VINAYAKAR MATRICULATION HIGHER SECONDARY SCHOOL, SIVAKASI.

12th Standard - CHEMISTRY

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Warm greetings

Dear students I think previous uploaded notes are very useful to you. Now we learn about the **HYDROXY COMPOUNDS AND ETHERS**.

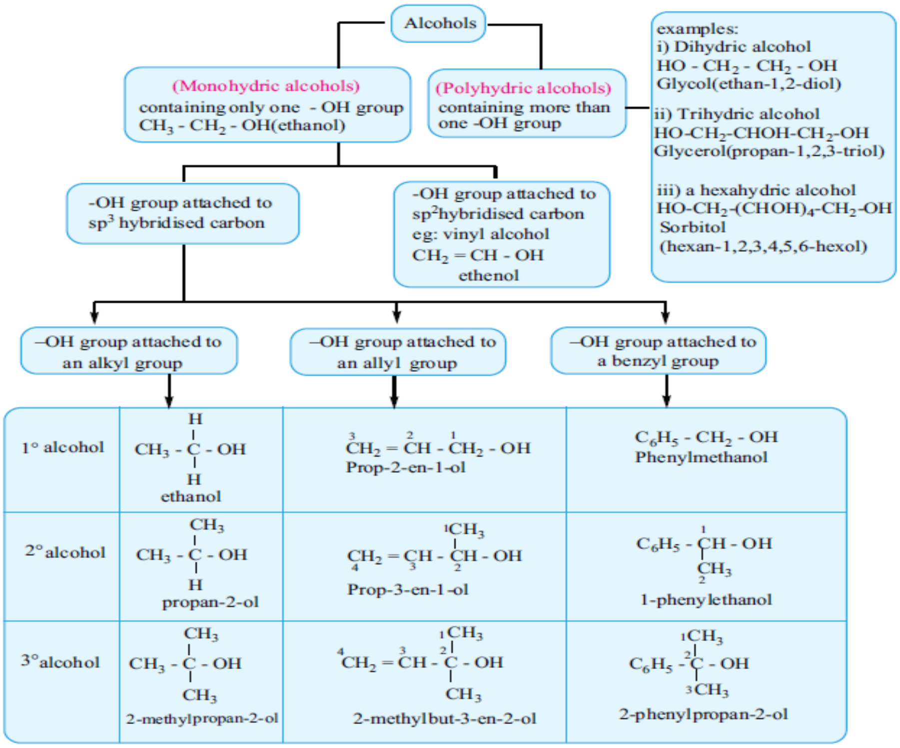
INTRODUCTION

The hydrolysis of an alkyl halide gives an alcohol, an organic compound containing hydroxyl (-OH) functional group. Many organic compounds containing –OH group play an important role in our body. For example, cholesteryl alcohol commonly known as cholesterol is an important component in our cell membrane. Retinol, the storage form of vitamin A, finds application in proper functioning of our eyes. Alcohols also find application in many areas like medicine, industry, etc.,

For example, methanol is used as an industrial solvent, ethyl alcohol an additive to petrol, isopropyl alcohol as a skin cleanser for injection, etc., The hydroxyl group of alcohol can be converted to many other functional groups. Hence, alcohols are important resource in synthetic organic chemistry. In this unit, we will learn the preparation, properties and uses of alcohols, phenols and ethers.

Classification of alcohols

Alcohols can be classified based on the number of hydroxyl groups and the nature of theCarbon to which the functional group (–OH) is attached.



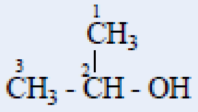
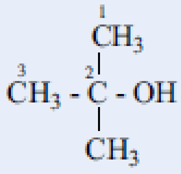
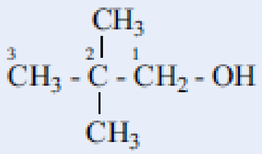
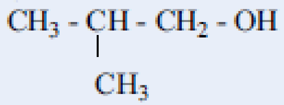
IUPAC Nomenclature

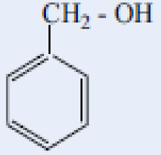
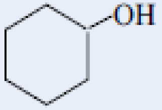
Naming the organic compounds according to IUPAC guidelines in XI standard. Let us recall the basic rules to name the alcohols.

