

Teacher Orientation :

Class – XII

Topic - Alcohol, Phenol and Ethers.

The following topics will be covered in this chapter.

Classification: Alcohol, Phenol and Ethers.

Nomenclature: Alcohol, Phenol and Ethers.

Structure of Functional Groups

Alcohols and Phenols: Preparation, Physical and Chemical Properties.

Ethers: Preparation, Physical and Chemical Properties.

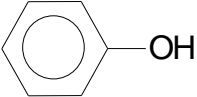
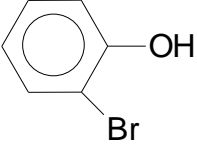
Student Orientation:

Topic - Alcohol, Phenol and Ethers.

Concept Detail:

Alcohol, Phenols and Ethers.

Here are the **general formula** and **examples** of each.

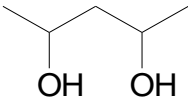
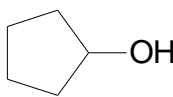
	alcohol	phenol	ether
general structure	$R-OH$		$R-O-R$
example structure	$\begin{array}{c} H & H \\ & \\ H-C & -C-OH \\ & \\ H & H \end{array}$		$\begin{array}{c} H & H & H \\ & & \\ H-C & -C-O & -C-H \\ & & \\ H & H & H \end{array}$
example name	ethanol or ethyl alcohol	o-bromo phenol or 2-bromo phenol	ethylmethyl ether or methoxy ethane

Nomenclature of Alcohols:

1. Select the longest chain containing the alcohol, -OH.
2. Number the chain with the -OH group getting the lowest possible number.
3. Replace the -e at the end of the suffix with -ol.
4. If there are more than one -OH group do not remove the -e from the suffix, but add a di- or tri- prefix to the -ol suffix.

5. Add a prefix number to indicate which carbon the –OH group is bonded to. This is not always necessary.

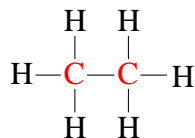
Examples:

ethanol	2-propanol or isopropyl alcohol (rubbing alcohol)	2,4-pentanediol	cyclopentanol
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{H} \quad \text{OH} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$		

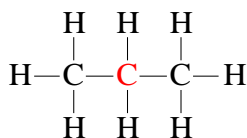
- For the first example there is no prefix number to indicate the location of the –OH group. The reason is that no matter which carbon the –OH group is attached to that carbon is carbon number one. The name 1-ethanol would be redundant.
- For the last example there is no prefix number to indicate the location of the –OH group. The reason is that no matter which carbon the –OH group is attached to that carbon is carbon number one. The name 1-cyclopentanol would be redundant.

Alcohols are often classified based on the classification of the carbon they are attached to. Remember the following diagrams.

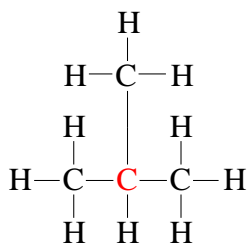
- primary carbon is bonded to one other carbon:
 - both of these carbons



- secondary carbon is bonded to two other carbons:
 - the center red carbon only

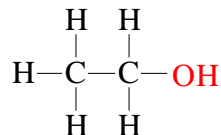


- tertiary carbon is bonded to three other carbons:
 - the center red carbon only

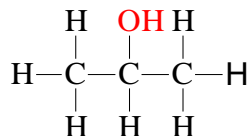


Following the format of the above diagrams, if we replace one hydrogen with a –OH group we get the following classifications of alcohols:

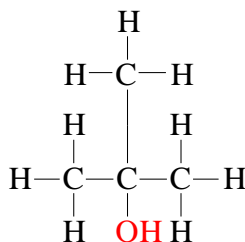
- 1°, primary alcohol has –OH group bonded to a carbon which is bonded to one other carbon:



- 2°, secondary alcohol has –OH group bonded to a carbon which is bonded to two other carbon:



- 3°, tertiary alcohol has –OH group bonded to a carbon which is bonded to three other carbon:



The classification dictates what types of reactions the alcohol will undergo. A simple test can be performed to determine which classification of alcohol is present.

Redox reactions (oxidation/reduction reactions) are very important to alcohols. The oxidation state of the carbon bonding to the functional group is important in determining what types of compounds could be formed.

