

Organic Chemistry

CHEM 145

2 Credit hrs

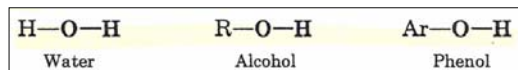
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Alcohols, Phenols and Ethers

Alcohols and Phenols

➡ Alcohols and phenols may be viewed as organic derivatives of water.



➡ Alcohols and phenols have a common functional group, the hydroxyl group, -OH.

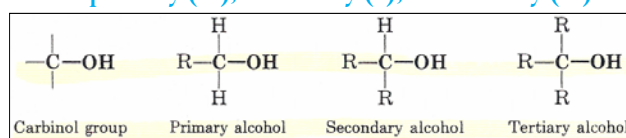
➡ In alcohols the hydroxyl group is attached to an alkyl group, -R.

➡ In phenols the hydroxyl function is attached to an aromatic ring, -Ar.

Classification and Nomenclature of Alcohols

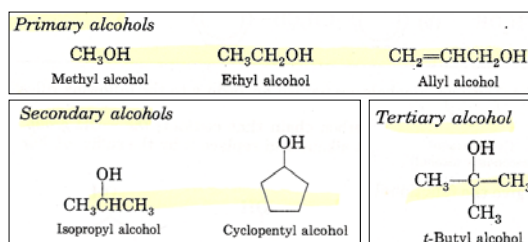
➡ Alcohols are subdivided into three classes: depends on the number of alkyl groups bonded to the carbon bearing the -OH, the so-called carbinol carbon.

primary (1°), secondary (2°), and tertiary (3°).



➡ The common names for the simplest alcohols consist of alkyl group attached to the hydroxyl function followed by the word *alcohol*.

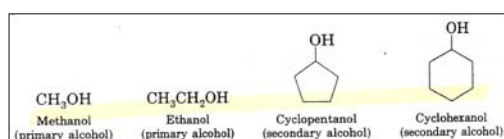
Alkyl alcohol



➡ In the IUPAC system, alcohols are named according to the following rules.

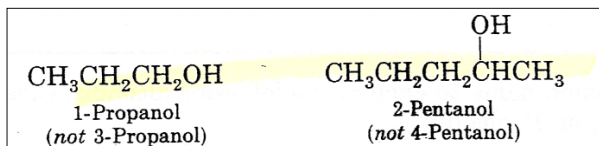
1. Select the longest continuous carbon chain that contains the -OH group.

Drop the -e ending of the parent alkane and replace it by the suffix -ol.



2. When isomers are possible,

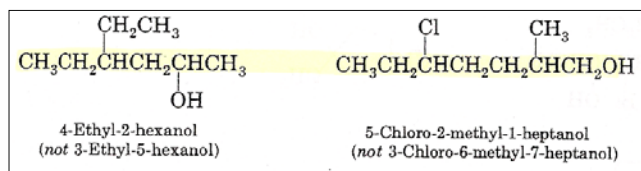
the chain is numbered so as to give the functional group (-OH) the *lowest possible number*.



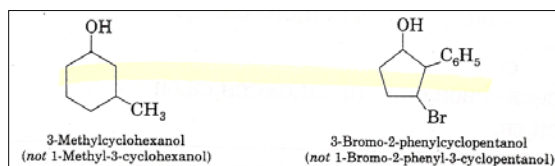
3. When alkyl side chains or other groups are present,

they are named alphabetically and their positions are indicated by a number.

The position of the functional group (-OH) is always given the **lowest possible number** at the end of the name.



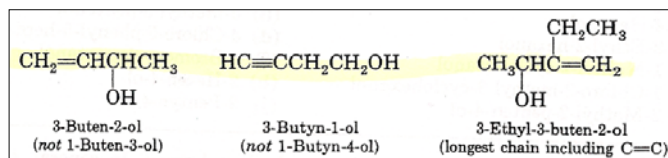
For *cyclic alcohols*, numbering always starts from the carbon bearing the -OH group.



4. If a molecule contains both an -OH group and a C=C or C-C triple bond,

The -OH group takes preference before the double or triple bonds in getting the lower number.

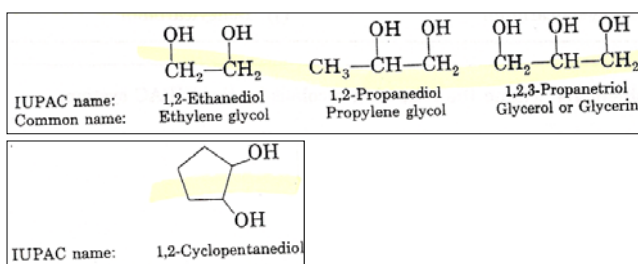
The name should include (if possible) both the hydroxyl and the unsaturated groups, **even if this does not make the longest chain the parent hydrocarbon**.