- Select the longest continuous chain of carbon atoms (root word) containing the functional group (-OH).
- Number the carbon atoms in the chain so that the carbon bearing the -OH group has the lowest possible number.
- Name the substituent (if any)
- Write the name of the alcohol as below.

Prefix	+	Root word	+	Primary suffix	+	Secondary suffix
(substituents)		(longest chain)		(Saturation /unsaturation)		(ol)

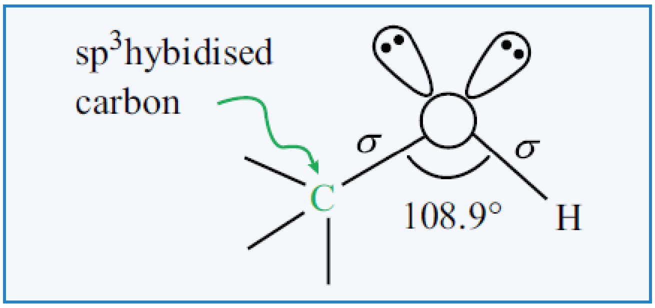
The following table illustrates the IUPAC nomenclature of alcohols.

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Isopropyl alcohol  $\overset{3}{C}H_3 - \overset{2}{C}H(\overset{1}{C}H_3) - OH$ Propan-2-ol	-	Prop	an~~e~~	2-ol
Tertiary butyl alcohol  $\overset{3}{C}H_3 - \overset{2}{C}(\overset{1}{C}H_3)(CH_3) - OH$ 2-methylpropan-2-ol	2-methyl	Prop	an~~e~~	2-ol
Neopentyl alcohol  $\overset{3}{C}H_3 - \overset{2}{C}(CH_3)_2 - \overset{1}{C}H_2 - OH$ 2,2-dimethylpropan-1-ol	2,2-dimethyl	Prop	an~~e~~	1-ol
Isobutyl alcohol  $\overset{3}{C}H_3 - \overset{2}{C}H(CH_3) - \overset{1}{C}H_2 - OH$ 2-methylpropan-1-ol	2-methyl	Prop	an~~e~~	1-ol

Benzyl alcohol  Phenylmethanol	Phenyl	Meth	an~~e~~	ol
Allyl alcohol $\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2-OH$ Prop-2-en-1-ol	-	Prop	2-en~~e~~	1-ol
Cyclohexyl alcohol  Cyclohexanol	-	Cyclohex	an~~e~~	ol
Glycerol $HO-CH_2-CH(OH)-CH_2-OH$ Propan – 1,2,3 – triol	-	Prop	an~~e~~	1,2,3 – triol

Structure of the functional group of alcohol.

The structure of -O-H group which is attached to a sp^3 hybridized carbon is similar to the structure of -O-H group attached to a hydrogen in water. i.e., 'V' shaped. In such alcohols, one of the sp^3 hybridized orbital of oxygen linearly overlap with the sp^3 hybridized orbital of carbon to form a C-O, ' σ ' bond and another sp^3 hybridized orbital linearly overlap with 1s orbital of hydrogen to form a O-H' σ ' bond. The remaining two sp^3 hybridized orbitals of oxygen are occupied by two lone pairs of electrons. Due to the lone pair – lone pair repulsion, the C-O-H bond angle in methanol is reduced to 108.9° from the regular tetrahedral bond angle of 109.5°.



Preparation of alcohols

The nucleophilic substitution reactions of alkyl halides with dilute alkali, conversion of alkenes to alcohols by hydration and the preparation of alcohols using Grignard reagent in XI standard. These reactions are summarised below.

Alkyl halides on heating with dilute aqueous NaOH gives alcohols. Primary alkyl halides undergo substitution by SN^2 reaction. Secondary and tertiary alkyl halides usually undergo nucleophilic substitution by SN^1 mechanism.

$$R\text{-}X+NaOH(aq)\xrightarrow{\Delta}R\text{-}OH+NaX$$

If R =t-butyl, the reaction proceeds through the formation of t-butyl carbocation

- Addition of water across the double bond of an alkene in presence of sulphuric acid gives alcohols. This addition reaction follows Markownikoff’s rule.