The oxidation state of carbon in various common compounds is as follows:

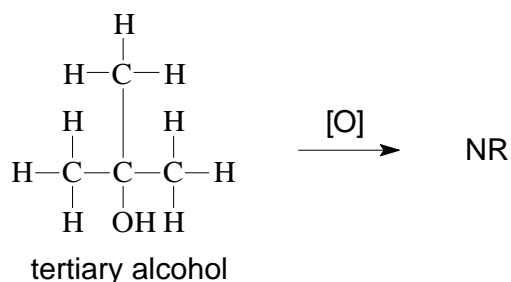
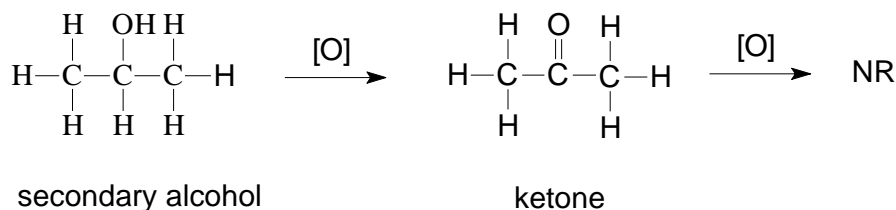
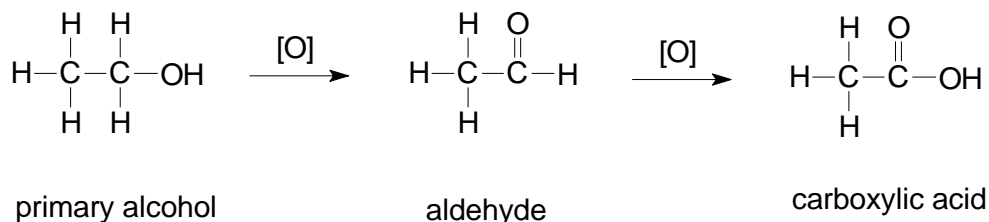
alkanes	→	alcohols	→	aldehydes	→	carboxylic acids	→	carbon dioxide
-4		-2		0		+2		+4
$ \begin{array}{c} \text{H}^+ \\ \\ \text{H}^+ - \text{C} - \text{H}^+ \\ \\ \text{H}^+ \\ -4 \end{array} $		$ \begin{array}{c} \text{H}^+ \\ \\ \text{H}^+ - \text{C} - \text{OH}^+ \\ \\ \text{H}^+ \\ -2 \end{array} $		$ \begin{array}{c} \text{O}^{-2} \\ \\ \text{H}^+ - \text{C} - \text{H}^+ \\ 0 \end{array} $		$ \begin{array}{c} \text{O}^{-2} \\ \\ \text{H}^+ - \text{C} - \text{OH}^+ \\ +2 \end{array} $		$ \begin{array}{c} \text{O}^{-2} = \text{C} = \text{O}^{-2} \\ +4 \end{array} $

In each step along carbon's path, from the alkanes to carbon dioxide, the carbon is oxidized and will lose 2 electrons.

For reactions involving alcohols an oxidizing agent such as potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is often used in acidic solutions and potassium permanganate, KMnO_4 , is often used in basic solutions. These by no means are the only chemicals used to oxidize alcohols. There are

many useful oxidizing agents available for experimentation and testing. The symbol [O] is often used as the short hand meaning for an oxidizing agent. This would be used when the reader is not concerned with which oxidizing agent is being used, but to simply to show that an oxidation took place.

The following are generalized reactions for the three classes of alcohols, 1°, 2° and 3°.



The oxidation of the primary alcohol ethanol, also known as grain alcohol which is the alcohol you find in wine, beer and spirits, is the least toxic of the alcohol classes. But a few fluid ounces of a secondary or tertiary alcohol can destroy a person's liver.

If you look at the products of this first reaction you will find an aldehyde is the first chemical produced by the oxidation of the ethanol. This is accomplished by enzymes found in most humans. Humans of certain ethnic backgrounds are able to produce more of these enzymes ethnicities. A person of German decent will normally have many more of these enzymes than a person of American Indian decent. This intermediate aldehyde is toxic to the liver organ, but as quickly as it is produced the body oxidizes this compound to a carboxylic acid. Carboxylic acids can easily be metabolized for energy use and will not harm your liver.

