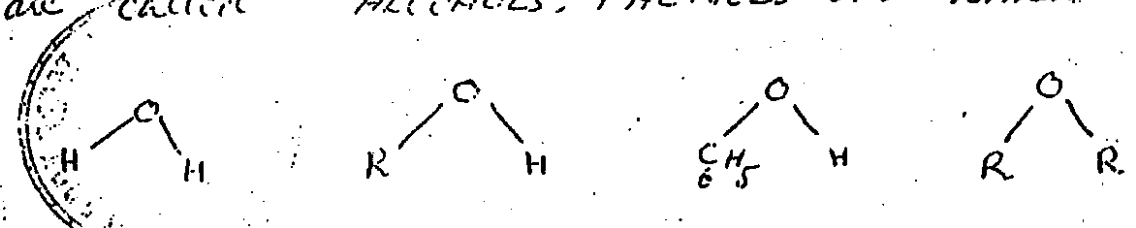
CHAPTER No. 11

ALCOHOLS, PHENOLS AND ETHERS.

INTRODUCTION:-

Alkyl or aryl derivatives of alcohol water are called ALCOHOLS, PHENOLS and ETHER.



WATER ALCOHOL PHENOL ETHER.

ALCOHOLS:-

When one alkyl hydrogen of water is replaced by alkyl group alcohols are formed.

PHENOLS:-

When hydrogen of water is replaced by phenyl group phenols are formed.

ETHERS:-

Ethers are formed by replacement of both hydrogens with alkyl or aryl group.

ALCOHOLS

Hydroxyl derivatives of alkane are called ALCOHOLS these are generally represented by following general formula "R-OH".

-R may be an alkyl group derived from aliphatic or alicylic hydrocarbon.

CLASSIFICATION OF ALCOHOLS:-

alcohols are classified as under.

i- MONOHYDRIC ALCOHOLS:- Alcohols having only one -OH group is called monohydric alcohols.

e.g; $CH_3CH_2CH_2OH$ $CH_3CH_2CH_2-CH_2-OH$.

ii- DIHYDRIC ALCOHOLS:- Alcohols having two -OH groups attached to alkyl groups are called dihydric alcohols e.g

$CH_2(OH)-CH_2(OH)$ (GLYCOL) $CH_3-CH(OH)-CH_2(OH)$ (1,2-Propanediol)

TRIHYDRIC ALCOHOLS:- The alcohols having three -OH groups attached to alkyl chain are called TRIHYDRIC ALCOHOLS e.g.

$CH_2(OH)-CH(OH)-CH_2(OH)$ (1,2,3 - Propanetriol)

Alcohols are further classified as follows:-

p- ALCOHOL

When α-carbon is attached to one carbon directly, the alcohol is called primary alcohol. e.g.

$CH_3CH_2-CH_2-OH$ (p-alcohol)

1- Propanol.

SEC. ALCOHOL:- If α-carbon is directly attached to two alkyl groups the alcohol is called SEC. ALCOHOL.

TER. ALCOHOL:- An alcohol in which α- carbon is directly attached with three carbons is called ter. alcohol

e.g. $CH_3-CH(OH)-CH_3$ (SEC. ALC).

$CH_3-C(CH_3)(CH_3)-OH$ (TER. ALC)

HOW TO DISTINGUISH B/W p, SEC, TER, ALCOHOLS

LUCAS TEST:- The pr. sec. and ter. alcohols can be distinguished by LUCAS TEST. In this test alcohol is treated with HCl and $ZnCl_2$ catalyst.

i) TER. ALCOHOLS produces an alkyl halide immediately with out heating. it is separated as oily layer.

$CH_3-C(CH_3)(CH_3)-OH + HCl \xrightarrow[R.T]{ZnCl_2} CH_3-C(CH_3)(CH_3)-Cl + H_2O$

ii) SEC. ALCOHOLS: produce an alkyl halide on 10-15 min. heating.

$CH_3-CH(CH_3)-OH + HCl \xrightarrow[\text{heat.}]{ZnCl_2,\ 10-15\ min} CH_3-CH(CH_3)-Cl + H_2O$

iii) P ALCOHOL:- produces an alkyl halide on prolong heating (for two hours).

$CH_3CH_2-OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$

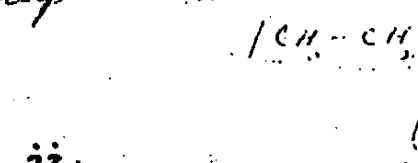
Here order of reactivity is

TER. ALCOHOL > SEC > p. ALCOHOL.