Some alcohols contain more than one hydroxyl group.

The suffix **-diol** is added to the name of the parent hydrocarbon when **two hydroxyl groups** are present, and the suffix **-triol** is added when there are **three -OH groups**.

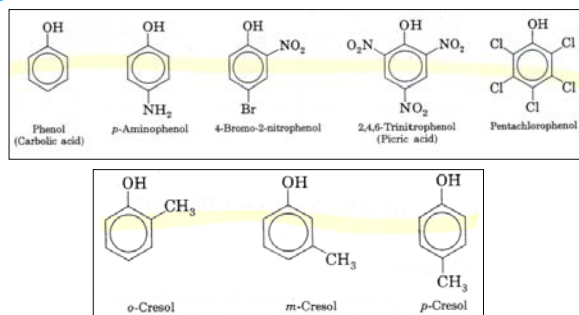
those containing two -OH groups on adjacent carbons are known as 1,2-glycols.



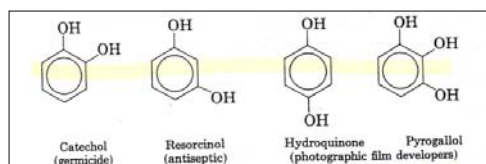
Alcohols that contain more than three hydroxyl groups per molecule are known as polyols.

Nomenclature of Phenols

Phenols are generally named as derivatives of the simplest member of the family, phenol.



Several important **hydroxysubstituted phenols** also have common names.



Physical Properties of Alcohols and Phenols

Monohydroxy Alcohols

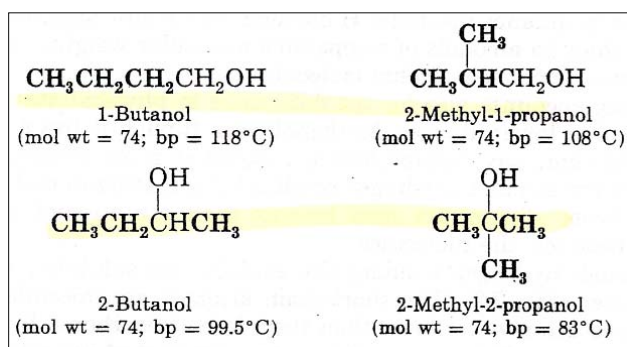
Table 7.1 Physical Properties of Straight-Chain Primary Alcohols

Name	Structure	Mp (°C)	Bp (°C)	Solubility in H ₂ O at 20°C
Methanol	CH ₃ OH	-97	64.5	completely soluble
Ethanol	CH ₃ CH ₂ OH	-115	78	completely soluble
1-Propanol	CH ₃ CH ₂ CH ₂ OH	-126	97	completely soluble
1-Butanol	CH ₃ (CH ₂) ₂ CH ₂ OH	-90	118	8.0 g/100 g H ₂ O
1-Pentanol	CH ₃ (CH ₂) ₃ CH ₂ OH	-78.5	138	2.3 g/100 g H ₂ O
1-Hexanol	CH ₃ (CH ₂) ₄ CH ₂ OH	-52	157	0.6 g/100 g H ₂ O

- ➡ The simplest alcohol, methanol, is a liquid at room temperature.
In contrast, alkanes from methane to butane are gases.
- ➡ The lower alcohols are completely miscible with water.
As the number of carbons in the alcohol increases, the solubility in water decreases.
- ➡ Series of normal alcohols,
The boiling points increase with increase in molecular weights.

➡ A comparison of boiling points among isomeric alcohols;

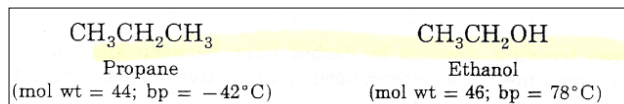
The boiling points decrease as the number of alkyl branches from the carbinol group increases.



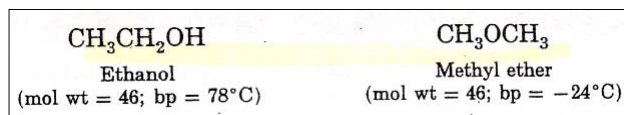
- ➡ The straight-chain isomers have larger molecular surfaces than do their branched-chain isomers.

Therefore, they have higher intermolecular interactions and, as a result, higher boiling points.

- ➡ The high values of the boiling points of alcohols compared with alkanes of similar molecular weights.



The **O—H bond** and not to the presence of oxygen can be proved by comparing the boiling point of ethanol with Alcohols, Phenols, that of its structural isomer, methyl ether:



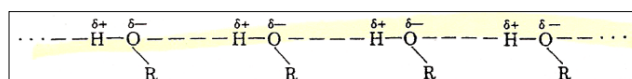
- ➡ Therefore, the large increase in boiling points of alcohols compared with alkanes (or ethers) also must be due to the O—H group.