Alcohol overdose can be accomplished by a few mechanisms, one is overloading of ethanol to the point that your liver can not produce enough enzyme to oxidize the ethanol to aldehyde and the aldehyde to a carboxylic acid. The aldehyde and ethanol persist in the liver and cause it to fail.

Another alcohol overdose can be accomplished by much smaller amounts if a secondary alcohol is consumed. As you can see, if you consumed a secondary alcohol a ketone will be produced. Then no reaction will occur. A ketone can not be oxidized inside most organisms. This can easily be accomplished by combustion, but if your liver is combusting the ketone in your system you have worries bigger than liver failure, like finding a fire extinguisher.

Back to our alcohol overdose scenario, since the ketone is not converted into another compound it sits in your liver. Your liver will fail with only a small ingestion of this secondary alcohol. By the way, this alcohol is isopropyl alcohol (2-propanol) otherwise known as rubbing alcohol.

Another alcohol overdose can be accomplished by even smaller amounts if a tertiary alcohol is consumed. Again, if you consumed a tertiary alcohol no reaction will occur. The tertiary alcohol will persist in your liver until it fails, then you will die.

Knowing the toxicity of the different classifications of alcohols to the human body, which class, 1°, 2° or 3°, do you think, causes the most deaths each year?

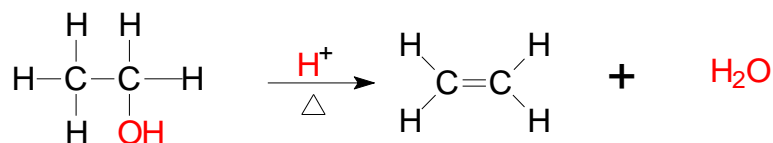
The 1°, as ethanol or drinking alcohol, has caused many thousands more deaths than the 2° and the 3° combined.

Here are two more reactions discussed previously that should still be included in this section:

1. Dehydration:

loss of a water

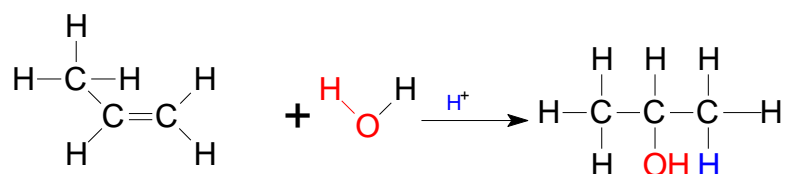
production of an unsaturated hydrocarbon



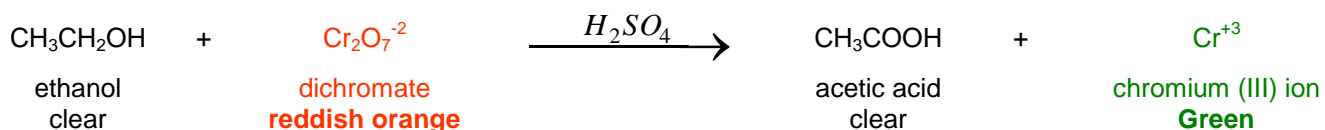
2. Hydration:

gain of a water

addition of the water across a double or triple bond

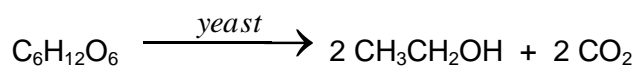


Real World Example:



This reaction is utilized by the inexpensive blood alcohol tests. You simply blow your breath into a small tube and the tube changes color from **reddish orange** to **green**.

Ethanol Production in Alcoholic Beverages:



Yeast converts the reactant glucose into ethanol and carbon dioxide. This is why beer and champagne are carbonated beverages. To keep some beverages from being carbonated, wine and spirits, a weak strain of yeast is used. This yeast dies in low concentrations of ethanol.

An interesting note, when you make ethanol in a lab by hydrating an alkene, an additive must be included in the solution to make it undrinkable. If not the government will tax this production.

Solubility and MP/BP of Alcohols:

The solubility and melting/boiling points of alcohols depend on two factors, the length of the carbon chain and the number of alcohols on the molecule. The longer the carbon chain, the

less soluble the alcohol will be. The BP and MP will also increase with carbon chain length. Longer carbon chained alcohols are less likely to mix with water. The longer the alcohols carbon chain, the better the chance that the alcohol will be a solid at room temperature.

