ALCOHOL

Preface

Organic compound having - OH group and hydroxy derivative of alkane or mono alkyl derivative of water is known as alcohol. **General alcohol** is used in beverage to stimulate nervous system but all other alcohols are poisonous in nature. This topic deals with its preparation from various organic compounds, its physical properties, various chemical properties, differentiation between 1º, 2º and 3º alcohol, Lucas test and Victor Meyer Test to differentiate alcohols

This book consists of theoritical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope bettter understanding of the chapter and to have better grasping level in the class.

Total number of Questions in **Alcohol** are :–

(i) In chapter Examples 12

(ii) Solved Examples 30

Total no. of questions 42

1. INTRODUCTION

(a) These are the organic compounds in which –OH group is directly attached with carbon.
(b) These are hydroxy derivatives of alkanes and mono alkyl derivatives of water.
(c) Their general formula is $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$.
(d) The hybridisation state of carbon is sp^3.
(e) Geometry is tetra hedral.
(f) In these compounds C-O bond length is 1.42 Å.
(g) These are of following types, depending upon the no. of OH groups.
(i) Monohydric alcohol:-
Contains one –OH group only, eg.C_2H_5OH
(ii) Dihydric alcohol :-
Contains two –OH groups. eg. glycol
(iii) Trihydric alcohol:-
Contains three –OH groups eg. glycerol
(iv) Polyhydric alcohol :-
Contains more than three - OH groups. eg, sorbitol, manitol.
(h) Alcohol shows chain, position & functional group isomerism. If chiral carbon atom is present, they shows optical isomerism.

2. METHODS OF PREPARATION

2.1 From Alkyl halides:-

Alkyl halides reacts with aq. KOH/aq. AgOH or H_2O and forms alcohol.

$$R-CH_2-X + K-OH\,(aq.) \longrightarrow R-CH_2OH + KX$$

$$R-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{CH}}}}-X + AgOH\,(aq.) \longrightarrow R-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{CH}}}}-OH + AgX$$

$$R-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-X + H-OH \longrightarrow R-\underset{\displaystyle R}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-OH + HX$$

2.2 From Alkenes :-

2.2.1 Hydration – Alkenes are catalytically hydrated by dilute mineral acid solution.

$$CH_2 = CH_2 + H_2O \xrightarrow{\text{dil } H_2SO_4} CH_3CH_2OH$$

$$R - CH = CH_2 + H_2O \xrightarrow{\text{dil } H_2SO_4} R-\underset{\displaystyle OH}{\overset{\displaystyle }{\underset{|}{\overset{|}{CH}}}}-CH_3$$

NOTE : Refer to chapter 'Alkenes' for mechanism of above reaction.

2.2.2 Oxymercuration – demercuration–

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds, which on reduction yield alcohols. (Markovnikov addition)

$$>C = C< + H_2O + Hg(OAc)_2 \longrightarrow$$

Mercuric acetate

$$-\underset{\displaystyle OH}{\overset{|}{C}}-\underset{\displaystyle Hg\,O\,Ac}{\overset{|}{C}}- \xrightarrow{NaBH_4} -\underset{\displaystyle OH}{\overset{|}{C}}-\underset{\displaystyle H}{\overset{|}{C}}-$$

Alcohol

NOTE : Refer to chapter 'Alkenes' for mechanism of above reaction.

2.2.3 Hydroboration – Oxidation :

(Anti–Markownikov orientation)

$$>C = C< + \frac{1}{2}(BH_3)_2 \longrightarrow \quad B$$

Alkene Diborane Tri alkyl borane

$$\xrightarrow[OH^-]{H_2O_2} -\underset{\displaystyle H}{\overset{|}{C}}-\underset{\displaystyle OH}{\overset{|}{C}}- + B(OH)_3$$

NOTE : Refer to chapter 'Alkenes' for mechanism of above reaction.

2.3 By Reduction of Carbonyl compounds :-

$$R-\underset{\displaystyle O}{\overset{\displaystyle }{\underset{\|}{\overset{\|}{C}}}}-H + 2H \xrightarrow{LiAlH_4/Na+C_2H_5OH} R-CH_2OH$$

1º alcohol

$$R-\underset{\displaystyle O}{\overset{\displaystyle }{\underset{\|}{\overset{\|}{C}}}}-R + 2H \xrightarrow{LiAlH_4/Na+C_2H_5OH} R-\underset{\displaystyle OH}{\overset{\displaystyle }{\underset{|}{\overset{|}{CH}}}}-R$$

2º alcohol

Note :

(i) We cannot obtain 3º alcohol from this method
(ii) If we use NaH as reductant then the process is called as '**Darzen's process**'.

2.4 By Reduction of Acid & its derivatives :-

$$R-\underset{\displaystyle O}{\overset{\displaystyle }{\underset{\|}{\overset{\|}{C}}}}-OH + 4H \xrightarrow{LiAlH_4} RCH_2OH$$

$$R-\underset{\underset{O}{\|}}{C}-X + 4H \xrightarrow{LiAlH_4} R\,CH_2OH + HX$$

$$R-\underset{\underset{O}{\|}}{C}-OR' + 4H \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

$$RCOOCOR + 8H \xrightarrow{LiAlH_4} 2\,RCH_2OH + H_2O$$

Important Note :- Acid amide does not form alcohol on reduction. It forms primary amine.

2.5 From Grignard reagent :

2.5.1 With oxygen : –

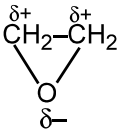
Grignard reagent forms alcohol of same no. of carbon atoms as in Grignard reagent.

$$2R-Mg-X + O_2 \xrightarrow[Al_2O_3]{\Delta} 2R-O-Mg-X$$

$$\xrightarrow{2HOH} 2ROH + 2\,Mg(X)OH$$

2.5.2 With ethylene oxide :

$$R^{\delta-}\leftarrow Mg^{\delta+}-X + \overset{\delta+}{C}H_2-\overset{\delta+}{C}H_2 \longrightarrow$$



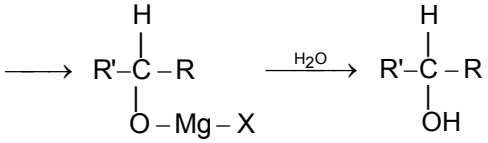
$$R-CH_2-CH_2-O-Mg-X$$

$$\xrightarrow{H_2O} R-CH_2-CH_2OH + Mg(X)OH$$

Alcohol with two carbon more than Grignard reagent

2.5.3 With carbonyl compounds :

$$R^{\delta-}\leftarrow Mg^{\delta+}-X +$$



Note :

(i) If R' = H , Product will be 1° alcohol.

(ii) If R' = R, Product will be 2° alcohol.

(iii) If carbonyl compound is ketone, product will be 3° alcohol.

(iv) It is the best method for preparation of alcohol because we can prepare every type of alcohols.

2.6 From Primary amines :-

$$R-NH_2 + HNO_2 \xrightarrow{HCl} R-OH + N_2 + H_2O.$$

But it is not a good method for preparation of alcohol because a number of byproducts are formed in this reaction like

alkyl chloride, alkyl nitrite, alkene and ether.

Note : -

In this reaction if we take ethyl amine then main product will be ethanol while if we take methyl amine, then main product will be dimethyl ether.