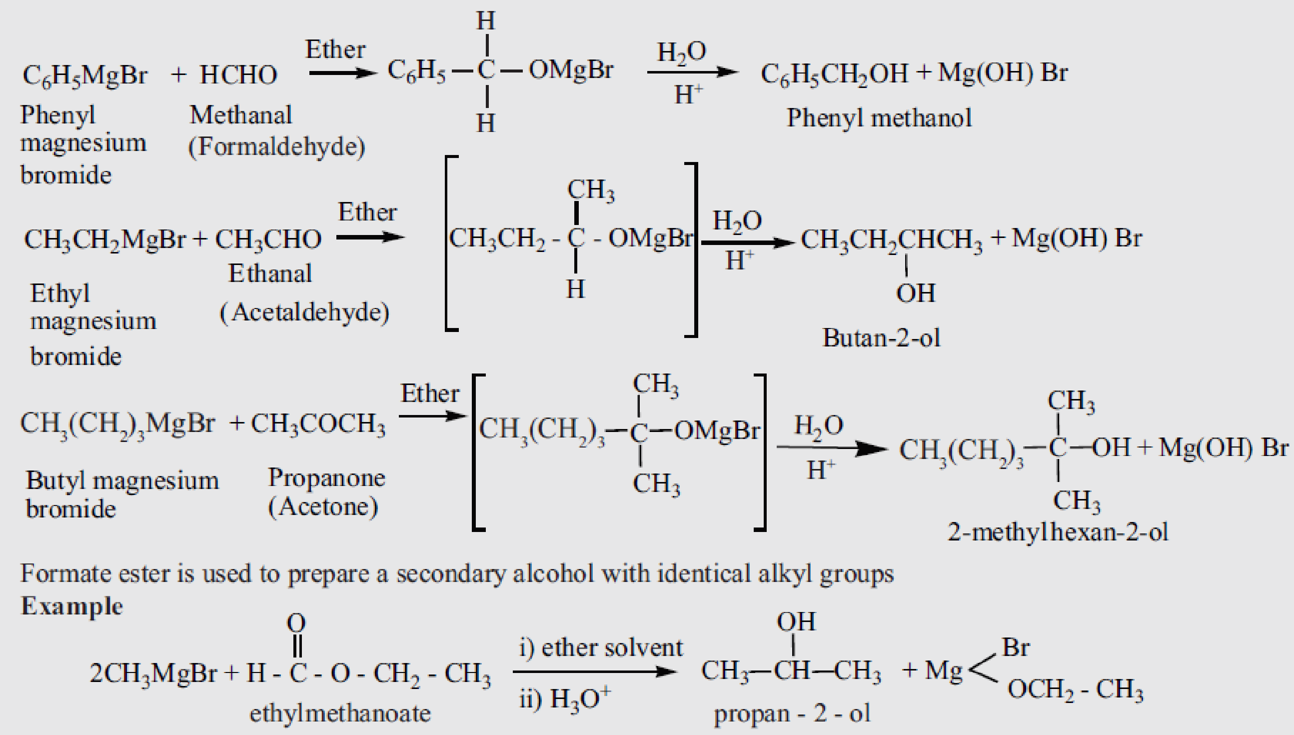
Example:

$$\underset{\text{propylene}}{CH_3\text{-}CH{=}CH_2}+H_2O\xrightarrow{Conc.H_2SO_4}\underset{\text{propan-2-ol}}{CH_3\text{-}CH(OH)\text{-}CH_3}$$

From Grignard reagent

Nucleophilic addition of Grignard reagent to aldehydes/ketones in presence of dry ether followed by the acid hydrolysis gives alcohols. Formaldehyde gives primary alcohol and other aldehydes give secondary alcohols. Ketones give tertiary alcohols.