➡ Hydrogen Bonding

The effect of the OH group on the physical properties of alcohols can be explained as follows.

The O—H bond is *highly polar*.

The oxygen, a highly electronegative atom carries a partial negative charge (δ^-), and the hydrogen a partial positive charge (δ^+).



- ➡ **Hydrogen bonding** accounts also for the differences in physical states between lower alcohols and lower alkanes.
- ➡ **Hydrogen bonding** also explains the solubility of the lower alcohols in water.
- ➡ When those alcohols are mixed with water,
 - They dissolve because of hydrogen bonding between the OH bond of the alcohol and the hydroxyl group of the water.
- ➡ As the number of carbons in an alcohol increases,
 - The nonpolar alkyl group becomes more and more important and the polar OH group becomes less important.

Diols and Triols

- ➡ Diols and triols are also miscible with water, but are only slightly soluble in alkanes

Table 7.2 Physical Properties of Some Alcohols and Number of OH Groups

Alcohol	Mol wt	Bp (°C)	Solubility in H ₂ O at 20°C	OH groups per molecule
1-Propanol	60	97	Soluble	1
1-Butanol	74	118.5	Soluble	1
Ethylene glycol (1,2-ethanediol)	62	197	Soluble	2
1-Pentanol	88	138	2.3 g/100 g H ₂ O	1
1-Hexanol	102	157	0.6 g/100 g H ₂ O	1
Glycerol (1,2,3-propanetriol)	92	290	Soluble	3

Phenols

- ➡ **Phenol** is a colorless, crystalline, low-melting solid, with a high boiling point, that is moderately soluble in water.
- ➡ Most other phenols also are solids, with slight solubility in water and high boiling points.
- ➡ The most significant physical property that distinguishes alcohols from phenols is the *acidity* of phenols.
- ➡ Acidities of Phenols and Alcohols Compared



- ➡ Why is the phenoxide ion more stable?

Because the negative charge on the oxygen is *dispersed* by *resonance* through the benzene ring.

No such delocalization of charge can take Place for the conjugate base of cyclohexanol

Reactions of Alcohols and Phenols

➡ **Alcohols** undergo two kinds of reactions:

➡ Those that involve the breaking of the oxygen-hydrogen bond (CO-H).

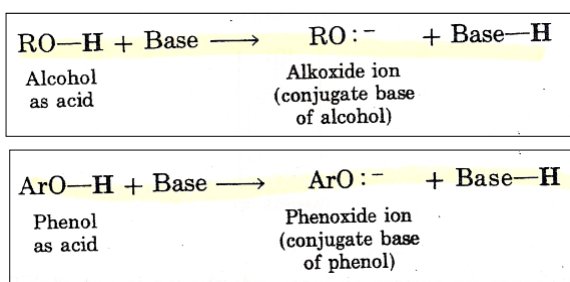
➡ Those that involve the rupture of the carbon-oxygen bond (C-OH).

➡ **Phenols** do not participate in reactions where the C-OH bond is broken.

➡ Alcohols and Phenols as Acids: Salt Formation.

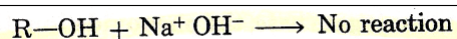
Alcohols and **phenols** can act as acids whenever they donate a proton to a base.

The base must be stronger than the conjugate base of the alcohol or the phenol.

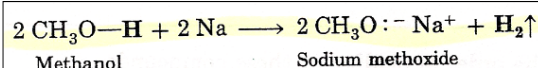


➡ Since alcohols are weaker acids than water,

it is not possible to form the salt of an alcohol in aqueous alkaline solutions.



➡ It is possible to form the salt by the action of active metals such as Na or K.

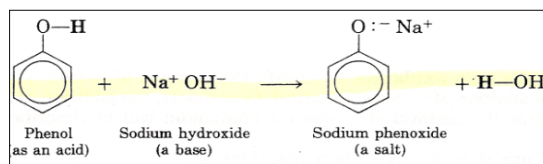


➡ The action of metallic sodium on an alcohol is similar to the reaction of metallic sodium with water.

➡ **Alkoxides** are strong bases, even stronger than hydroxides.

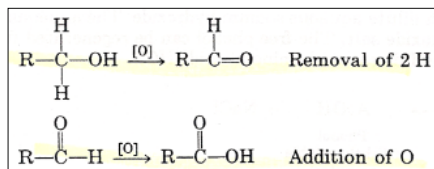
Alkoxides are used extensively in the synthesis of ethers

➡ It is possible to obtain **phenoxide** salts from aqueous solutions of alkali.



