ring.The nucleophile attacks the less crowded carbon from the side opposite the carbon-oxygen bond.

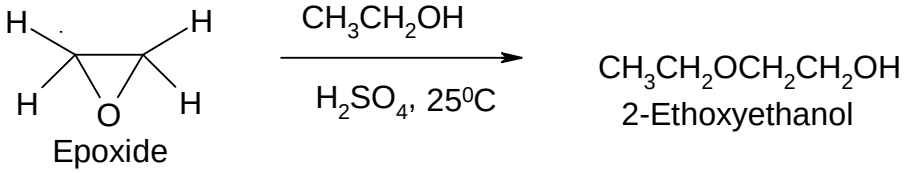


Bond formation with the nucleophile accompanies carbon-oxygen bond breaking and a substancial portion of the strain in the three –membered ring is relieved as it begins to open at the transition state.The initial product is an alkoxide anion, which rapidly abstracts a proton from the solvent to give β-substituted alcohol as the isolated product.



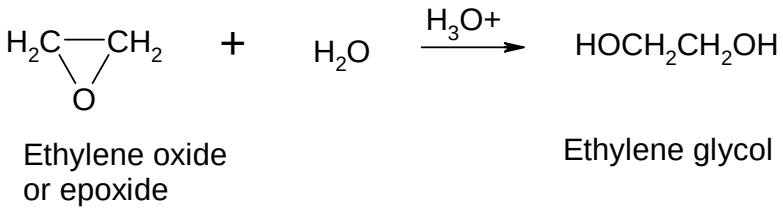
(ii) **Acid catalyzed ring opening**

Epoxides can also undergoes ring opening to give 2-substituted derivatives by involving an acid an a reactant, or under conditions of acid catalysis:

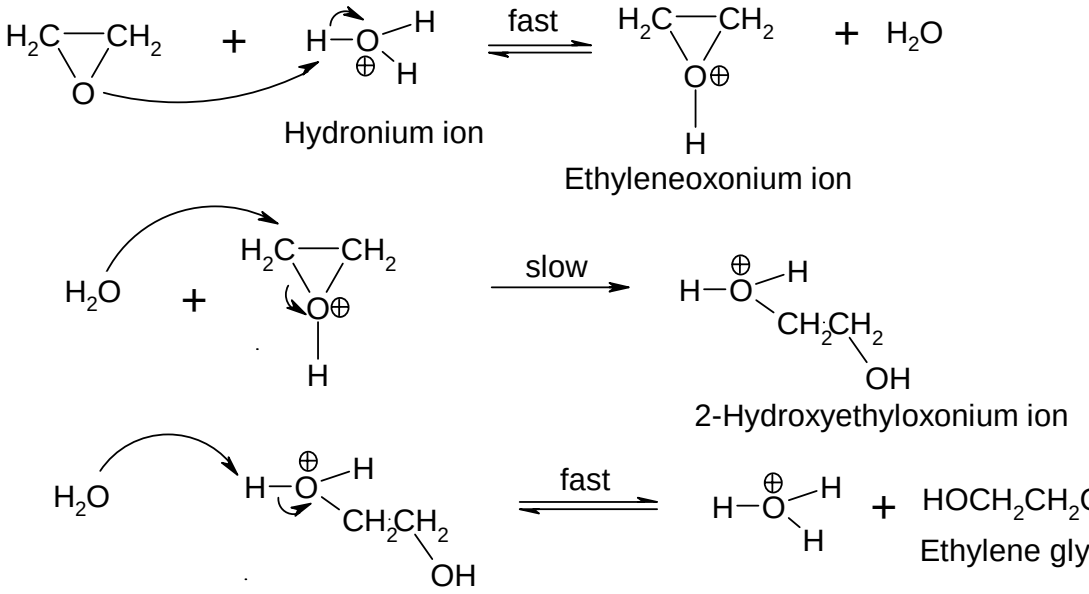


In this case, the species that is attacked by the nucleophile is not the epoxide itself but rather its conjugarte acid. The transition state for ring opening has a fair measure of carbocation character. Breaking of the ring carbon-oxygen bond is more advanced than formation of the bond to the nucleophile. Because carbocation character develops at the transition state, therefore substitution is favoured at the carbon that can better support a developing positive charge.