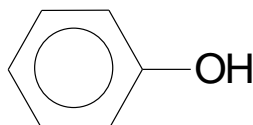
More alcohols on the chain will increase the chains solubility. The more alcohols on the carbon chain, the better the chance that the alcohol will be a solid at room temperature.

Longer means less soluble, less alcohols means less soluble.

Shorter means more soluble, more alcohols means more soluble.

Phenols:

A phenol is a simply an $-OH$ bonded to a benzene ring.

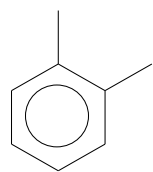


This compound is a solid, but is normally used in a liquefied form by dissolving in any number of solvents. Phenol is very corrosive to human skin. It can chew through your skin in a few seconds. Having said this, many phenol derivatives can be found in different foods, see below.

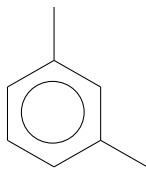
vanilla	cloves	BHT butyrate hydroxytoluene or 2,6-di-t-butyl-4-methyl phenol

The disubstituted nomenclature for aromatics applies to the phenol.

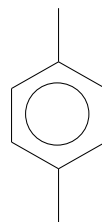
Remember the following relationships for substitutions of benzene rings.



ortho



meta

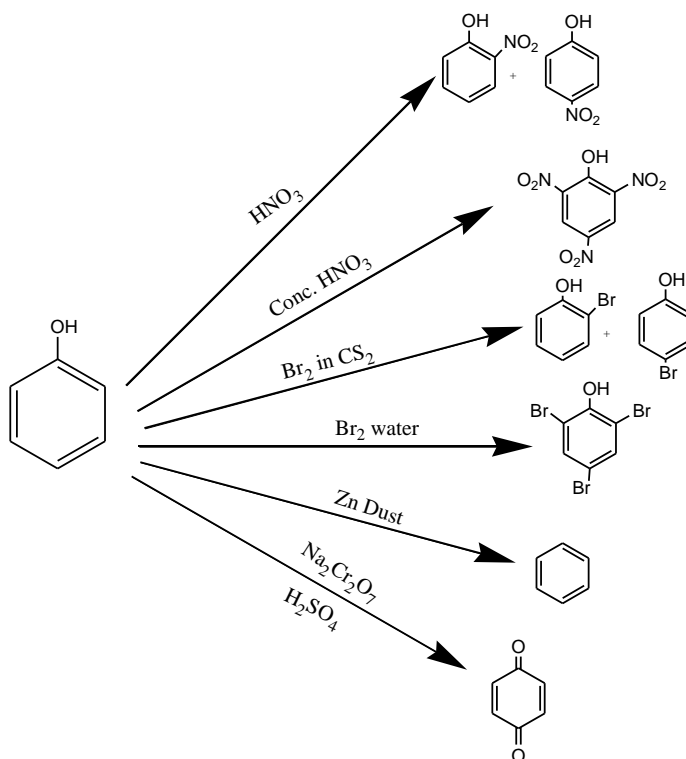


para

Examples:

Structure		
name	meta-amino phenol	para-methyl phenol
name	m-amino phenol	p-methyl phenol
name	3-amino phenol	4-methyl phenol

Reactions of Phenols:



Ethers:


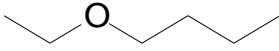
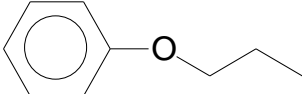
An ether is a hydrocarbon with an oxygen sandwiched between the carbons. They are very useful in organic chemistry. They tend to be very good solvents, much like water, and have relatively low reactivity. They are very resistant to oxidizing agents like potassium dichromate and potassium permanganate, as well as most acids and bases if the temperature is near room temperature.

Ether Nomenclature:

There are two predominate methods of naming ethers. The first is the common method and is most useful with simple ethers.

For the first method, if the carbon chains on either side of the oxygen are considered alkyl groups you simply name the groups then write ether.

