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Distinction between Primary, secondary and Tertiary alcohols :—

The Primary, secondary and tertiary nature of monohydric alcohol can be determined by following methods :—

(i) By oxidation :— This test is based on the fact that three types of monohydric alcohols give different oxidation products on oxidation with acidified Potassium dichromate ($K_2Cr_2O_7/H_2SO_4$).

a. A primary (1°) alcohol on oxidation first gives an aldehyde then carboxylic acid containing the same number of carbon atoms as the original alcohol.

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

ethyl alcohol — Acetaldehyde — Acetic acid

b. A Secondary (2°) alcohol on oxidation first gives ketone containing same number of carbon atom, but on prolonged action of oxidising it further oxidised into carboxylic acid or a mixture of acids containing lesser number of carbon atoms than the original alcohol.

$$(CH_3)_2CHOH \xrightarrow{[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

isopropyl alcohol — Acetone

$$CH_3-CO-CH_3 \xrightarrow{[O]} CH_3COOH + HCOOH \xrightarrow{[O]} CO_2 + H_2O$$

Acetone — Acetic acid — Formic acid

c. A Tertiary (3°) alcohol can not be oxidised ~~and~~ under these conditions. However, under drastic oxidation the carbon chain is ruptured to give ketones and acids both having fewer number of carbon atoms than the original alcohol.

$$2\,(CH_3)_3COH \xrightarrow[\text{conc. } HNO_3]{[O]} \left[CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \right]$$

2-methylpropene

$$\left[CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \right] \xrightarrow{[O]} CH_3-\overset{CH_3}{\overset{|}{C}}=O \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$$

Acetone → Acetic acid

2. <u>Lucas test</u> :- This test depends upon the different behaviour of alcohol towards Lucas reagent (conc. HCl + anhydrous $ZnCl_2$) at room temperature to form alkyl halide.

a. Tertiary alcohol reacts immediately forming a ppt of alkyl chloride.

b. If turbidity appears after 5 minutes (Sometime) the alcohol is Secondary. and

c. If the solution remains clear i.e. no turbidity is formed the alcohol is Primary. because it doest not react with Lucas reagent at room temp. it requires high temp.

$$R_3COH \xrightarrow{\text{Lucas reagent}} R_3CCl + H_2O$$

3° alcohol → Alkyl halide

$$R_2CHOH \xrightarrow{\text{Lucas reagent}} R_2CHCl + H_2O$$

2° alcohol → Alkyl halide (After few minute)

$$RCH_2OH \xrightarrow[\text{At room temp.}]{\text{Lucas reagent}} \text{no reaction}$$

1° alcohol

3. <u>Victor Meyer's test</u> :- This test depends upon the different behaviour of Nitro alkane towards nitrous acid. The process consist in treating the alcohol under examination with conc. HI or red P and Iodine to form the corresponding alkyl iodide followed by treatment with silver nitrite to form Nitro alkane. It is then treated with nitrous acid and the solution is made alkaline by addition of excess of caustic Soda. The appearance of :-

a. Blood red colour indicates the presence of 1^0 alcohol.

b. Blue colour indicates the presence of 2^0 alcohol and

c. No colour indicates the presence of 3^0 alcohol.

$$\underset{1^0\ \text{alcohol}}{RCH_2OH} \xrightarrow{HI} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2$$

$$RCH_2NO_2 \xrightarrow{HONO} R-\underset{\underset{NOH}{\|}}{C}-NO_2$$

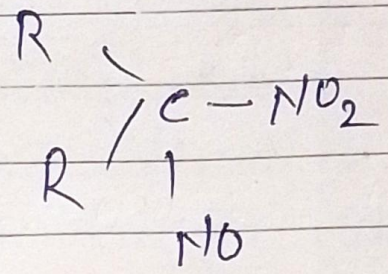
Nitrolic acid

$$R-\underset{\underset{NOH}{\|}}{C}-NO_2 \xrightarrow{NaOH} \text{Blood red colour}$$

$R_2CHOH \xrightarrow{HI} R_2CHI \xrightarrow{AgNO_2} R_2CHNO_2$

2^0 alcohol

$\downarrow$ HONO



Blue colour $\xleftarrow{NaOH}$

Pseudo nitrol

$R_3COH \xrightarrow{HI} R_3CI \xrightarrow{AgNO_2} R_3C\text{-}NO_2$

3^0 alcohol

$\downarrow$ HONO

No reaction

$\downarrow$ NaOH

colourless