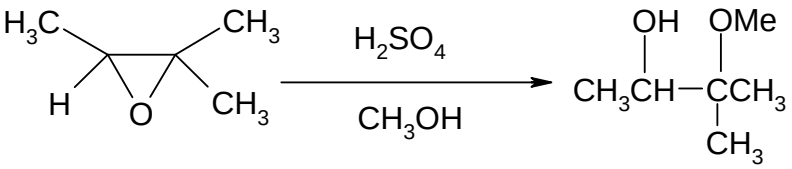
Reaction :



Mechanism:

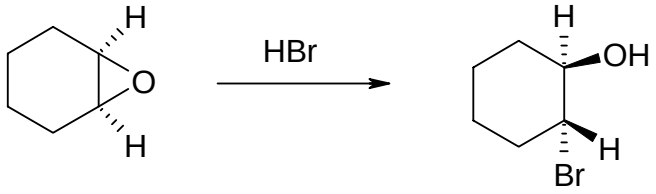


Thus in this case substitution promotes at the position that bears the greater number of alkyl groups.



2,2,3-Trimethyloxirane

3-Methoxy-3-methylbutan-2-ol

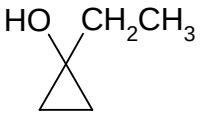


1,2-Epoxycyclohexane

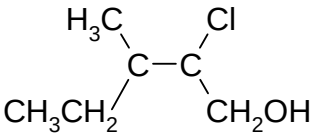
trans-2-Bromocyclohexanol

QUESTIONS

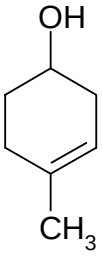
1. Give the systematic (IUPAC) name for the following alcohols.



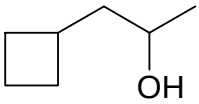
(a)



(b)

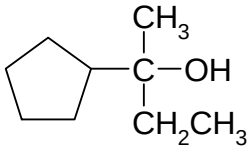


(c)

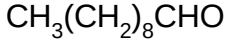


(d)

2. Write structures of the compounds whose IUPAC names are as follows:
   (a) Cyclohexylmethanol
   (b) 3,5-Dimethylhexane-1,3,5-triol
   (c) 1-Phenylpropan-2-ol
   (d) 2-Methylbutan-2-ol
3. What do you understand by the term "Hydroboration-oxidation"? Give the orientation and mechanism of this reaction.
4. Predict which is more soluble in water (a) hexan-1-ol or cyclohexanol (b) heptan-1-ol or 4-methylphenol.
5. How is ethanol prepared? Give properties and uses of ethanol.
6. Show how you would synthesize the following alcohols from compound containing not more than 5 carbon atoms.

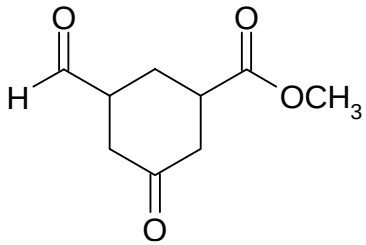


7. Predict the product, which you would expect from the reaction of $NaBH_4$ with the following compounds.

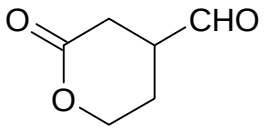


(a)

(b)



(c)

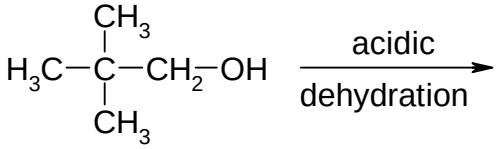


(d)

8. Briefly define each term and give an example: (a) PCC oxidation, (b) chromic acid oxidation and (c) tosylate esters.
9. Write short notes on:
   (i) Hydrogen bonding in alcohols.
   (ii) Dehydration of butan-2-ol.
   (iii) Oxymercuration-demercuration.
10. Discuss the following properties of alcohols:
   (i) Ester formation.
   (ii) Reaction with halogen acids.
   (iii) Reaction with phosphorus trihalides.
   (iv) Reaction with alkali metals.
11. Draw the structure of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.
12. What is fermentation? How is alcohol manufactured from molasses and starch?
13. How will convert

(i) Methanol into ethanol and vice versa.
(ii) Ethanol into propane and vice versa.
(iii) A primary alcohol into a secondary alcohol.
(iv) A secondary alcohol into a tertiary alcohol.
(v) A primary alcohol into a tertiary alcohol.