Examples based on Methods of Preparation of Alcohol

Ex.1 Which of the following reaction is called as 'Bouveault-Blanc reduction' -

(A) Reduction of acyl halide through Na/C_2H_5OH

(B) Reduction of ester through Na/C_2H_5OH

(C) Reduction of anhydride through Na/C_2H_5OH

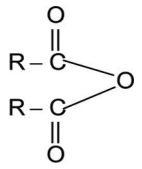
(D) Reduction of carbonyl compounds through Na/C_2H_5OH

(Ans.D)

Sol. Reduction of carbonyl compounds through Na/C_2H_5OH is called as Bouveault–Blanc reduction.

Ex.2 Acid derivative which does not give alcohol on reduction:-

(A) $R-\underset{\underset{O}{\|}}{C}-X$ (B) $R-\underset{\underset{O}{\|}}{C}-NH_2$

(C) $R-\underset{\underset{O}{\|}}{C}-OR'$ (D) 

(Ans. B)

Sol. Acid amide forms primary amine on reduction.

Ex. 3 In which of the following reaction alcohol is not formed-

(A) $R - CH = CH_2 + H_2O \xrightarrow[High\ pr.]{H^+}$

(B) $R - COCl + 2H_2 \xrightarrow{LiAlH_4}$

(C) $(R - CO)_2\,O + 4\,H_2 \xrightarrow{LiAlH_4}$

(D) $R - CH_2 - CH_3 + H_2O \xrightarrow[High\ pr.]{H^+}$

(Ans. D)

Sol. Alkanes are paraffins. They do not form alcohol on hydrolysis.

3. PHYSICAL PROPERTIES

(a) Alcohols are colourless with specific smell liquid. They are soluble is water due to H-bonding. These are partially soluble in organic solvents.

(b) They are liquid in nature up to 12-carbon.

(c) Melting point and Boiling point

$$\alpha \text{ molecular mass } \alpha \frac{1}{\text{No. of branches}}$$

(d) Boiling point of alcohols are higher than equivalent ethers. It is due to H-bonding.

(e) Alcohols are poisonous in nature also. Poisonous character increase with increment in molecular weight or branching. Ethanol is exception, which is non-poisonous in nature. It is most useful organic solvent.

(f) Methanol causes blindness.

(g) Isopropyl alcohol is called as rubbing alcohol.

(h) Cholestrol is also an example of complex alcohol which is called notorious alcohol because it causes heart attack.

(i) Viscous nature of alcohol is directly proportional to H-bonding or number of -OH groups. That is why we can say alcohol is less viscous than glycerol & manitol is more viscous than glycerol.

(j) Ethanol is liquid while glucose is solid. It is due to more H-bonding in glucose.

Examples based on Physical properties of Alcohol

Ex.4 Which one of the following alcohol has highest boiling point -

(A) Methanol (B) Ethanol

(C) Propanol (D) Isopropanol **(Ans.C)**

Sol. Boiling point $\propto$ molecular weight

$$\propto \frac{1}{\text{No. of branches}}$$

Ex.5 Dimethyl ether and ethanol have same molecular weight but boiling point of ethanol is greater than dimethyl ether, cause of this is that dimethyl ether -

(A) Having less no. of branches

(B) Arrangement of hydrogen is different

(C) Due to hydrogen bonding in alcohol

(D) None of these **(Ans.3)**

Sol. Due to hydrogen bonding in alcohol boiling point of alcohol is high.

4. CHEMICAL PROPERTIES

Chemical reactions of alcohols are classified in the following three types :-

4.1 Reaction of H atom of –OH group of Alcohols

4.2 Reaction of OH group of Alcohols

4.3 General reaction of Alcohols.

4.1 Reaction of H atom of –OH group of Alcohols :-

These are the reactions in which alcohol shows acidic character.

4.1.1 Reaction with Na :-

$$2R{-}O{-}H + Na \longrightarrow 2R - O - Na + H_2\uparrow$$

The acidic order of alcohols is

MeOH > 1º > 2º > 3º

4.1.2 Esterification / Reaction with carboxylic acid :-

$$R{-}O{-}H + H{-}O{-}\underset{\underset{O}{\|}}{C}{-}R \xrightarrow{\text{conc.}H_2SO_4} R{-}\underset{\underset{O}{\|}}{C}{-}O{-}R + H_2O$$

ester

Mechanism :-

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$R-\underset{\underset{O}{\|}}{C}-\ddot{O}-H + H^+ \longrightarrow R-\underset{\underset{O\ H}{\|\ |}}{C}-\overset{\oplus}{\ddot{O}}-H \xrightarrow{-H_2O}$$

$$R-C^+ \xrightarrow{ROH} R-\overset{\oplus}{O}-\underset{\underset{O}{\|}}{C}-R \xrightarrow{-H^+} R-\underset{\underset{O}{\|}}{C}-OR$$

Note :- The above reaction is laboratory method of ester preparation.

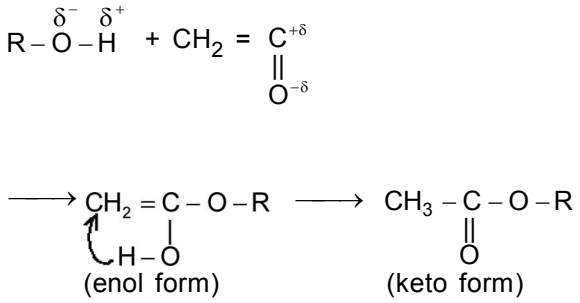
4.1.3 Reaction with Acid derivatives :-

$$R{-}O{-}H + X-\underset{\underset{O}{\|}}{C}-R \xrightarrow{\text{Conc.}H_2SO_4}$$

$$R-O-H + R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R \longrightarrow R-O-\underset{\underset{O}{\|}}{C}-R + HX$$

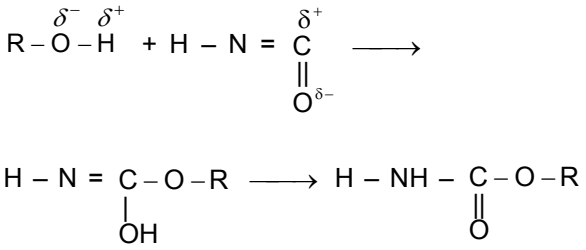
$$\xrightarrow{\text{Conc.}H_2SO_4} R-\underset{\underset{O}{\|}}{C}-O-R$$

4.1.4 Reaction with Ketene :-



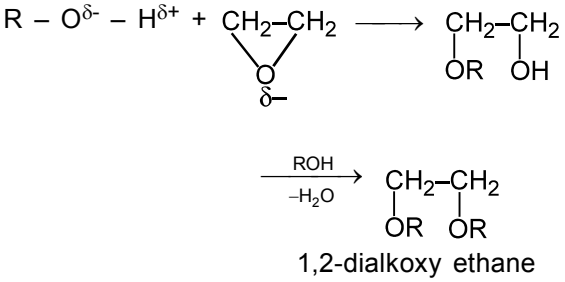
(enol form) (keto form)

4.1.5 Reaction with Isocyanic Acid :-



amino ester (urethane)

4.1.6 Reaction with ethylene oxide :-



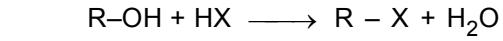
1,2-dialkoxy ethane

4.1.7 Reaction with Diazomethane :-

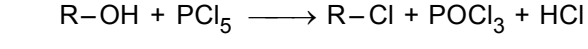
(ether)

4.2 Reaction of – OH group of Alcohols :-

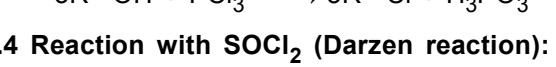
4.2.1 Reaction with dry HX (Grove's Process) :–



