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MATRIC NO: 19/ENG05/031

COURSE CODE: CHE 102

1. Alcohols are very important organic compounds. Discuss briefly their classification and give one example each.

Primary alcohols

In a primary (1°) alcohol, the carbon atom that carries the -OH group is only attached to one alkyl group. Some examples of primary alcohols are shown below:

CH₃-CH₂-OH CH₃-CH₂-CH₂-OH CH₃-CH-CH₂-OH

ethanolpropan-1-ol2-methylpropan-1-olNotice that the complexity of the attached alkyl group is irrelevant. In each case there is only
one linkage to an alkyl group from the CH2 group holding the -OH group. There is an exception
to this. Methanol, CH3OH, is counted as a primary alcohol even though there are no alkyl
groups attached to the -OH carbon atom.

Secondary alcohols

In a secondary (2°) alcohol, the carbon atom with the -OH group attached is joined directly to two alkyl groups, which may be the same or different. Examples include the following:

| ÓН | ÓН | ÓН |
|-------------|----------------|---|
| СН₃-॑ĊН-СН₃ | CH₃-ĊH-CH₂-CH₃ | CH ₃ -CH ₂ -CH-CH ₂ -CH ₃ |

propan-2-ol butan-2-ol pent-3-ol

Tertiary alcohols

In a tertiary (3°) alcohol, the carbon atom holding the -OH group is attached directly to three alkyl groups, which may be any combination of the same or different groups. Examples of tertiary alcohols are given below:

2-methylpropan-2-ol 2-methylbutan-2-ol

2. Discuss the solubility of alcohols in water, organic solvents

Small alcohols are completely soluble in water; mixing the two in any proportion generates a single solution. However, solubility decreases as the length of the hydrocarbon chain in the alcohol increases. At four carbon atoms and beyond, the decrease in solubility is noticeable; a two-layered substance may appear in a test tube when the two are mixed. Consider ethanol as a typical small alcohol. In both pure water and pure ethanol, the main intermolecular attractions are hydrogen bonds.



Both of these are held together mainly by hydrogen bonding.

In order to mix the two, the hydrogen bonds between water molecules and the hydrogen bonds between ethanol molecules must be broken. Energy is required for both of these processes. However, when the molecules are mixed, new hydrogen bonds are formed between water molecules and ethanol molecules.



New hydrogen bonds are set up between ethanol and water molecules.

The energy released when these new hydrogen bonds form approximately compensates for the energy needed to break the original interactions. In addition, there is an increase in the disorder of the system, an increase in entropy. This is another factor in deciding whether chemical processes occur. Consider a hypothetical situation involving 5-carbon alcohol molecules.



The hydrocarbon chains are forced between water molecules, breaking hydrogen bonds between those water molecules. The -OH ends of the alcohol molecules can form new hydrogen bonds with water molecules, but the hydrocarbon "tail" does not form hydrogen bonds. This means that many of the original hydrogen bonds being broken are never replaced by new ones.

In place of those original hydrogen bonds are merely van der Waals dispersion forces between the water and the hydrocarbon "tails." These attractions are much weaker, and unable to furnish enough energy to compensate for the broken hydrogen bonds. Even allowing for the increase in disorder, the process becomes less feasible. As the length of the alcohol increases, this situation becomes more pronounced, and thus the solubility decreases.

3. Show the three steps in the industrial manufacture of ethanol. Equations of reaction are mandatory

1.BY THE HYDROLYSIS OF HALOALKANES

Haloalkanes when boiled with aqueous solution of an alkali hydroxide or moist silver oxide furnish alkanols.

| RX + | KOH(aq) - | \longrightarrow ROH \cdot | + 1 | XX |
|---|--------------------|---------------------------------------|-----|------|
| Haloalkane | | Alkanol | | |
| C ₂ H ₅ Br + | KOH(<i>aq</i>) — | $\longrightarrow C_2H_5OH$ | + | KBr |
| C ₂ H ₅ Br + Bromoethane | AgOH — Moist | $\longrightarrow C_2H_5OH$ Ethanol | + | AgBr |

Primary alkyl halides give good yield of alcohols. However, tertiary alkyl halides, in this reaction give, mainly alkene due to dehydrohalogenation.