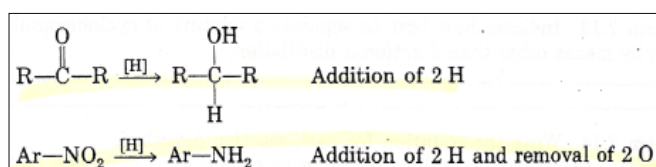
Oxidation

➡ **Oxidation** is the **removal of H** from a compound and/or the **addition of O** to a compound.



➡ An **oxidizing agent** is the chemical reagent that does the oxidation.

➡ **Reduction** is the **addition of H** to a compound and/or the **removal of O** from a compound.

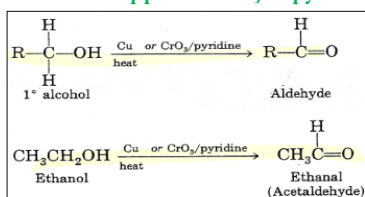


➡ A **reducing agent** is a substance that does the reduction.

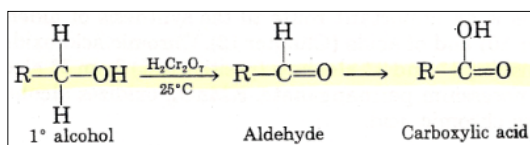
Oxidation of Alcohols

➡ Oxidation of alcohols gives different products depending on the **class of alcohols** that is oxidized and on the **kind of oxidizing agent** that is used.

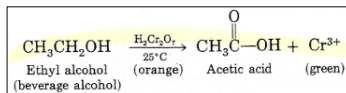
➡ **Primary alcohols** yield **aldehydes** when treated with **mild oxidizing agents** such as **hot metallic copper** or **CrO₃ in pyridine**.



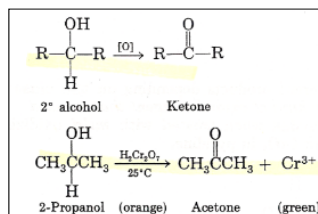
➡ with **stronger oxidizing agents**, such as **chromic acid**, **H₂Cr₂O₇**, or **neutral potassium permanganate**, **KMnO₄**, the **intermediate aldehydes** formed initially are oxidized further to **carboxylic acids**.



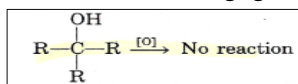
➡ **Chromic acid** is prepared by adding sulfuric acid to potassium dichromate, giving an orange solution.



➡ **Secondary alcohols**, when treated with **any of the oxidizing agents** mentioned previously, **yield ketones**.



➡ **Tertiary alcohols** do **not react** with oxidizing agents.



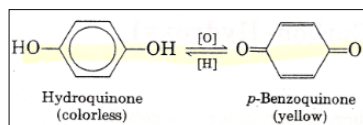
➡ **Neutral potassium permanganate, KMnO_4** , oxidizes alcohols in the same manner as does chromic acid.

Oxidation of Phenols

➡ Some **phenols** are **oxidized slowly** by **oxygen in the air alone**; in that case, we say that the phenol has undergone **autoxidation**.

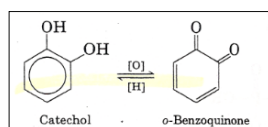
➡ The food, petroleum, rubber, and plastic industries take advantage of the autoxidation to incorporate them as **antioxidants** in their products.

➡ **Hydroquinone** is oxidized to the yellow, stable *p*-benzoquinone.



Hydroquinone is the primary reducing agent used.

➡ **Catechol** is oxidized in a similar manner to *o*-benzoquinone.



***o*-Quinones** are not as stable as the para isomer.

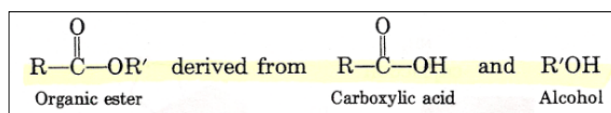
➡ In intermediary metabolism in human beings, certain substances obtained from proteins contain catechol as part of the molecule.

Reactions Involving Carbon-Hydroxyl Bond Breaking

The cleavage of the C-OH bond is applicable to alcohols only

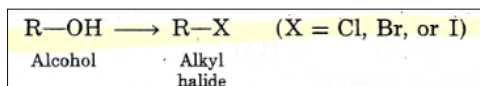
A. Esters

➡ **Organic esters**, derived from a carboxylic acid and an alcohol.



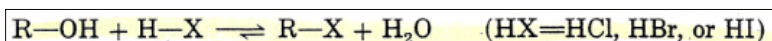
B. Replacement of the OH Group by Halide: Alkyl Halides

➡ The hydroxyl group of alcohols can be replaced by halide to form **alkyl halides**.