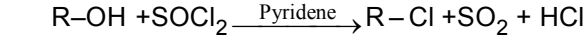
4.2.2 Reaction with PCl_5 :–



4.2.3 Reaction with PCl_3 : –



4.2.4 Reaction with $SOCl_2$ (Darzen reaction): –



4.2.5 Reaction with ammonia : –

4.2.6 Reaction with HNO_3 : –

(conc.) alkyl nitrate

(soluble ester)

Mechanism :-

alkyl nitrate

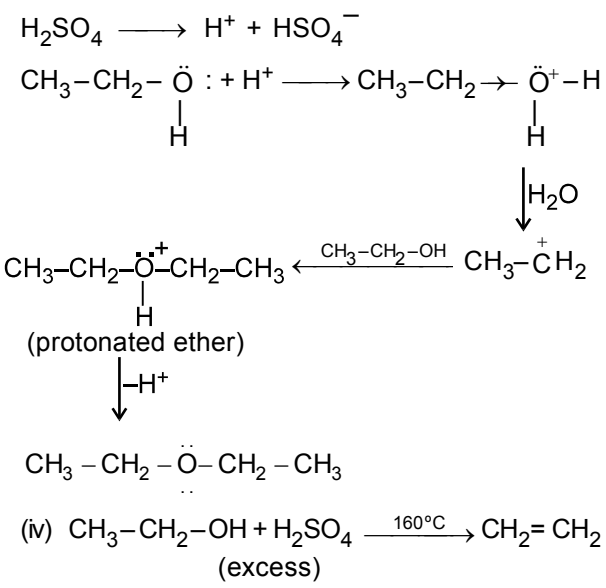
4.2.7 Reaction with H_2SO_4 :-

diethyl sulphate

stable upto

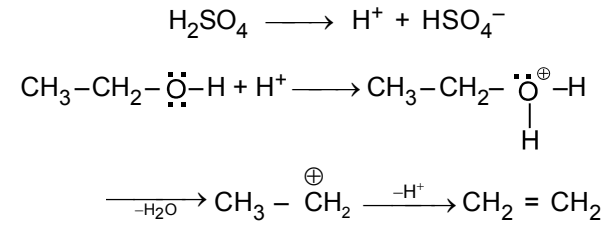
(80-100ºC)

Mechanism :-



(iv) $CH_3-CH_2-OH + H_2SO_4 \xrightarrow[\text{(excess)}]{160°C} CH_2= CH_2$

Mechanism :-



Note :-

In the above reaction excess of ethanol is present so, intermediate carbocation satisfies itself by elimination.

4.3 General reaction of Alcohols :-

4.3.1 Reduction :-

$R-O-H + 2\ HI \xrightarrow[150°C]{Red P} R - H$

4.3.2 Oxidation :

(i) Primary alcohol initially forms aldehyde on oxidation and on further oxidation forms respective acid.

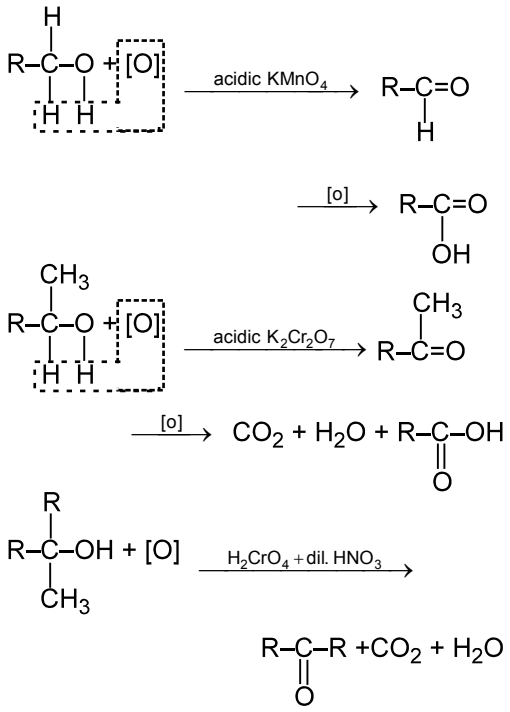
(ii) Secondary alcohol initially forms respective ketone on oxidation which on further oxidation forms acid of less carbon. Oxidation of ketone is slightly difficult than aldehyde due to stability so, we use strong oxidising agent for oxidation.

(iii) Tertiary alcohols are resistant to oxidation in normal conditions but on taking strongest oxidising agent like chromic acid in dilute nitric acid then they form less carbon ketone.

(iv) For oxidation of 1° alcohol, acidic $KMnO_4$ is used as oxidant while for 2° alcohol acidic $K_2Cr_2O_7$ (more strong than $KMnO_4$) is used.

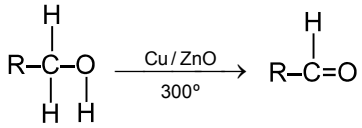
(v) For both (1° and 2° alcohol) we can use common oxidising agent also, like chromic acid in dilute H_2SO_4. Colour of this solution is orange and it turns into green colour due to Cr^{+3}.

(vi) Reacting species of solution is $HCrO_4^-$.

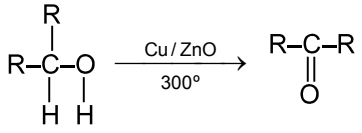


(ketone of lesser carbon)

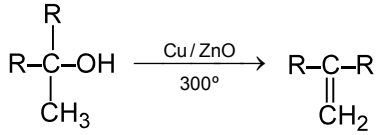
4.3.3 Catalytic Oxidation / Dehydrogenation :-



1° alcohol aldehyde



secondary alcohol ketone

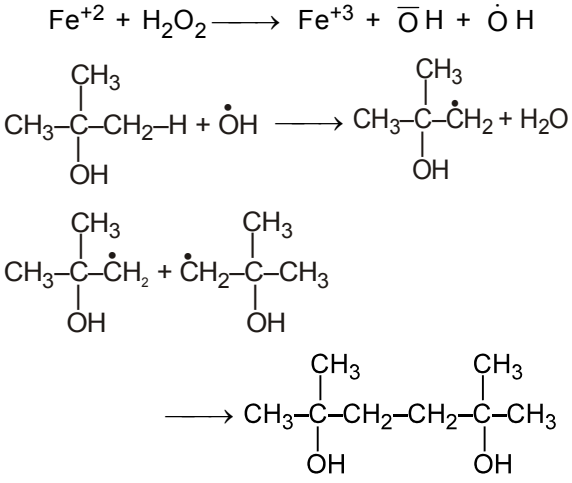


tert. alcohol alkene

(**Note : –** This is dehydration process.)

4.3.4 Oxidation through Fenton's Reagent :–

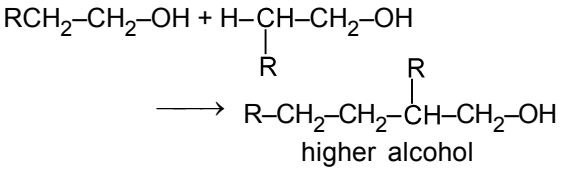
Higher and branched alcohols are converted into diols through Fentons reagent. ($FeSO_4 + H_2O_2$) is Fenton's reagent.



2,5-dimethyl hexandiol-2,5

4.3.5 Self Condensation : -

When alcohol is heated with sodium ethoxide then by self condensation they convert into higher alcohol.



higher alcohol

Note : –

The above reaction is called as '**Guerbet's Reaction**'.