Examples:



$$\underset{\text{Phenyl magnesium bromide}}{C_6H_5MgBr}+\underset{\text{Methanal (Formaldehyde)}}{HCHO}\xrightarrow{\text{Ether}}C_6H_5-\overset{H}{\underset{H}{C}}-OMgBr\xrightarrow[H^+]{H_2O}\underset{\text{Phenyl methanol}}{C_6H_5CH_2OH}+Mg(OH)Br$$

$$\underset{\text{Ethyl magnesium bromide}}{CH_3CH_2MgBr}+\underset{\text{Ethanal (Acetaldehyde)}}{CH_3CHO}\xrightarrow{\text{Ether}}\left[CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-OMgBr\right]\xrightarrow[H^+]{H_2O}\underset{\text{Butan-2-ol}}{CH_3CH_2\underset{OH}{C}HCH_3}+Mg(OH)Br$$

$$\underset{\text{Butyl magnesium bromide}}{CH_3(CH_2)_3MgBr}+\underset{\text{Propanone (Acetone)}}{CH_3COCH_3}\xrightarrow{\text{Ether}}\left[CH_3(CH_2)_3-\overset{CH_3}{\underset{CH_3}{C}}-OMgBr\right]\xrightarrow[H^+]{H_2O}\underset{\text{2-methylhexan-2-ol}}{CH_3(CH_2)_3-\overset{CH_3}{\underset{CH_3}{C}}-OH}+Mg(OH)Br$$

Formate ester is used to prepare a secondary alcohol with identical alkyl groups

Example

$$2CH_3MgBr+\underset{\text{ethylmethanoate}}{H\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}CH_3}\xrightarrow[\text{ii) }H_3O^+]{\text{i) ether solvent}}\underset{\text{propan - 2 - ol}}{CH_3-\overset{OH}{CH}-CH_3}+Mg\begin{cases}Br\\OCH_2\text{-}CH_3\end{cases}$$

Hydroboration

Diborane reacts with an alkene to form trialkyl borane which on treatment with H_2O_2 in presence of NaOH gives an alcohol. (Refer reactions of diborane) The overall reaction is hydration of an alkene. This reaction yields an anti-Markownikoff's product.

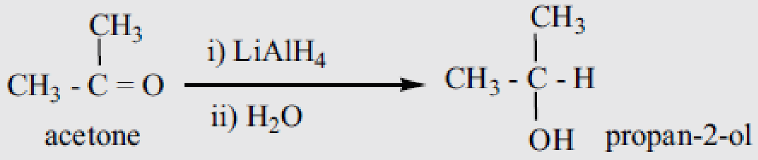
$$6CH_3-CH=CH_2+B_2H_6 \longrightarrow \underset{\text{Tripropylborane}}{2(CH_3-CH_2-CH_2)_3B}$$

$$(CH_3-CH_2-CH_2)_3B+3H_2O_2 \xrightarrow{OH^-} \underset{\text{propan-1-ol}}{3CH_3-CH_2-CH_2-OH}+B(OH)_3$$

Reduction of carbonyl compounds

Reduction of aldehydes/ketones with $LiAlH_4$ in the presence of solvents like THF (Tetrahydrofuran) followed by hydrolysis gives alcohols. Unlike other reducing agents such as Raney Ni, Na-Hg/H_2 O, the lithium aluminium hydride does not reduce the carbon**–**carbon double bond present in the carbonyl compound and hence it is a best reagent to prepare unsaturated alcohols.

Examples:



$$\underset{\text{acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} \xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-H \quad \text{propan-2-ol}$$

$$C_6H_5\text{-}COOH \xrightarrow[(ii)H_2O]{(i)LiAlH_4} C_6H_5CH_2OH$$

Benzonic acid Phenyl methanol(Benzyl alcohol)

$$CH_3COOCH_2CH_3 \xrightarrow[(ii)H_2O]{(i)LiAlH_4} 2CH_3CH_2OH$$

Ethyl ethanoate Ethanol
(ethyl acetate)

$$CH_3\text{-}CH=CH\text{-}CHO \xrightarrow[(ii)H_2O]{(i)LiAlH_4} CH_3\text{-}CH=CH\text{-}CH_2OH$$

crotonaldehyde crotyl alcohol
(prop-2-enal) (but-2-en-1-ol)