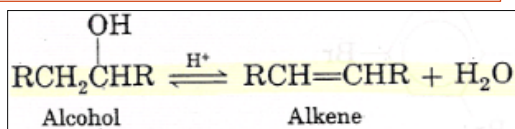


➡ **Reaction with hydrogen halides: Lucas test.**

➡ Treatment of alcohols with aqueous concentrated hydrogen halides H-X, or with anhydrous H-X, give alkyl halides.



C. Dehydration of Alcohols: Formation of Alkenes



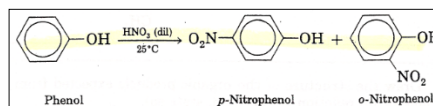
1. Dehydration of alcohols is **catalyzed by acids**.
2. Elimination of H₂O involves a **carbocation as an intermediate**.
3. The ease of dehydration of alcohols follows the order;
 $3^\circ > 2^\circ > 1^\circ > \text{methanol}$
which is also the order of ease of formation and stability of carbocations.
4. The carbocation loses a proton to give an **alkene**.
5. If more than one alkene can be formed,

The major one is the one that has the greater number of alkyl groups bonded to C=C (*Saytzeff's rule*).

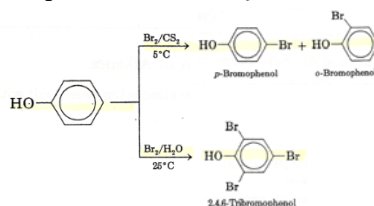
Reactions of Alcohols and Phenols

Reactions on the Aromatic Ring of Phenols

➡ **Nitration of phenol** goes so rapidly that *dilute nitric acid* at room temperature must be used.



➡ **Halogenation** takes place *without catalyst*.



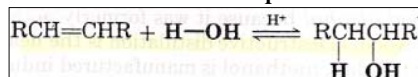
➡ **The products depend on the solvent used.**

- ♦ In *aprotic solvents* (solvents that do not release protons) (CCl_4 , CS_2)-bromination gives a mixture of *o*- and *p*-bromophenol.
- ♦ In *protic solvents* (solvents that can release protons) (H_2O)-halogenation gives a trisubstituted phenol is produced.

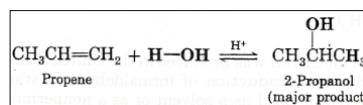
Preparation of Alcohols

A. Hydration of Alkenes

1. Addition of water to a double bond in the presence of an *acid catalyst, H^+* .



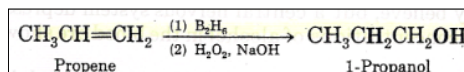
2. The addition follows *Markovnikov's rule*.



3. It is *not possible to prepare primary alcohols* except Ethanol.

B. Hydroboration-Oxidation

➡ The addition of **diborane, B_2H_6** , followed by *oxidation with alkaline hydrogen peroxide*.



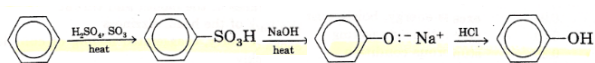
The net result is the addition of H_2O across $\text{C}=\text{C}$ in an *anti-Markovnikov* manner.

Preparation of Phenols

The Alkali Fusion of Sulfonates

➡ The alkali fusion of sulfonates involves the following steps;

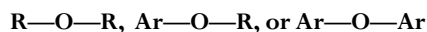
1. **Sulfonation** of an aromatic ring.
2. **Melting (fusion)** of the aromatic sulfonic acid with sodium hydroxide to give a **phenoxide salt**.
3. **Acidification** of the phenoxide with HCl to produce the **phenol**.



Ethers

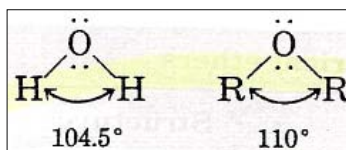
Structure of Ethers

➡ General formula of an **ether**;



➡ **Ethers** as water molecules in which each hydrogen has been replaced by an organic group.

➡ The geometry of simple ethers is similar to that of water.



➡ The ether is classified as

➤ **Symmetrical ethers**;

When the organic groups attached to the oxygen are **identical**.

➤ **Unsymmetrical ethers (mixed ethers)**;

When the organic groups attached to the oxygen are **different**.

Nomenclature of Ethers

➡ **Simple ethers are given common names.**

➤ The organic groups are named first in **alphabetical order**; then the word **ether** is added.

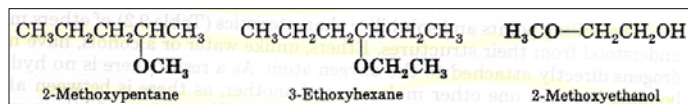
➤ **Methyl phenyl ether** has the special name **anisole** (oil of anis).