Examples based on Chemical Reactions of Alcohol

Ex.6 Reactivity order of alcohols towards Na will be -

(A) 3º > 2º > 1º > MeOH

(B) MeOH > 1º > 2º > 3º

(C) 2º > 1º > 3º > MeOH

(D) 1º = 2º = 3º = MeOH **(Ans. B)**

Sol. In the above reaction O–H bond breaks and acidic character appears. The acidic strength of the alcohol isMeOH > 1º > 2º > 3º

Ex.7 In the esterification of alcohol by carboxylic acid, proton is given by –

(A) Alcohol (B) Conc. H_2SO_4

(C) Acid carboxylic (D) None of these

(Ans.B)

Sol. H_2SO_4 is a strong acid and the corboxylic acid behaves as base in presence of H_2SO_4. The mechanism of the reaction also proves it.

Ex.8 2-methyl 2-propanol with Fenton's reagent gives -

(A) 1,2-methyl propene -1

(B) 2-methyl propene -2

(C) 2,5-dimethyl hexanediol-2,5

(D) 2,2,3,3 - tetramethyl butane

(Ans.C)

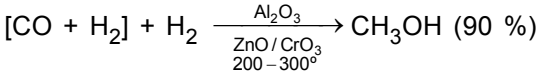
Sol. Fenton's reagent proceeds the reaction by Free radical mechanism to give 2,5-dimethyl hexanediol.

5. INDUSTRIAL PRODUCTION OF ALCOHOL

5.1 Preparation of methanol : -

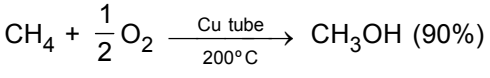
Methanol is also called as carbinol or wood spirit.

5.1.1 From Water Gas :-



5.1.2 From Methane : -

CH_4 gives methanol on partial oxidation in Cu tube.



5.1.3 By destructive distillation of wood : -

When wood is heated in absence of air in iron retorts at 400ºC then following products are formed.

(i) Wood Gases : - These are mixture of natural gases like CH_4, N_2, H_2 , CO_2, SO_2 etc.

(ii) Pyroligneous acid : - It is also called as pyro acid. It is brownish sticky liquid.

(iii) Wood tar : - Blackish viscous liquid used in formation of road and also preservation of wood. It is used in formation of deodrant.

(iv) Wood coke : - It is used as a fuel.

5.1.4 By Pyroligneous Acid : -

It contains acetic acid (8-10%) acetone (.5 - 2%), methanol (2 - 5%) and remaining water.

(i) Removal of Acetic acid : - Acetic acid is separated by adding base $Ca(OH)_2$. It forms calcium acetate with acetic acid.

(ii) Removal of Acetone : - We can remove acetone by fractional distillation because boiling point of acetone is 56ºC and boiling point of methanol is 65º C.

(iii) Removal of water : - We can remove impurities of water by using anhydrous calcium chloride or anhydrous magnesium chloride or anhydrous $CuSO_4$. These forms additional crystal salt with methanol.

anhy. $CaCl_2 + CH_3OH \longrightarrow CaCl_2 \cdot 4CH_3OH$

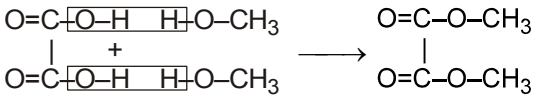
anhy. $MgCl_2 + CH_3OH \longrightarrow MgCl_2 \cdot 6CH_3OH$

anhy. $CuSO_4 + CH_3OH \longrightarrow CuSO_4 \cdot 2CH_3OH$

we get pure methanol on steam distillation

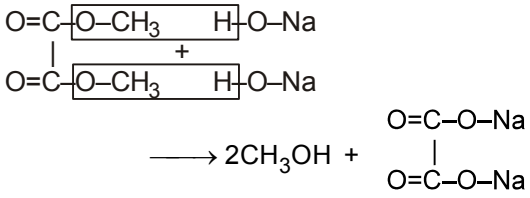
or

we can use oxalic acid to separate water impurities.



oxalic acid methanol — methyl oxalate(solid)

we get pure methanol on alkaline hydrolysis



5.2 Preparation of Ethanol : -

5.2.1 From Ethene : -

By hydration with dil. H_2SO_4

$CH_2=CH_2 + H - OH \xrightarrow{\text{dil. } H_2SO_4} CH_3-CH_2-OH$

5.2.2 General Definitions : -

(i) Fermentation : - In presence of microbes like yeast break down of complex organic compounds into simple compounds is called fermentation. It is an exothermic process. The term 'Fermentation' was proposed by **Lebeig**.

(ii) Yeast is unicellular living parasite plant.

(iii) **Enzymes : -** Nitrogenous high molecular weight complex compound which converts complex organic compound in simple organic compound without taking part in reactions are called enzymes. They are also called as biocatalyst. They are made of protein.

(iv) They are sensitive to temperature, concentration and pH.

(v) Temperature at which enzymes are maximum efficient is called optimum temperature. For yeast enzyme it is 20 – 35º C.

(vi) Temperature at which enzymes are destroyed, is called thermal death point (TDP) > 60º. At low temperature they becomes inactive.

(vii) They always work in dilute solution. They cannot work in conc. solution.

(viii) Their working pH range is 6.5 - 7.5 (slightly acidic slightly basic).

(ix) Boric acid and mercuric salt are inhibitors.

(x) Food of yeast cell is ammonium phosphate or ammonium sulphate.

5.2.3 Preparation of ethanol from sugar : -

(i) **Molasses : -** Waste product in sugar industry is called molasses. It is a mixture of sugar (30%) and invert sugar (32-40%).

(ii) **Invert sugar : -** Combine form of glucose and fructose is called as invert sugar.

$C_{12}H_{22}O_{11} + H_2O$

$$\xrightarrow[\text{invertase enzyme}]{\text{yeast cell}} C_6H_{12}O_6 + C_6H_{12}O_6$$

glucose fructose

$$C_6H_{12}O_6 \xrightarrow[\text{zymase enzyme}]{\text{yeast cell}} C_2H_5OH + CO_2 + H_2O$$

Note : Glucose and fructose are functional isomers.

5.2.4 Preparation of ethanol from starch :-

(i) Starch solution is technically called 'Mesh'

(ii) Crushed germinated barley solution is called 'Malt'.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\text{starch}]{\text{diastase}} \underset{\text{maltose (wort)}}{nC_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{maltose}]{\text{maltose}} \underset{\text{glucose (monosaccharide)}}{2C_6H_{12}O_6}$$

$$2C_6H_{12}O_6 \xrightarrow{\text{zymase}} C_2H_5OH + CO_2 + H_2O + \text{energy}$$

(iii) From both of the methods conc. of ethanol achieved is 10-12% which is called 'Wash'.