14. Why are alcohols acidic in nature? Compare and explain the acidic nature of 1°, 2° and 3° alcohols.
15. Give the mechanism of the reaction of the Grignard's reagent with carbonyl compounds giving alcohols.
16. Discuss the basis of the Lucas test for differentiating between 1°, 2° and 3° alcohols.
17. (a) Why the boiling points of alcohols are much higher than those of the corresponding alkanes?
(b) How will you synthesise:
(i) butan-1-ol and
(ii) butan-2-ol from butane?
(c) How can you distinguish between a primary, secondary and tertiary alcohol using Victor Meyer test?
18. Briefly discuss the mechanism of dehydration of alcohols.
19. Predict the major product of the following reactions showing its mode of formation.



20. Predict the products of the following reactions:

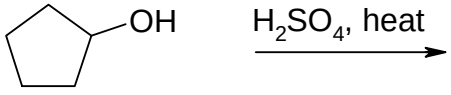
(i) Ethyl alcohol —(Conc. Hydrochloric acid, room temperature)→

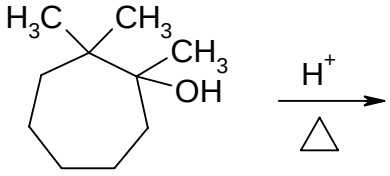
(ii) Ethyl alcohol —($KMnO_4$)→

(iii) *tert*-Butyl alcohol —(Conc. Hydroiodic acid, room temperature)→

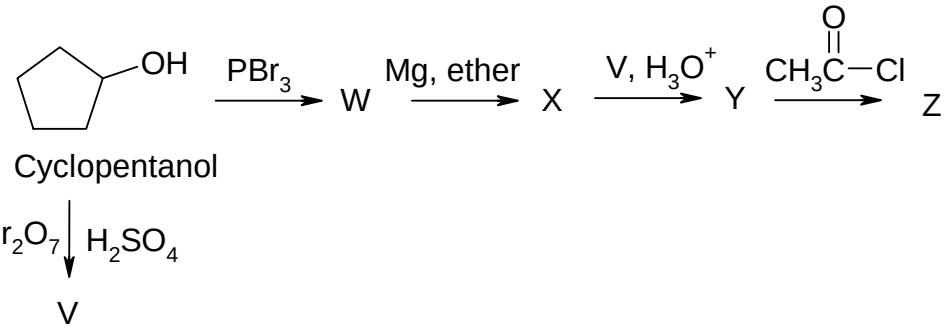
(iv) Cyclohexanol —(Conc. boiling Hydrochloric acid)→

(v) 1-Methylcyclohexanol —(Sulphuric acid)→

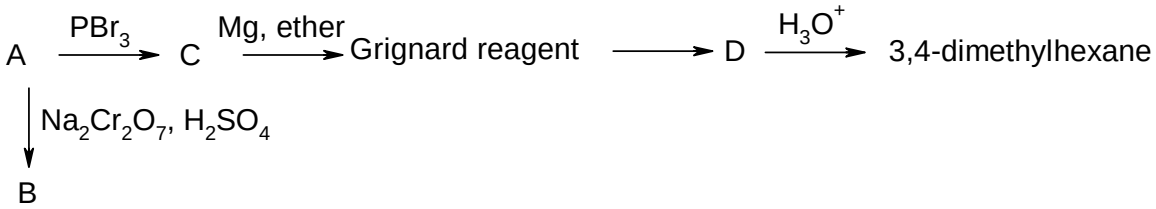
(vi) 

(vii) 

21. Explain why reactions of ammonia with ethyl chloride proceeds readily to give ethyl amine, where as with ethyl alcohol it does not.
22. Esterification is a reversible reaction. Explain with its mechanism?
23. Give the structure of the intermediates and products.



24. Give the structure of the intermediates and products. Product A is optically active alcohol.



25. How are the following conversion carried out?

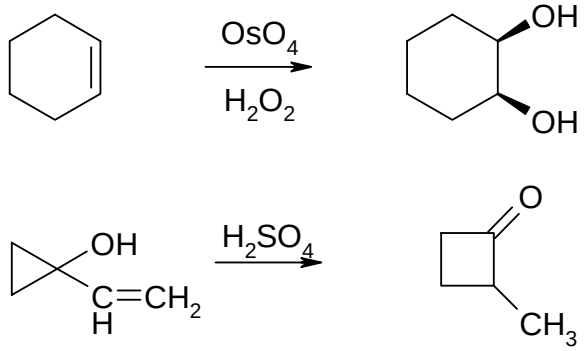
(a) Benzyl chloride ⟶ Benzyl alcohol
(b) Ethyl chloride ⟶ Propan-1-ol
(c) Methyl bromide ⟶ 2-Methylpropan-2-ol
(d) Propane ⟶ Propan-2-ol
(e) Benzoic acid ⟶ Benzaldehyde

26. An organic compound having molecular formula $C_5H_{12}O$ gives a ketone on oxidation. On dehydration, an alkene is formed, which on oxidation gives acetone and acetic acid. Assign the structure to the compound and the reaction product.