➡ **Complicated ethers are named according to the IUPAC system.**

➤ The ethers are considered as **alkoxy (RO-)** derivatives of a parent compound

➤ Specific **alkoxy groups**; **methoxy**, $\text{CH}_3\text{O-}$, **ethoxy** $\text{CH}_3\text{CH}_2\text{O-}$, etc.

➤ The names of a few ethers according to the IUPAC system are



Methyl ether	$\text{CH}_3\text{—O—CH}_3$	Ethyl methyl ether	$\text{CH}_3\text{—O—CH}_2\text{CH}_3$
Ethyl ether	$\text{CH}_3\text{CH}_2\text{—O—CH}_2\text{CH}_3$	Ethyl-n-propyl ether	$\text{CH}_3\text{CH}_2\text{—O—CH}_2\text{CH}_2\text{CH}_3$
Vinyl ether	$\text{CH}_2=\text{CH—O—CH}=\text{CH}_2$	<i>t</i> -Butyl methyl ether	$(\text{CH}_3)_3\text{C—O—CH}_3$
Phenyl ether		Methyl phenyl ether (anisole)	

Physical Properties of Ethers

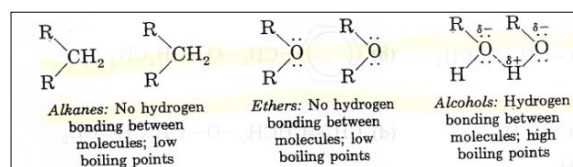
➡ **Ethers**, unlike water or alcohols, have no hydrogens directly attached to the oxygen atom.

➤ So, there is no hydrogen bonding between one ether molecule and another.

➡ The **boiling points** of ethers

➤ Lower than those of **alcohols** of comparable molecular weights.

➤ About the same as those of **alkanes**, of comparable molecular weights.

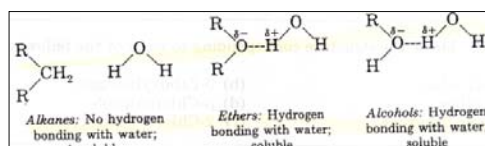


➡ **Solubility in water**

➤ Ethers behave much like alcohols of similar molecular weights.

This is because the oxygen atom in ethers, as in alcohols, is capable of hydrogen bonding with water molecules.

➤ **Alkanes**, of course, are insoluble because no hydrogen bonding with water is possible.



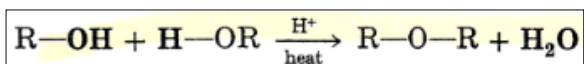
Structure	Name	Mol wt	Bp (°C)	Solubility in H ₂ O at 20°C
$CH_3CH_2CH_3$	propane	44	-42	insoluble
CH_3OCH_3	methyl ether	46	-24	soluble
CH_3CH_2OH	ethanol	46	78	soluble
$CH_3CH_2CH_2CH_3$	n-butane	58	-0.5	insoluble
$CH_3CH_2OCH_2CH_3$	ethyl methyl ether	60	8	soluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	soluble
$CH_3(CH_2)_3CH_3$	n-pentane	72	35	insoluble
$CH_3CH_2OCH_2CH_2CH_3$	ethyl ether	74	36	7.5 g/100 g
$CH_3(CH_2)_2CH_2OH$	1-butanol	74	118	7.9 g/100 g
$CH_3(CH_2)_5CH_3$	n-heptane	100	98	insoluble
$CH_3(CH_2)_2O(CH_2)_2CH_3$	n-propyl ether	102	91	0.2 g/100 g
$CH_3(CH_2)_4CH_2OH$	1-hexanol	102	157	0.6 g/100 g

Preparation of Ethers

- ➡ There are *two general methods* for synthesizing ethers.
 - The dehydration of alcohols is used *commercially* and in the *laboratory* to make certain *symmetrical ethers*.
 - The Williamson synthesis General *laboratory* method used to prepare all kinds of ethers, *symmetrical* and *unsymmetrical*.
- ➡ Both methods depend on *alcohols as starting materials*.
- ➡ Both methods involve *nucleophilic substitution (S_N) reactions*.

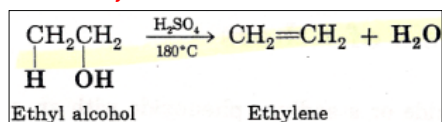
Ethers by Dehydration of Alcohols

It takes place in the presence of acid catalysts (H_2SO_4 , H_3PO_4) (*intermolecular reaction*).

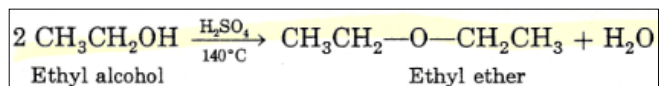


B. Scope and Limitations

- When ethyl alcohol is dehydrated by *sulfuric acid at $180^\circ C$* , the dominant product is *ethylene*.