(iv) Distillation of wash is done in special apparatus 'Coffee's still', which is based on counter current method. From this distillation yield of alcohol is 90%, which is called Raw spirit.

$$\text{Raw spirit} \xrightarrow{\text{Fractional distillation}} \underset{\text{(rectified spirit)}}{95.5\%\ C_2H_5OH + 4.5\%\ H_2O}$$

(v) Further purification is done in the following ways : -

$$95.5\%\ C_2H_5OH + 4.5\%\ H_2O \xrightarrow{\text{Fractional distillation}} \underset{(64^oC)}{C_6H_6} + \underset{(78.5\ ^oC)\ (99.7\%)}{H_2O + C_2H_5OH} + \underset{(68^oC)}{\text{Remaining } C_6H_6 + CH_3CHO}$$

$$\underset{(99.7\%)}{C_2H_5OH} + \text{Ca metal} \xrightarrow{2-3\ \text{days}} \underset{(100\%)}{C_2H_5OH} + Ca(OH)_2$$

$$\underset{(99.7\%)}{C_2H_5OH} + \underset{\text{white}}{\text{anhy. } CuSO_4} \longrightarrow \underset{(100\%)}{C_2H_5OH} + CuSO_4 \cdot 5H_2O$$

Examples based on Industrial Production of Alcohol

Ex.9 When methane is passed in copper tube at 200ºC with air, it gives -
(A) Methanol (B) Ethanol
(C) Acetylene (D) Ethene
(Ans.A)

Sol. This is the industrial method of preparation of methanol in which 90% yield is given

Ex.10 Acetic acid is removed from pyroligneous acid by the passing it in -
(A) Al $(OH)_3$ solution
(B) Ba $(OH)_2$ solution
(C) Ca $(OH)_2$ solution
(D) Ethanol **(Ans.C)**

Sol. $Ca(OH)_2$ react with acetic acid to give calcium acetate which on treatment with dil acid gives acetic acid.

$$(CH_3COO)_2\ Ca + H_2SO_4 \rightarrow CaSO_4 + 2CH_3COOH$$

Ex.11 Crushed germinated barley solution is called-
(A) Mesh (B) Malt
(C) Wort (D) Wash
(Ans.B)

Sol. Malt is the germinated barley solution rich in diastase enzyme and used to convert starch (Mesh) into maltose (wort). 10-12% ethanol solution is known as 'wash'

6. DIFFERENCE BETWEEN PRIMARY, SECONDARY & TERTIARY ALCOHOLS

6.1 By Oxidation Reaction :-

Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary alcohols are resistant to oxidation.

6.2 By Catalytical Oxidation / Dehydrogenation :

Primary alcohol gives aldehyde on oxidation, secondary alcohol gives ketone and tertiary gives alkene (dehydration takes place in this condition to tertiary alcohols.)

6.3 Lucas Test :-

A mixture of (anhydrous $ZnCl_2$ + Conc. H_2SO_4) is called as **Lucas Reagent.**

(i) 3º alcohol gives white ppt. with lucas reagent in 2-3 seconds only.

(ii) 2º alcohol takes 9 - 10 minutes.

(iii) 1º alcohol does not gives white ppt. at room temperature.

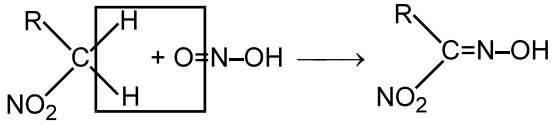
6.4 Victor Meyer Test : -

This test is also known as RBW (Red, Blue, White) test.

(a) $R-CH_2-OH \xrightarrow{Red\ P/I_2} R-CH_2-I \xrightarrow[-AgI]{AgNO_2}$

$R - CH_2 - NO_2 + HNO_2$

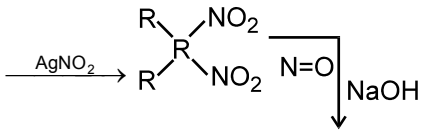
nitrate



nitrolic acid

$\xrightarrow{NaOH}$ red solution

(b) $R_2-CH-OH \xrightarrow{Red\ P/I_2} R_2-CH-I$



nitrosoderivative NaOH (blue ppt.)

Pseudonitrile

(c) $R_3-C-OH \xrightarrow{Red\ P/I_2} R_3-C-I \xrightarrow{AgNO_2}$

$R_3-C-NO_2 \xrightarrow{HNO_2}$ no. reaction.

6.5 Difference between Methanol and Ethanol :-

Methanol	Ethanol
1. When CH_3OH is heated on Cu coil it gives formalin like smell.	1. Ethanol does not give formalin like smell.
2. When CH_3OH is heated with salicylic acid in H_2SO_4 (conc.) then methyl salicylate is formed which has odour like winter green oil	2. No such odour is given by ethanol
3. It does not give haloform or Iodoform test.	3. It gives haloform

Examples based on Difference Between Alcohols

Ex.12 Which one test is also known as RBW test-

(A) Lucas test

(B) Victor Meyer test

(C) Carbilamine test

(D) Mullican-Barker test **(Ans.B)**

Sol. In victor - Meyer test, 1º alcohol give Red ppt, 2º alcohol Blue ppt and 3º alcohol no ppt, therefore according to colour of ppt this is also known as RBW test.

ALCOHOL

GMP

(1) Alkene $\xrightarrow{H_2O}$

(2) RX $\xrightarrow[\text{or aq. } K_2CO_3 \text{ or moist } Ag_2O]{\text{aq. NaOH or aq. KOH}}$

(3) R - O - R $\xrightarrow{\text{dil. } H_2SO_4}$

(4) RCOOR $\xrightarrow[-RCOOH]{\text{dil. } H_2SO_4}$

(5) 1º amine $\xrightarrow{HNO_2}$

Exception - Methyl amine gives CH_3-O-CH_3 or ether

(6) Aldehyde or ketone $\xrightarrow[\text{Darzon reduction}]{NaH}$

(1º alc.) (2º alc.)

(7) Acid or Acid derivative $\xrightarrow[\text{Bouveault–Blanc reduction}]{Na/EtOH}$

(8) HCHO or Ald.or ketone $\xrightarrow[H_2O]{R-MgX}$

(1º alc) (2ºalc) (3º alc.)

(9) RMgX $\xrightarrow[H_2O]{O_2}$

(10) CH_3MgBr $\xrightarrow[H_3O^+]{CH_2-CH_2 \text{ (O)}}$

(11) Sugar $\xrightarrow{\text{Fermentation}}$

Formation of EtOH by fermention -

(1) Cane sugar $\xrightarrow[\text{Sucrose}]{\text{Crystallization}}$ Molasses $\xrightarrow[\text{hydrolysis}]{\text{Invertase}}$ Invert sugar $\xrightarrow[\text{Fermentation}]{\text{zymase}}$ EtOH

(2) Grain → Starch $\xrightarrow[HOH]{\text{Diastase}}$ Maltose $\xrightarrow[\text{hydrolysis}]{\text{Maltase}}$ Glucose $\xrightarrow[\text{Fermentation}]{\text{Zymase}}$ EtOH

R-OH

GR

(1) $\xrightarrow[\text{or KI } + H_3PO_4 \text{ or } SOCl_2 \text{ or } SO_2Cl_2]{HX \text{ or } PX_3 \text{ or } PX_5}$ RX

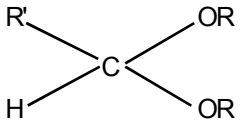
(2) $\xrightarrow{\text{Red P/HI}}$ RH

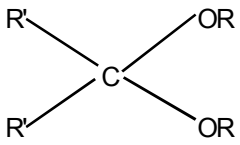
(3) $\xrightarrow{NH_3}$ 1º , 2º , 3º amines

(4) $\xrightarrow[ThO_2]{H_2S}$ R - SH Thiol

(5) $\xrightarrow{Na}$ RONa

(6) $\xrightarrow{CH_3MgX}$ CH_4

(7) $\xrightarrow[\text{dry HCl}]{\text{ald.R'–CHO}}$  Acetal

(8) $\xrightarrow[\text{dry HCl}]{\text{Ketone R'COR'}}$  Ketal

(9) $\xrightarrow{R'COZ}$ R'COOR ester (Z = OH,Cl, $OCOCH_3$)