27. Compound A, $C_7H_{10}O_2$ gave compound B, $C_{11}H_{20}O_4$ on treatment with acetyl chloride in pyridine. Dehydration of A gave compound C, C_7H_{12} , which gave no Diels-Alder adduct with maleic anhydride. Hydrogenation of C gave D, C_7H_{16} . Compound C readily decolorized bromine, yielding E which in turn gave F, C_7H_8 , on treatment with alcoholic KOH. Compound F gave precipitate with $[Ag(NH_3)_2]^+$ and liberated 2 moles of methane on treatment with CH_3MgI. Hydrogenation of F yielded D. Compound C was oxidized by $KMnO_4$ to compound G (a diacid) which readily lost CO_2 , giving compound H. Treatment with isopropyl magnesium bromide first with CO_2 & then with H_2O gave H. Identify A to H.

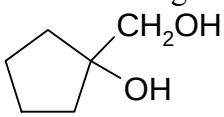
28. What are di- and trihydric alcohols? Give one example of each and four properties of each.

29. Predict the mechanism

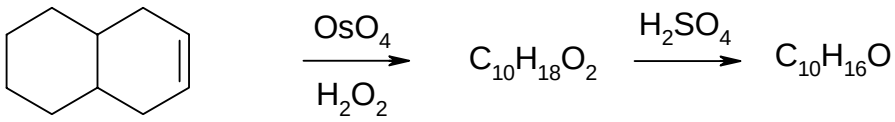


30. Predict the products formed by periodic acid cleavage of the following diols:

(a) $CH_3CH(OH)CH(OH)CH_3$ (b)

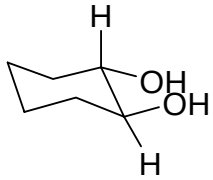


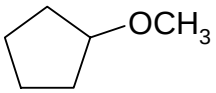
31. Identify the reaction and products in the scheme

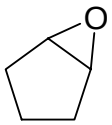


32. Give common names for the following compounds

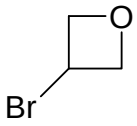
(a) $(CH_3)_2CH-O-CH(CH_3)CH_2CH_3$ (b) $Ph-O-C_2H_5$

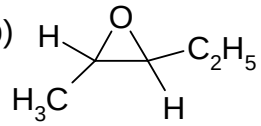
(c) 

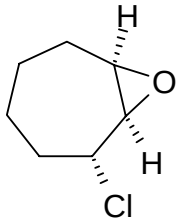
(d) 

(e) 

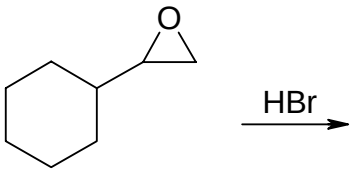
33. Give IUPAC names for the following compounds

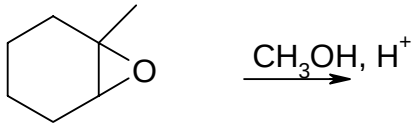
(a) 

(b) 

(c) 

34. Predict the products

(a) 

(b) 

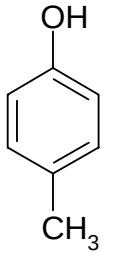
(c) $t\text{-}BuO^-K^+ + n\,BuBr \longrightarrow$

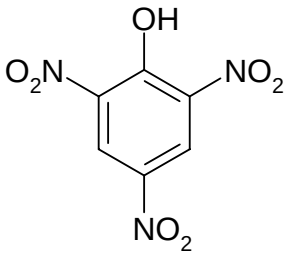
35. How is glycerol prepared on large scale? Give its three uses.

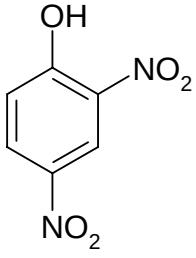
36. What happens when glycerol reacts with (i) sodium metal (ii) HCl (iii) heated with $KMnO_4$ (iv) Conc. HNO_3 (oxidation) (v) $Bi(NO_3)_3$ (vi) oxalic acid (vii) acetyl chloride (viii) PCl_5 under appropriate conditions.