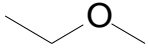
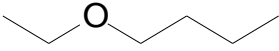
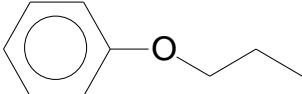
Examples:

		
ethylmethylether	butylethylether	phenylpropylether

The other method follows the official **IUPAC** rules:

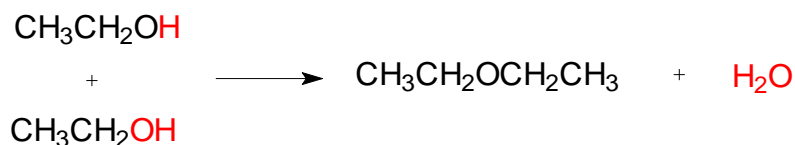
1. Determine the longest alkyl chain for the root name.
2. Treat the oxygen and the remaining carbons as a side chain.
3. The prefix includes the alkyl chain with a suffix of oxy for the oxygen.

Examples:

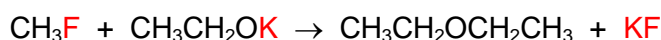
		
methoxyethane	1-ethoxybutane	1-phenoxypropane

Preparation of Ethers:

1. Dehydration of two alcohols:



2. Alkyl halide and alkoxide:

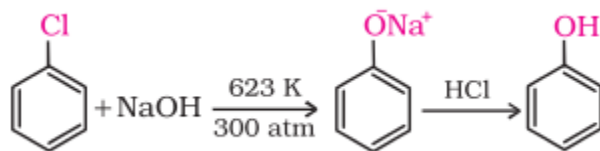


3. Williamson synthesis: This reaction is used for the synthesis of symmetrical and unsymmetrical ethers.



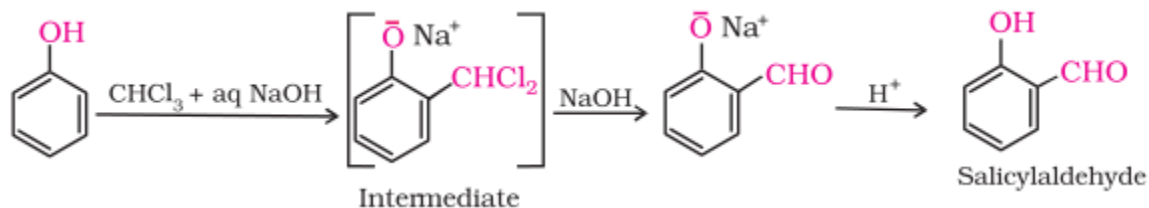
Important Named Reactions of Alcohols, Phenols And Ethers

1. Dow's Process: This process is used for the formation of phenols from chlorobenzene.



a.

2. Reimer Tiemann Reaction: In this reaction, salicylaldehyde (2-Hydroxy benzaldehyde) is prepared on reaction of phenols with chloroform while salicylic acid (2-Hydroxy benzoic acid) is formed when phenols are treated with carbon tetrachloride.



a.

3. Kolbe's Reaction: In this reaction, salicylic acid is prepared by the reaction of sodium phenoxide with carbon dioxide followed by acidification.

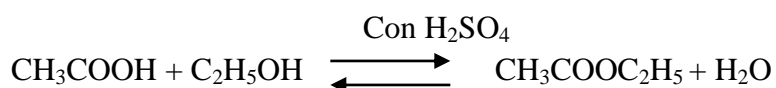


a.