(10) $\xrightarrow{H_2SO_4}$ $ROSO_2OH$ (Alkyl hydrogen sulphate)

(11) $\xrightarrow{HNO_3}$ $RONO_2$ (Alkyl nitrate)

(12) $\xrightarrow{PhSO_2Cl}$ RSO_2Ph (Alkyl benzene sulphonate)

(13) $\xrightarrow{CH\equiv CH}$ H_3C - CH $(OR)_2$ Acetal

(14) $\xrightarrow{CH_2N_2}$ R - O - CH_3 Ether

(15) $\xrightarrow{CH_2-CH_2 \text{ (O)}}$ RO - CH_2 - CH_2 - OH Alkoxyalkanol

(16) $\xrightarrow{CH_2=C=O}$ $ROCOCH_3$ Ester

(17) $\xrightarrow{\text{Dehydration}}$ Alkene

(18) $\xrightarrow[1^0 \text{ or } 2^0 \text{ alcohol , Cu or ZnO , } 300^0C]{\text{Catalytic dehydrogenation}}$ Aldehyde or ketone

Exception - 3º alc → Alkene

(19) 1ºalc. $\xrightarrow{[O]}$ Aldehyde $\xrightarrow{[O]}$ Acid (same no. of C-atom)

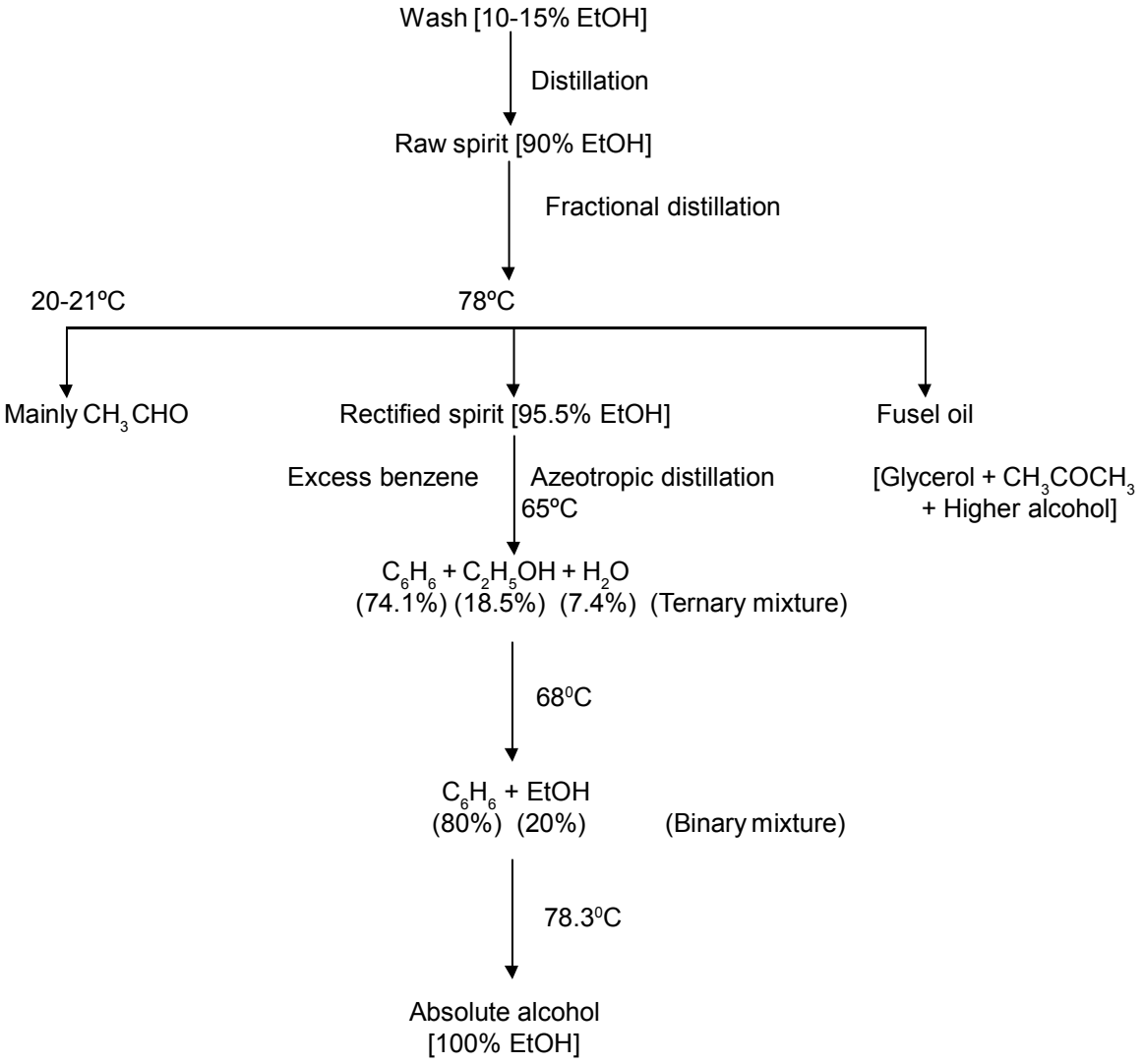
(20) 2ºalc. $\xrightarrow{[O]}$ Ketone $\xrightarrow{[O]}$

(21) 3ºalc. $\xrightarrow{[O]}$

(22) 1º or 2ºalc. $\xrightarrow[\text{(orange)}]{O\ HCrO_4^-}$ Aldehyde or ketone + Cr^{+3} (green)

(23) 3º alc $\xrightarrow[\text{(orange)}]{O,\ HCrO_4^-}$ No reaction (No. green colour)

WASH - ABSOLUTE ALCOHOL



SOLVED EXAMPLES

Ex.1 Which is not an alcohol –

(A) CH_2 = CH-CH_2OH (B) CH_2OH. CH_2OH

(C) C_6H_5 CH_2OH (D) C_6H_5OH

Ans. (D)

Sol. In the given compounds C_6H_5OH is not an alcohol. It is a phenol in which a –OH group is attached to a benzene ring. Alcohols are regarded as monoalkyl derivatives of water or hydroxy derivative of hydrocarbons. Rest of the alcohol shown above are primary alcohols.

Ex.2 Which of the following statements is false:

(A) A primary alcohol has CH_2OH group

(B) A secondary alcohol has two carbon atoms

(C) A tertiary alcohol has a minimum of four carbon atoms

(D) A primary alcohol with a branched chain has a minimum of four carbon atoms.

Ans.(B)

Ex.3 Ethyl acetate on reaction with the following reagents gives ethanol -

(A) P + HI (B) Na/C_2H_5OH

(C) $LiAlH_4$ (D) All above

Ans.(D)

Sol. Ethyl alcohol is formed by the treatment of all the above reagents like P + HI / Na & EtOH / $LiAlH_4$ on ethyl acetate. The reduction takes place as follows :

$$CH_3COOC_2H_5 \xrightarrow{+2H} CH_3CHO + C_2H_5OH$$

ethyl ethanoate

$$\downarrow +2H$$

CH_3CH_2OH

ethanol

Ex.4 $C_2H_5NH_2 \xrightarrow[\text{reagent}]{\text{Tilden}} B \xrightarrow{NH_3} C \xrightarrow[+HNO_2]{HCl} D$

the product D is an-

(A) Alcohol (B) Ether

(C) Alkyne (D) All above

Ans. (A)

Sol. In the above reaction the product D is C_2H_5OH (Ethanol) The reaction takes place as follows :

$$C_2H_5NH_2 \xrightarrow[-N_2,-H_2O]{\text{Tilden reagent (NOCl)}} C_2H_5Cl \xrightarrow{+NH_3} C_2H_5NH_2 \xrightarrow[-N_2-HCl]{+HNO_2/HCl} C_2H_5OH$$

Ex.5 Which of the following compound does not give an alcohol as the main product by the reaction with HNO_2-

(A) Ethyl amine (B) n-Propylamine

(C) Methyl amine (D)Isopropyl amine

Ans. (C)

Sol. Primary amines react with ($NaNO_2$ + dil HCl) to give a mixture of products consisting of an alcohol with same number of carbon atoms as amine, an alkyl nitrite, an alkyl halide, an alkene etc. However methyl amine does not give an alcohol as the main product by the reaction with HNO_2.