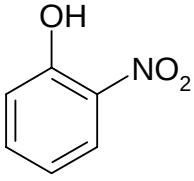
37. Complete the following reactions:
    (a) 1,2-Dichloroethane + aq, KOH solution.
    (b) Ethane + alkaline $KMnO_4$ solution.
    (c) Ethane + HOCl.
    (d) Glycol + sodium metal.
    (e) Glycol + PCl_5.
    (f) Glycol + acetyl chloride.
    (g) Glycol is oxidized.
    (h) Glycol is heated with fused $ZnCl_2$.
    (i) Glycol + PI_3.
    (j) Glycol + acetaldehyde in acidic medium.

38. When one mole of each of the following compounds is treated with HIO_4, what will be the product and how many moles of HIO_4 would be consumed.
    (i) $CH_3CHOHCH_2OH$
    (ii) $HOCH_2CHOHCHOHCH_3$
    (iii) $HOCH_2CHOHCHO$
39. Assign structures to A, B and C in the following:
    (i) A + one mole of $HIO_4 \rightarrow CH_3COCH_3 + HCHO$
    (ii) $B + 3HIO_4 \rightarrow 2HCOOH + 2HCHO$
    (iii) $C + 2HIO_4 \rightarrow 2HCOOH + HCHO$
40. Complete the following equations:
    1. Glycol distilled with conc. H_2SO_4.
    2. Propene + chlorine at 500°C.
    3. 1,2,3-trichloropropane + aq. KOH solution.
    4. Glycerol + PCI_5.
    5. Glycerol heated with HI.
    6. Glycerol + Hydrochloric acid.
    7. Glycerol heated with $KHSO_4$.
    8. Glycerol + conc. HNO_3.
    9. Glycerol + acetic anhydride.
41. What are ethers? Comment briefly on their structure.
42. How are ethers prepared? Give their general properties and uses. Select an important member of ether series to illustrate your answer.
43. Write mechanism on cleavage of ether by acids.
44. (a) Explain why ethers are slightly soluble in water.
    (b) Why ethers are slightly polar? Does this polarity affect their b.p. as compared to alkanes?
45. Give two methods with mechanism for the preparation of methyl ether.
46. (a) Briefly describe the chemistry of industrial preparation of ethyl ether and its important users.
    (b) Give important reactions of ethers.
47. Out of the following two methods for synthesizing methyl tertiary-butyl ether which one is preferable and why?
    (k) Sodium methoxide + *tert*-butyl chloride
    (l) Sodium *tert*-butoxide + methyl chloride
48. Indicate the most probable mechanism for the following reactions.
    (i) Di-*iso*-propyl ether and hot hydrobromic acid
    (ii) Dimethyl ether and hot hydrobromic acid.
49. Why Phenols are more acidic than alcohols?
50. Arrange the following compounds in increasing order of their acidic nature.









51. How will you carry out the following conversions
    a. Phenol → benzene
    b. Phenol → aniline
    c. Phenol → anisole
    d. Phenol → phenolphthalein
    e. Phenol → Salicyaldehyde

f. Phenol → Picric acid

52. How will you distinguish between phenol and benzyl alcohol?

53. Write short notes on
    g. Reimer and Tiemann's reaction
    h. Kolbe's reaction
    i. Schotten Baumann reaction

54. An organic compound dissolves in aqueous NaOH and imparted a violet colour to $FeCl_3$. Its solution in aqueous NaOH when heated with CCl_4 followed by hydrolysis gave an acid B, which on acetylation with acetic anhydric yields aspirin? What are A and B?

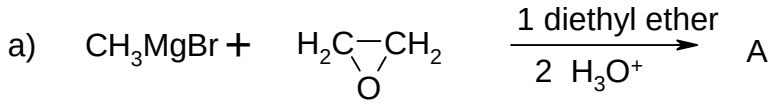
55. How will you synthesize phenol from
    j. Cumene
    k. Chlorobenzene
    l. Benzenesulphonic acid

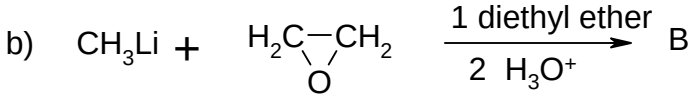
56. How will you separate a mixture of *o*-nitrophenol & *p*-nitrophenol?

57. Explain the mechanism involved in the Fries rearrangement by taking a suitable example.

58. How will expoxides directly be prepared from corresponding alkenes? Explain with mechanism.

59. Complete the following reactions





60. Explain the mechanism of acid catalysed ring opening of expoxides.