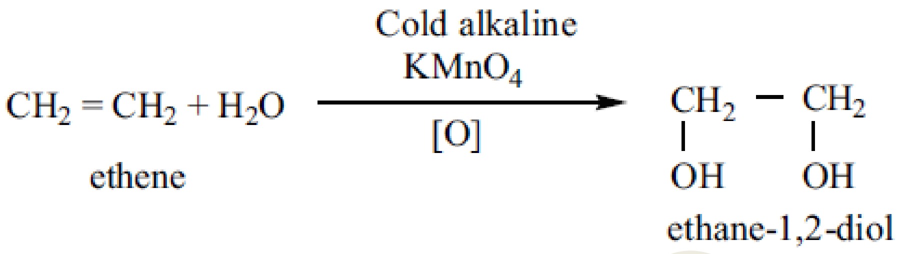
When two or more functional groups are present in a molecule a less vigorous sodium borohydride is used as a reducing agent to reduce the more reactive group. For example, if a compound contains both carbonyl and carboxyl group, it preferentially reduces the carbonyl group.

$$RCOCH_2CH_2COOH \xrightarrow[H_3O^+]{NaBH_4} RCHOH\text{-}CH_2CH_2COOH$$

4-alkyl- 4- hydroxybutanoic acid

Preparation of glycol

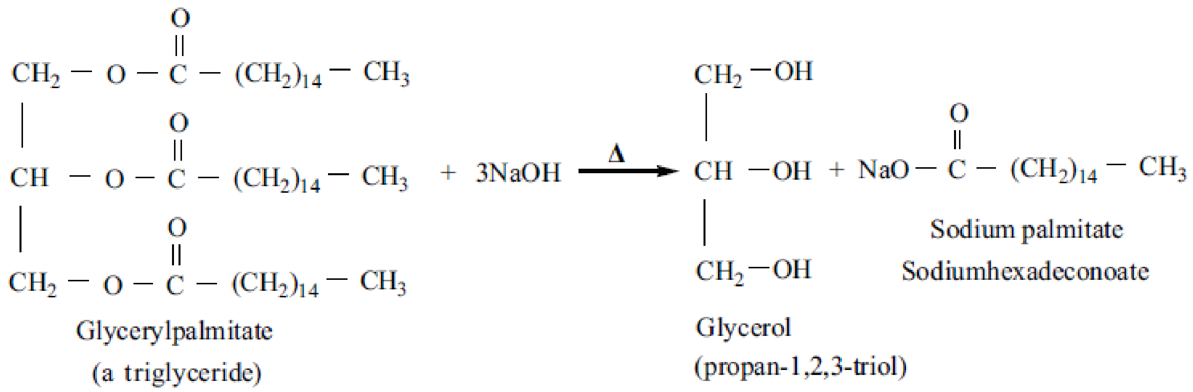
The hydroxylation of ethylene using cold alkaline solution of potassium permanganate (Baeyer's reagent) gives ethylene glycol.



$$\underset{\text{ethene}}{CH_2=CH_2+H_2O} \xrightarrow[{[O]}]{\text{Cold alkaline } KMnO_4} \underset{\text{ethane-1,2-diol}}{\underset{OH\quad\ \ OH}{CH_2-CH_2}}$$

Preparation of glycerol

Glycerol occurs in many natural fats and it is also found in long chain fatty acids in the form of glyceryl esters (Triglycerides). The alkaline hydrolysis of these fats gives glycerol and the reaction is known as saponification.