Ex.6 Which of the following is a method of preparing a primary alcohol-

(A) Reduction of ketone

(B) Hydrolysis of the adduct obtained from a Grignard reagent and ethanal

(C) Oxidative alkaline hydrolysis of adduct obtained from an alkene and borane

(D) Hydrolysis of adduct obtained from a G.R. and a ketone

Ans. (C)

Sol. A primary alcohol can be obtained by oxidative alkaline hydrolysis of adduct obtained from an alkene and borane.

$$(CH_3CH_2CH_2)_3B \xrightarrow[OH^-]{H_2O_2} CH_3CH_2CH_2\text{-}OH$$

trialkyl borane propanol

Ex.7 Which of the following reductants is used in Bouveault Blanc reduction-

(A) Zn + HCl (B) $LiAlH_4$

(C) Na + C_2H_5 OH (D) Ni + H_2

Ans. (C)

Sol. The reductants used in Bouveault Blanc reduction are Na + C_2H_5OH. The reduction takes place as follows

$$CH_3CO\text{-}OC_2H_5 \xrightarrow[Na/C_2H_5OH]{+2H} CH_3CHO + C_2H_5OH$$

ethyl acetate

$$\downarrow +2H$$

CH_3CH_2OH

ethanol

The reduction of an ester with Na and C_2H_5OH is known as Bouveault Blanc reduction.

Ex.8 The correct order of solubility of 1º, 2º and 3º alcohol in water is-

(A) 3º > 2º > 1º (B) 1º > 2º > 3º

(C) 3º > 1º > 2º (D) None of these

Ans.(A)

Sol. There is a great braching in 3º alcohol and it causes a reduction in intermolecular forces (H-bonding). Hence the solubility in water increases in the order 3º > 2º > 1º as H-bond with water is formed more easily.

Ex.9 Methanol can be distinguished from ethanol by-

(A) Heating with I_2 and alkali

(B) Treating with schiff's reagent

(C) Treating with CrO_3 solution in dil. H_2SO_4

(D) Treating with Lucas reagent

Ans.(A)

Sol. Methanol can be distinguished from ethanol by heating with I_2 and NaOH. Ethanol undergoes the reaction and forms a yellow ppt. of CHI_3.

$$CH_3CH_2OH \xrightarrow[+NaOH]{+I_2} CH_3CHO \xrightarrow{+I_2}$$

ethanol

$$CI_3.CHO \xrightarrow[HCOONa]{+NaOH} CHI_3 \text{ (iodoform)}$$

Methanol does not undergo above reaction

Ex.10 In the reaction involving C - OH bond, the order of reactivity is-

(A) 1º > 2º > 3º (B) 3º > 2º > 1º

(C) 2º > 3º > 1º (D) None of these

Ans. (A)

Sol. In reaction involing C-O bond, the reactivity order is 3º > 2º > 1º alcohol. This is due to +I effect of alkyl group which increases the electron density of oxygen which is greatest in case of 3º alcohol. In case of reactivity order is 1º > 2º > 3º, because electrons density is more in O-H bond and hydrogen tends to separate as proton.

Ex.11 Ethanol on reaction with acetic anhydride gives-

(A) Acetic ester

(B) Formic ester

(C) Ethanoic acid

(D) Acetic ester and Ethanoic acid both

Ans. (D)

Sol. Ethanol on reaction with acetic anhydride gives acetic ester and ethanoic acid both. It is called esterification reaction. The reaction takes place as follows :

$$CH_3CO.O.COCH_3 \xrightarrow{+HOC_2H_5} CH_3COOH + CH_3COOC_2H_5$$

acetic anhydride — aceticacid

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

acetic acid — ethanol — ethyl acetate

Ex.12 HBr reacts fastest with-

(A) 2-Methyl propan-2-ol

(B) Propan-1-ol

(C) Propan-2-ol

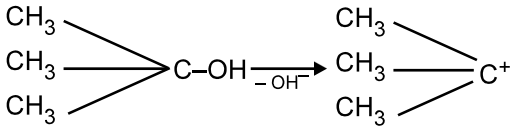
(D) 2-Methyl propan-1-ol

Ans. (A)

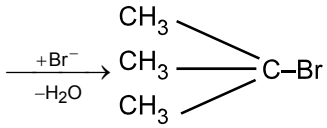
Sol. HBr reacts fastest with 2-methyl propan-2-ol, because it is a tertiary alcohol and the reactivity of the alcohols is in the order

t > s > p

The reaction takes place by S_N^I mechanism.



2-methyl propan-2-ol



2-bromo-2-methyl propane

Ex.13 The name of the compound B in the following sequence is-

$$CH_3CHOHCH_3 \xrightarrow{PCl_5} A \xrightarrow[KOH]{alc} B$$

(A) Propene (B) Propane

(C) Propyne (D) Propanol

Ans. (A)

Sol. The name of the compound B in the given sequence is propene. The reaction takes place as follows :

$$CH_3CHOH.CH_3 \xrightarrow{PCl_5} CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow[-KCl/H_2O]{alc\,KOH} CH_3-CH=CH_2$$

isopropyl alcohol — isopropyl chloride — propene

Alc. KOH is used in elimination reaction for dehydro halogenation of an alkyl halide.

Ex.14 Which of the following compound can give most stable carbonium ion during dehydration with H_2SO_4-
(A) $(CH_3)_2CHCH_2OH$
(B) $(CH_3)_3COH$
(C) $CH_3(CH_2)_2CH_2OH$
(D) $CH_3CHOHCH_2CH_3$ **Ans. (B)**

Sol. The stability of carbonium ions follows the order 3º > 2º > 1º. The tertiary butyl alcohol give teritary butyl carbonium ion,

$$(CH_3)_3COH \rightarrow (CH_3)_3C^+ + OH^-$$

Ex.15 When 3, 3-dimethyl -butanol -2 is heated with conc. H_2SO_4, the main product formed is-
(A) 3, 3-Dimethyl butene -1
(B) 2, 3-Dimethyl butene -2
(C) 2, 3-Dimethyl butene -1
(D) Cis and Trans isomers of the product obtained in (3rd)

Ans. (B)

Sol.

$$CH_3-\underset{\underset{CH_3OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{|}{CH}-CH_3 \xrightarrow[-H_2O]{Conc.H_2SO_4}$$

3,3 - dimethyl butanol -2

$$CH_3-\overset{\overset{CH_3}{|}}{\overset{+}{C}}-CH-CH_3 \xrightarrow{Rearangement}$$

$$CH_3-\overset{\overset{CH_3}{|}}{\overset{+}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{-H^+} CH_3-\overset{\overset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3$$

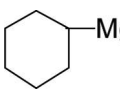
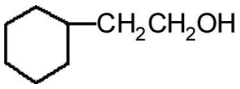
2,3 - dimethyl butene -2