4. Williamson synthesis: This reaction is used for the synthesis of symmetrical and unsymmetrical ethers.



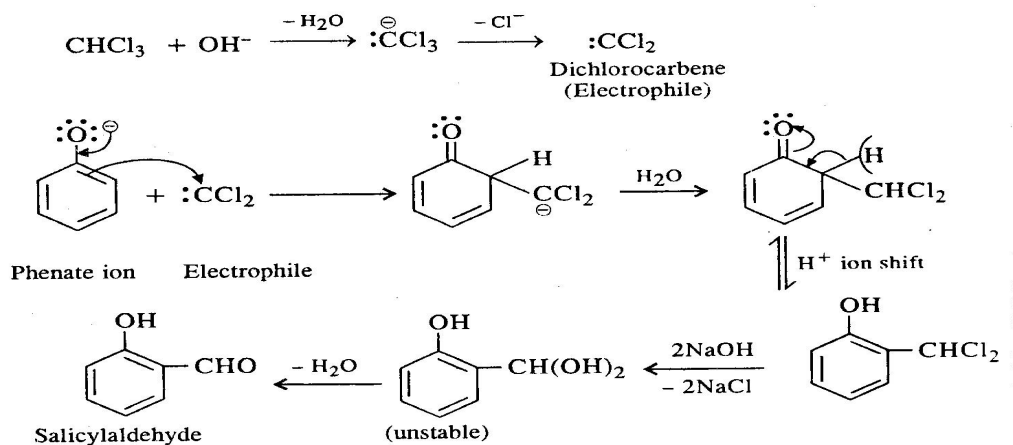
5. ESTERIFICATION



Important Mechanisms

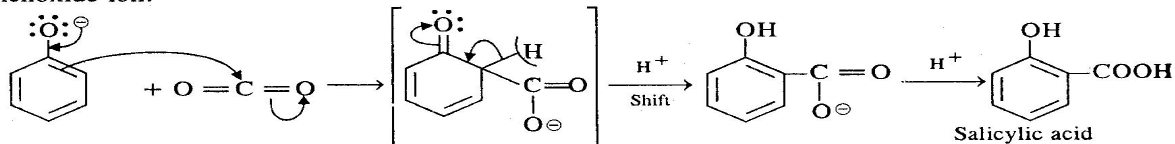
1. REIMER TIEMANN

Mechanism. It is an example of electrophilic substitution but the electrophile is dichlorocarbene (:CCl₂)



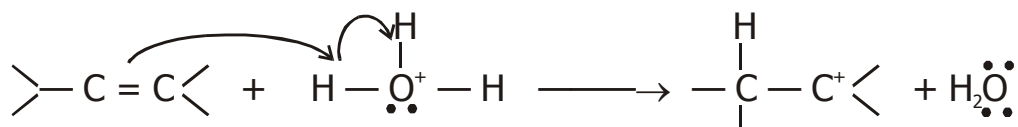
2. KOLBE SCHMIDT REACTION

Mechanism. The mechanism involves the electrophilic attack of CO₂ on highly activated phenoxide ion.

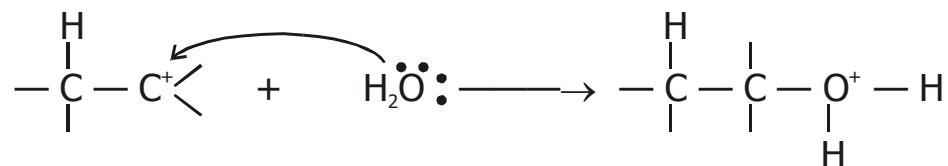


3. HYDRATION OF ETHENE TO YIELD ETHANOL.

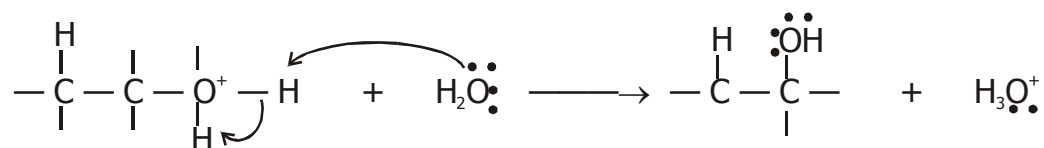
Step (i) : — Protonation of alkene to form carbocation by electrophilic attack :



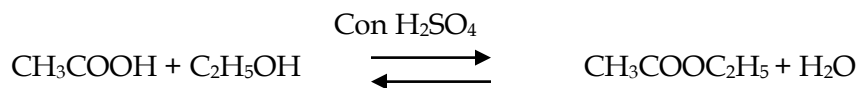
Step (ii) : — Nucleophilic attack of water on carbocation :