Glycerylpalmitate
(a triglyceride)

Glycerol
(propan-1,2,3-triol)

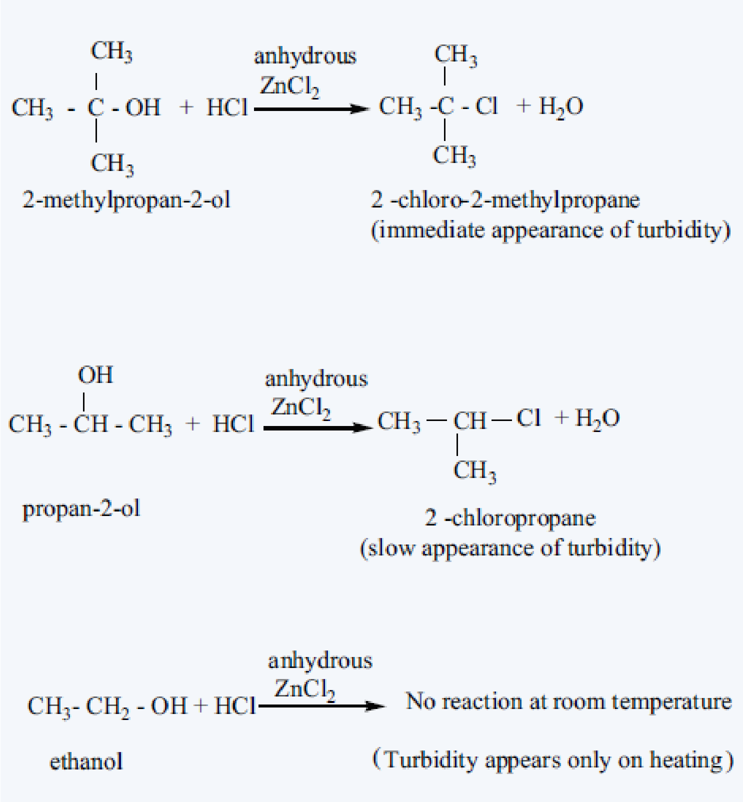
Sodium palmitate
Sodiumhexadeconoate

Methods to differentiate primary, secondary and tertiary alcohols

The following tests are used to distinguish between 1°, 2° and 3° alcohols.

a) Lucas test

When alcohols are treated with Lucas agent (a mixture of concentrated HCl and anhydrous $ZnCl_2$) at room temperature, tertiary alcohols react immediately to form a turbidity due to the formation of alkyl chloride which is insoluble in the medium. Secondary alcohols react within 10 minutes to form a turbidity of alkyl chloride where primary alcohols do not react at room temperature.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + HCl \xrightarrow[ZnCl_2]{anhydrous} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + H_2O$$

$$CH_3-\overset{OH}{CH}-CH_3 + HCl \xrightarrow[ZnCl_2]{anhydrous} CH_3-\underset{CH_3}{CH}-Cl + H_2O$$

$$CH_3-CH_2-OH + HCl \xrightarrow[ZnCl_2]{anhydrous} \text{No reaction at room temperature}$$