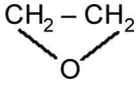
Ex.16 Which of the following yields 2-butene on dehydration with conc. H_2SO_4-
(A) 2-Methyl-2-butanol
(B) 2-Propanol
(C) 2-Methyl-2-propanol
(D) Secondary butyl alcohol

Ans.(D)

Sol. $CH_3CHOHCH_2CH_3 \xrightarrow[-H_2O]{Conc.H_2SO_4}$

$CH_3 - CH = CH - CH_3$
2-butene

Ex.17  forms 
on reaction with :

(A) $CH_3 - CHO$ (B) 
(C) $CH_3 - CH_2 - CHO$ (D) 

Ans. (B)

Ex.18 Identify Z in the following series

$$C_2H_5OH \xrightarrow{PBr_3} X \xrightarrow{Alc.\ KOH}$$

$$Y \xrightarrow[(ii)\ H_2O + Heat]{(i)\ H_2SO_4} Z$$

(A) $CH_2 = CH_2$ (B) CH_3CH_2OH
(C) $CH_3CH_2OCH_2CH_3$ (D) CH_3OH

Ans. (B)

Sol. $C_2H_5OH \xrightarrow[H_2SO_4]{PBr_3} CH_3CH_2Br \xrightarrow{alc.\ KOH}$

$$CH_2 = CH_2 \xrightarrow[H_2O+Heat]{H_2SO_4} CH_3CH_2OH$$

Ex.19 Pyrolignious acid is the source of -
(A) Wood gas + wood charcoal
(B) Woodtar + acetic acid
(C) Acetone + methanol + Aceticacid
(D) Ethanol + acetone + acetic acid

Ans.(C)

Sol. Pyrolignious acid is the brown aqueous upper layer of the liquid distillation and contains about (i) 5% methanol (ii) 0.5% acetone (iii) 10% acetic acid and rest water, hence it is a source of acetone, methanol and acetic acid.

Ex.20 $[C_2H_5OH + CH_2N_2]$ leads to the product :
(A) Higher alcohol (B) Simple ether
(C) Lower alcohol (D) Mixed ether

Ans. (D)

Ex.21 Ethanol cannot be dried by anhydrous $CaCl_2$ due to the formation of the following solvated product-
(A) $CaCl_2.\ 2C_2H_5OH$
(B) $2CaCl_2.\ 3C_2H_5OH$
(C) $CaCl_2.\ 4C_2H_5OH$
(D) $CaCl_2.\ C_2H_5OH$ **Ans. (C)**

Sol. Ethanol forms a solid derivative with metallic salt in which alcohol molecule shows

solvation phenomena e.g. $CaCl_2 . 4C_2H_5OH$

That is why alcohols cannot be dried by anhydrous $CaCl_2$.

Ex.22 The enzyems A, B and C in the reaction sequence are-

$$(C_6H_{10}O_5)_n \xrightarrow{A} C_{12}H_{22}O_{11} \xrightarrow{B} C_6H_{12}O_6$$

$$\xrightarrow{C} C_2H_5OH$$

(A) Invertase, Maltase, Zymase

(B) Diastase, Maltase, Zymase

(C) Maltase, Zymase, Invertase

(D) Diastase, Zymase, Maltase

Ans. (B)

Sol. The enzymes A, B and C in the reaction sequence are Diastase, Maltase and Zymase.

$$(C_6H_{10}O_5)_n \xrightarrow{\text{Diastase}} C_{12}H_{22}O_{11}$$

starch maltose

$$\xrightarrow{\text{Maltase}} C_6H_{12}O_6 \xrightarrow[-CO_2]{\text{Zymase}} C_2H_5OH$$

glucose ethanol

The production of ethanol by the above method is called fermentation of starchy materials.

Ex.23 Phenol and ethanol are distinguished by the reaction with-

(A) Red litmus (B) $NaHCO_3$

(C) $FeCl_3$ (D) NaOH

Ans. (C)

Sol. Phenol is weakly acidic in nature while alcohol is neutral. Phenol and ethanol are distinguished by the reaction with $FeCl_3$. Phenol gives a green or red colour with $FeCl_3$, while ethanol does not give it

Ex.24 The Lucas test is used to determine the type of-

(A) Amines (B) Alcohols

(C) Acids (D) Phenols

Ans. (B)

Sol. The Lucas reagent is a solution of $ZnCl_2$ + HCl. It is used to determine the type of alcohols. On adding it, tertiary alcohols give an immediate white turbidity. Secondary alcohols give turbidity in five minutes and primary alcohols give turbidity in half an hour or more.

It is used to distinguish among various types of alcohols.

Ex.25 Which of the following is least reactive towards $ZnCl_2$ and con. HCl mixture-

(A) 2-Butanol

(B) 1-Butanol

(C) 2-Methyl 2-butanol

(D) All of the above **Ans. (B)**

Sol. The primary alcohol 1-butanol is least reactive towards Lucas reagent $ZnCl_2$ and Con.HCl. It gives a white turbidity in half an hour or above. This test is used for the distinction between primary, secondary and tertiary alcohols and konwn as Lucas test.

Ex.26 Primary, secondary and tertiary alcohols are distinguished by-

(A) Oxidation method

(B) Lucas test

(C) Victor meyer test

(D) All of the above

Ans. (D)

Sol. Primary, secondary and tertiary alcohols are distinguished by all the above methods like oxidation method, Lucas test & victor Meyer test. Out of these the last method is the most effective method of distinguishing alcohols.

Ex.27 $C_2H_5OH \xrightarrow{P/I_2} A \xrightarrow{AgNO_2} B \xrightarrow{HNO_2} C$, Product [C] is-

(A) Pseudonitrolic acid

(B) Nitrolic acid

(C) Nitro ethane

(D) Ether

Ans. (B)

Sol. The product 'C' is Nitrolic acid. The reaction takes place as follows :

$$C_2H_5OH \xrightarrow{P+I_2} C_2H_5I \xrightarrow[A]{+AgNO_2} C_2H_5NO_2$$

$$\xrightarrow[B]{+HNO_2} CH_3\text{-}\underset{\underset{N\text{-}OH}{\|}}{C}\text{-}NO_2 \xrightarrow{NaOH} \text{Red colour}$$

(C) nitrolic acid

The above reaction is used for the identification of primary alcohols by Victor Meyer's method

Ex.28 Power alcohol contains-

(A) Rectified spirit + petrol

(B) Petrol + benzene + spirit

(C) Methanol + ethanol + benzene

(D) Methanol + benzene + petrol

Ans. (B)

Sol. Power alcohol is a mixture of spirit, benzene and petrol. This is used as a substitute for petrol in the automobile engines to generate power, in the countries poorer in petroleum resources. A small amount of ether or tetraline is also added.

Ex.29 Absolute alcohol is obtained from rectified spirit by-

(A) Rectification

(B) Fractional distillation

(C) Azeotropic distillation

(D) Denaturation **Ans. (C)**

Sol. Absolute alcohol is obtained from rectified spirit by azeotropic distillation. Some benzene is added to the rectified spirit and then distilled. A three component mixt. containing ethanol (18.5%) benzene (74.1%) and water (7.4%) is obtained at 65ºC.

Ex.30 $CH_3-\underset{\diagdown\,O\,\diagup}{CH-CH}-CH_3$, is the anhydride of :

(A) 1,2–Butane diol (B) 2,2–Butane diol

(C) 2,3–Butane diol (D) 1,1–Butane diol

Ans. (C)