Secondary alkyl halides give a mixture of alkanol and alkene.

This method is not very useful for preparing alcohols because haloalkanes are themselves obtained from alcohols. However, the preparative utility of this method lies in the preparation of aromatic alcohols. For example,



2. BY HYDRATION OF ALKENES

Alkenes are obtained by cracking of petroleum. They are easily converted to alkanols by the addition of water in presence of tetraoxosulphate (VI) acid.

$$\begin{array}{c} \mathrm{H_2C} = \mathrm{CH_2} + \mathrm{H_2O} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{CH_3} \xrightarrow{} \mathrm{CH_2} \xrightarrow{} \mathrm{OH} \\ \\ \mathrm{Ethene} \end{array}$$

In case of unsymmetrical alkenes, the addition takes place according to Markownikov's rule.



3. BY OXO PROCESS

Alkenes react with carbon monoxide and hydrogen in the presence of octacarbonyl dicobalt [Co(CO)4h as catalyst and at high temperature and pressure to yield aldehydes. Catalytic hydrogenation of aldehydes gives primary alkanols.



4. Show the reaction between 2-methylpropanal and butylmagnesiumchloride Hint: Grignard synthesis

 $\mathbf{2C_4CIMgH_9} + \mathbf{4C_4H_8O} \rightarrow \mathbf{3C_8H_{16}O} + \mathbf{2MgCI} + \mathbf{H_2O}$

- 5. Show the reaction between 2-methyl propanone and butylmagnesiumchloride Hint: Grignard synthesis. Note: show all structures
- 6. Show the reduction reaction of 2-methylpropanone
- 7. Show the reduction reaction of 2-methylpropanal

In general, the **hydrogen**ation is supposed to reduce the compound by adding two **hydrogens** somewhere. The easiest place to add them is wherever the molecule is *most electrophilic*, so it would have to be across the carbonyl group. The C=O bond has the most electron density, and oxygen's higher electronegativity polarizes the bond to be partially positively charged nearer the carbon.



One actual example of <u>hydrogenation</u> (i.e. reduction) of an aldehyde is using LiAlH4 and then an acid workup.



We see this weird behavior from hydrogen since AIH3 is a lewis acid. due to its empty p orbital. It binds to the tetrahedral complex to allow favorable distribution of the carbonyl's electron density into the empty p orbital.

8. Propose a scheme for the conversion of propan-1-ol to propan-2-ol.

<u>Aim:</u>

To convert propan-1-ol to propan-2-ol

Things required:

- Concentrated sulfuric $acid(H_2SO_4)$
- Water

Process involved:

- 1. Dehydration of propan-1-ol to propene.
- 2. Hydrolysis of propene to propan-2-ol

<u>Steps:</u>

1. Dehydration of propan-1-ol to propene.

• When propan-1-ol is treated with concentrated sulfuric $acid^{(H_2SO_4)}$ the phenomenon called dehydration occurs due to which a water molecule from propan-1-ol gets eliminated. • Due to this propan-1-ol gets converted into propene. The reaction involved is as follows:<u>2.</u> <u>Hydrolysis of propene to propan-2-ol</u>

• Propene can be hydrolysed to propan-2-ol in accordance with mechanism called as Markownikoffs addition.

• It states that when an unsymmetrical reagent the negative part of the reagent gets attached itself to the carbon atom of the alkene which has a smaller number of hydrogen atoms.

• In this case, the unsymmetrical reagent used in H_2O which is composed of H^+ and OH^- part.

• Due to hydrolysis of water, the negative part attaches itself to the propene and thus convert it as propan-2-ol.

• The reaction involved is as follows:

 $CH_3 - CH = CH_2 \xrightarrow{H_2O} CH_3 - CH_2 - OH - CH_3$