- To prepare ethyl ether
 - ◆ Dissolve ethyl alcohol in sulfuric acid at *ambient temperature*.
 - ◆ Heat the solution to $140^\circ C$ while adding more alcohol.

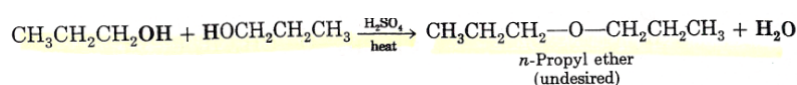
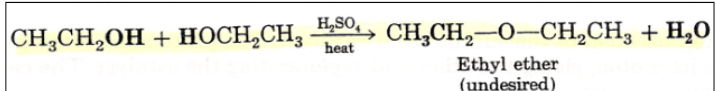
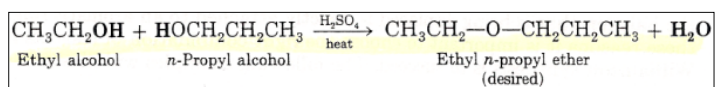


- Generally, the dehydration of alcohols is limited to the preparation of symmetrical ethers.

► **Example;**

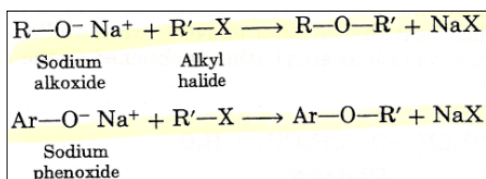
Assume you needed **Ethyl *n*-propyl ether**.

It can be prepared by dehydrating a mixture of **ethyl alcohol** and ***n*-propyl alcohol**.



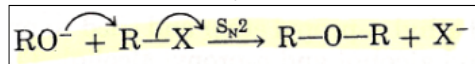
The Williamson Synthesis of Ethers

- The reaction of a **sodium alkoxide** or a **sodium phenoxide** with an **alkyl halide** to form an ether.



- The reaction goes by an **S_N2 mechanism**.

The alkoxide (or phenoxide) ion serves as a strong nucleophile and displaces the halide ion from the alkyl halide.



- The S_N2 mechanism does not work well,

- (1) if the approach of the **nucleophile** is hindered by **bulky groups** in the alkyl halide.
- or (2) if the **halogen** that is being displaced is directly **attached to an aromatic ring**.

➤ For these reasons

It is important to choose the right combination of reagents if the Williamson synthesis is to succeed.

➤ Example 1;

Preparation of *t*-butyl methyl ether, $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$.

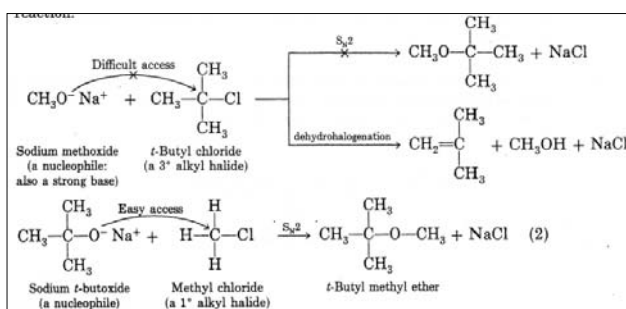
◆ In theory, this could be done by either of two reactions.

1. You could react sodium methoxide, $\text{CH}_3\text{O}^-\text{Na}^+$, with *t*-butyl chloride, $(\text{CH}_3)_3\text{C}-\text{Cl}$.

This combination leads to dehydrohalogenation to an alkene, an elimination reaction.

2. You could react sodium *t*-butoxide, $(\text{CH}_3)_3\text{C}-\text{O}^-\text{Na}^+$, with methyl chloride, CH_3Cl .

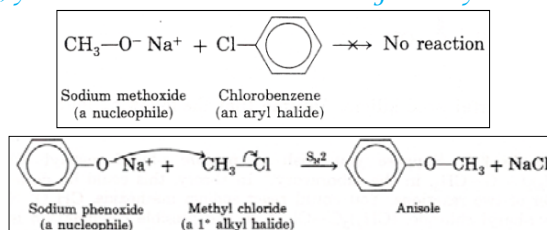
This route gives the desired ether by substitution.



➤ Example 2;

Assume you need to synthesize methyl phenyl ether (anisole), $\text{CH}_3-\text{O}-\text{C}_6\text{H}_5$, by the Williamson method.

In theory, you could obtain anisole in either of two ways.



➤ Summary of the Williamson synthesis

1. The Williamson synthesis is the preferred laboratory method for making ethers.

The reaction goes by an S_N2 mechanism.

2. To prepare a mixed ether, it is necessary to choose the proper combination of reagents.

3. To obtain the best yields of mixed dialkyl ethers, we select a 1° rather than a 2° or 3° alkyl halide and react it with a sodium alkoxide

4. To prepare an alkyl aryl ether, we must be careful not to pick a combination in which one of the reagents has a halogen directly attached to an aromatic ring.