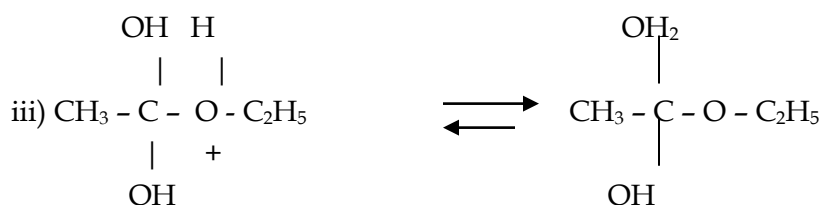
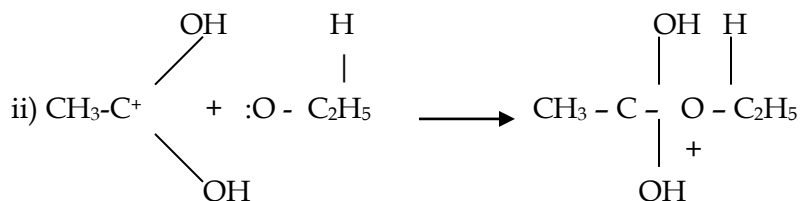
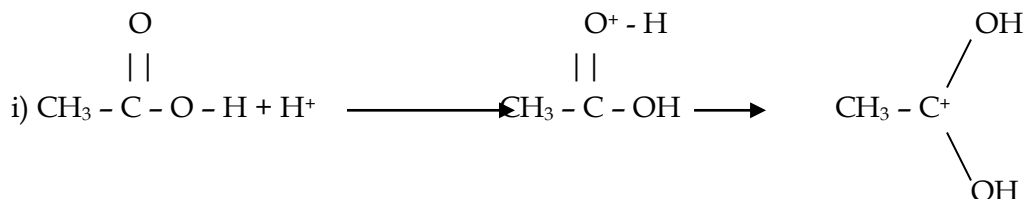
Step (iii) : — Deprotonation to form an alcohol :

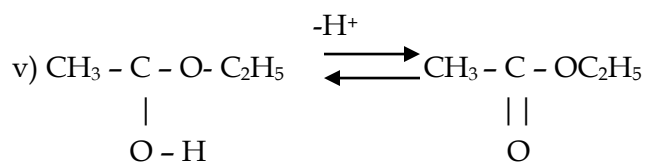


4. ESTERIFICATION



Mechanism:





Identification Test :

- Lucas Test: To differentiate between primary, secondary and Tertiary alcohol.
 - 3° alcohol + Lucas Reagent ----- \rightarrow immediate turbidity
 - 2° alcohol + Lucas Reagent ----- \rightarrow turbidity after heating
 - 1° alcohol + Lucas Reagent ----- \rightarrow No turbidity
- FeCl_3 Test : To differentiate between alcohol and phenol.
 - Alcohol + FeCl_3 ----- \rightarrow No Change
 - Phenol + FeCl_3 ----- \rightarrow Change in colouration of FeCl_3

Activity

- To differentiate between primary, secondary and Tertiary alcohol.
- To differentiate between alcohol and phenols.

Instant Diagnosis Question

- What do you mean by 1° , 2° , 3° alcohols?
- Alcohols have higher boiling points than corresponding ethers, why?
- What is Lucas reagent?

Formative Assignment

- What is the main product obtained when vapors of t-butyl alcohol are passed over copper at 300°C ?
- Phenol has smaller dipole moment than methanol. Why ?
- Explain the following
 - (a) Cyclohexanol is more soluble in water than 1-Hexanol.
 - (b) Propane 1,3-diol is more soluble in the water than propan-1-ol.
- Riemer-Tieman Reaction.
- Kolbe's Reaction.
- Esterification.
- Why is preparation of ethers by acid catalysed dehydration of 2° and 3° alcohols not a suitable method ?

Level Wise Assignment:

Level 1

- Arrange the following compounds in the increasing order of acid strength.
Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol
- Di-tert butyl ether cannot be made by Williamson's synthesis. Why ?
- Arrange the following alcohols in the order of increasing reactivity towards Lucas Reagent: 2-butanol, 1-butanol, 2-methyl-2-propanol

Level 2:

1. How will you account for the following :

Ethers possess a net dipole moment even if they are symmetrical in structure ?

2. The treatment of alkyl chlorides with aq KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are the major products. Explain.
3. How is tert-butyl alcohol obtained from acetone ?

Level 3:

1. An organic compound A with molecular formula C_6H_6O gives a characteristic colour with aq. $FeCl_3$ Solution. When A is treated with CO_2 and NaOH at 410 K, under pressure, it gives compound B which on acidification gives compound C. compound C react with acetyl chloride to give d which is a popular pain killer. Deduce the structures of A, B, C and D and explain all the reactions involved.
2. Explain why dehydration of alcohols to form alkenes is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3 ?
3. An ether A ($C_5H_{12}O$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis form compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.

Project:

To make Roadmap of whole chapter.