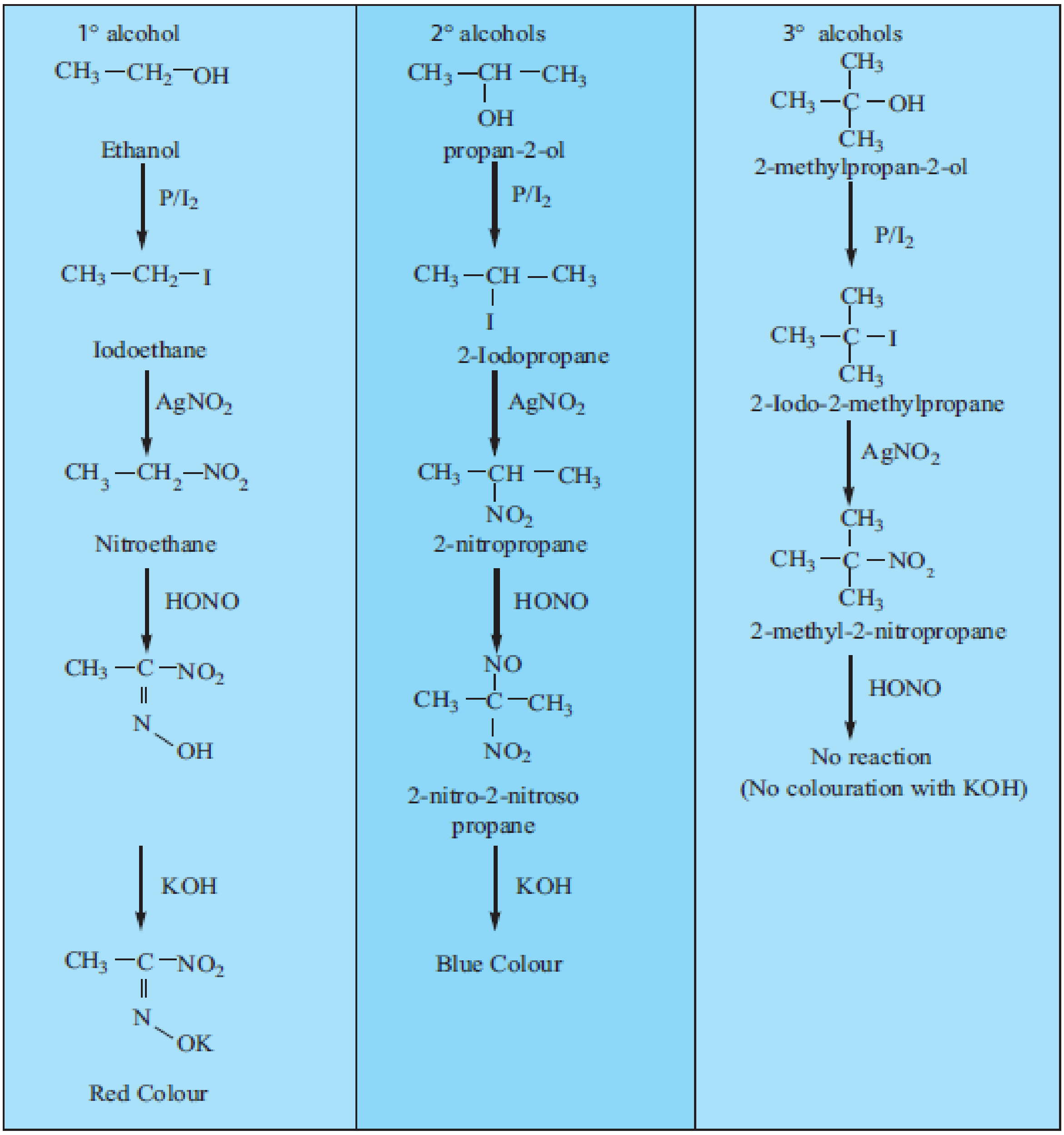
b) Victor Meyer's test

This test is based on the behaviour of the different nitro alkanes formed by the three types of alcohols with nitrous acid and it consists of the following steps.

- Alcohols are converted into alkyl iodide by treating it with I_2 /P.
- Alkyl iodide so formed is then treated with $AgNO_2$ to form nitro alkanes.
- Nitro alkanes are finally treated with HNO_2 (mixture of $NaNO_2$ HCl /) and the resultant solution is made alkaline with KOH.

Result

- ✓ Primary alcohol gives red colour
- ✓ Secondary alcohol gives blue colour.
- ✓ No colouration will be observed in case of tertiary alcohol.


1° alcohol
CH3—CH2—OH
Ethanol
P/I2
CH3—CH2—I
Iodoethane
AgNO2
CH3—CH2—NO2
Nitroethane
HONO
CH3—C—NO2 = N—OH
KOH
CH3—C—NO2 = N—OK
Red Colour
2° alcohols
CH3—CH—CH3 OH
propan-2-ol
P/I2
CH3—CH—CH3 I
2-Iodopropane
AgNO2
CH3—CH—CH3 NO2
2-nitropropane
HONO
NO CH3—C—CH3 NO2
2-nitro-2-nitroso propane
KOH
Blue Colour
3° alcohols
CH3 CH3—C—OH CH3
2-methylpropan-2-ol
P/I2
CH3 CH3—C—I CH3
2-Iodo-2-methylpropane
AgNO2
CH3 CH3—C—NO2 CH3
2-methyl-2-nitropropane
HONO
No reaction
(No colouration with KOH)

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