Reactions of Ethers

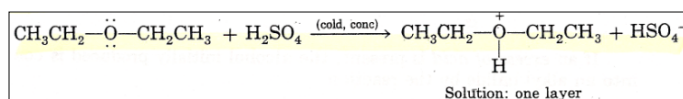
⇒ Ethers are quite stable compounds.

⇒ The ether linkage does not react with bases, reducing agents, oxidizing agents, or active metals.

⇒ Ethers react only under strongly acidic conditions.

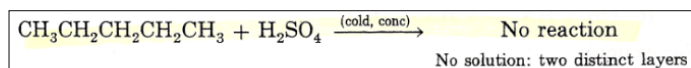
A. Reaction with Cold Concentrated Acids

➤ An ether, acting as a base, donates an electron pair to a hydrogen ion to form a protonated ether.



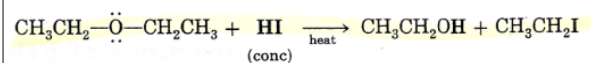
Protonated ethers, once produced, are soluble in the cold concentrated acid solution.

➤ Since alkanes do not react with, and are insoluble in, cold concentrated acid solutions.



B. Cleavage of Ethers by Hot Concentrated Acids

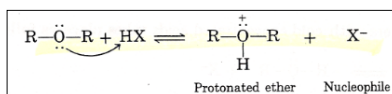
➤ When **ethers** are heated in concentrated acid solutions, the ether linkage is broken



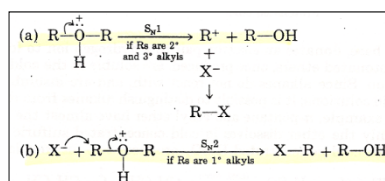
► The acids most often used in this reaction are HI, HBr, and HCl.

► The cleavage of **ethers** involves two steps:

(1) A protonated ether is formed.



(2) When heated, the protonated ether undergoes cleavage.

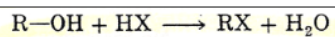


The cleavage occurs by an S_N1 .

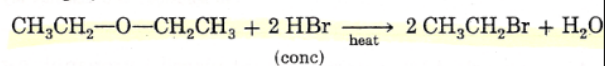
The cleavage occurs by an S_N2 .

depending on the structure of the ether.

➤ If an *excess of acid* is present, the alcohol initially produced is converted into an alkyl halide by the reaction.

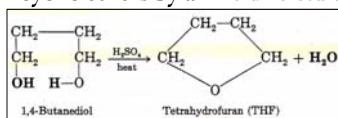


For example,

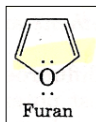


Cyclic Ethers

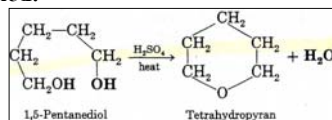
- It is possible to obtain cyclic ethers by an *intramolecular reaction*.



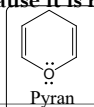
- THF is so named because it is related to the unsaturated cyclic ether *furan*.



- When 1,5-pentanediol is heated in acid, the six-membered ring ether *tetrahydropyran* is obtained.

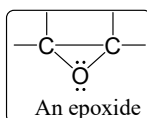


- Tetrahydropyran is so called because it is related to the unsaturated ether *pyran*.

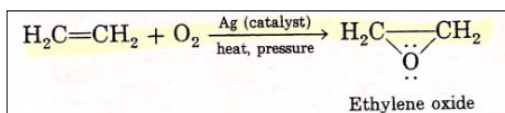


Epoxides

- Epoxides are cyclic ethers in which the ether oxygen is part of a three membered ring.

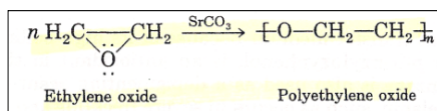


- The simplest and most important epoxide is *ethylene oxide*.
- Ethylene oxide is prepared commercially by air oxidation of ethylene.

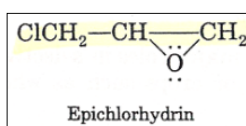


- Epoxides undergo many reactions that other ethers do not.
- Their reactivity is due to the **strain in the three-membered ring**, which is relieved when the epoxide ring is opened after a reaction has taken place.

- Examples of ring-opening reactions of ethylene oxide that form commercially important products are



- **Polyethylene oxide** is used as an additive by fire departments under the name **Rapid-Water**.
- Another important epoxide is **epichlorhydrin**.



- Ring-opening reactions of **epichlorhydrin** with a number of reagents produce epoxy resins.
- **Epoxy resins** are polymers used as protective coatings because of their resistance to chemicals