NOMENCLATURE OF ALCOHOLS:-

Alcohols are named according to following I.U.P.A.C rules.

RULE-i. Longest carbon chain containing -OH group is selected. e.g.



(3-Methyl-3-pentanol.)

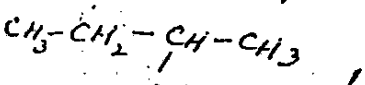
RULE-ii: Suffix "ol" is added to parent hydrocarbon by replacing "e", at the end. e.g.

CH_3-CH_2-OH (Ethanol).

RULE-iii: If there are more than one -OH groups suffix diol, triol, etc is added. e.g.

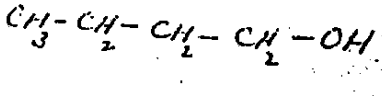
(1,2-Ethanediol)

RULE-iv. -OH must get lowest possible number. e.g.



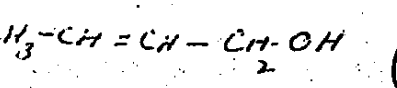
(2-Butanol)

RULE-v. Position of -OH group is indicated by a number placed before the name.



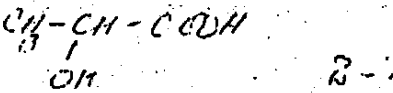
(1-Butanol)

RULE.vi. Unsaturated alcohols are named so that OH group gets the lower number, rather than point of unsaturation.



(2-Butene-1-ol).

RULE-vii. In presence of any other functional group of higher priority, -OH is named as a substituent it is called HYDROXY GROUP. e.g.



2-Hydroxy-Propanoic acid.

PREPARATION OF ALCOHOLS.

(i)- PREPARATION OF METHANOL

(WOOD SPIRIT.)

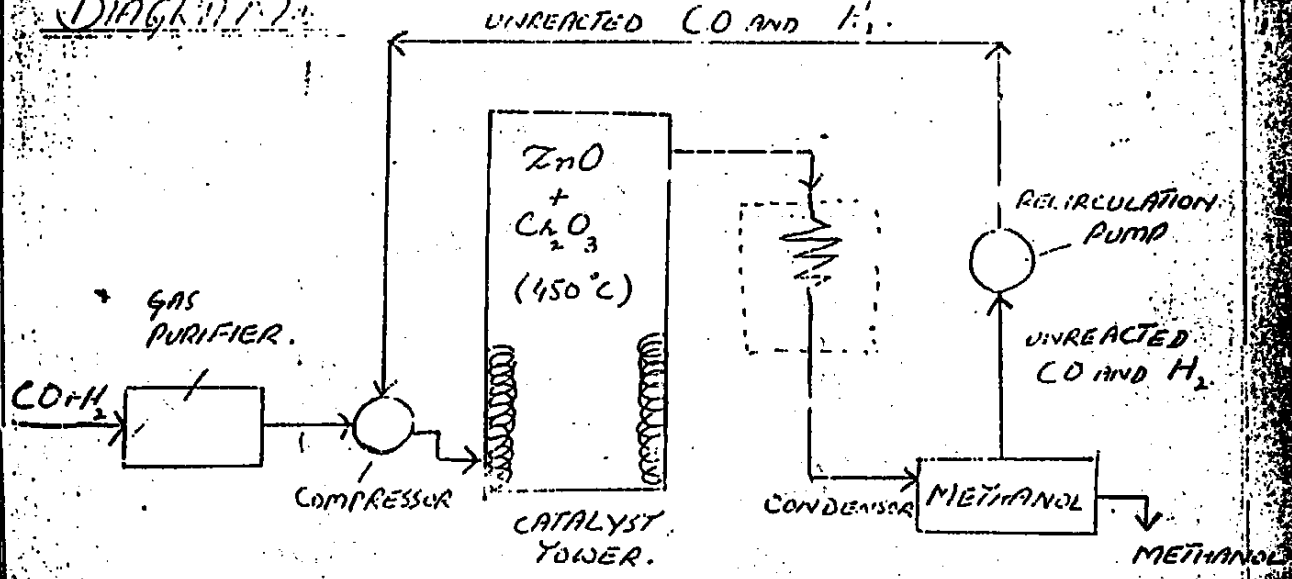
Methanol is obtained from water gas ($CO + H_2$).

Mixture of ($CO + H_2$) is compressed under a pressure of 200 atm. It is passed in reaction chamber by means of coiled pipes. In this chamber catalyst is heated - upto 450 - 500°C. Gases react to form methanol vapours. Vapours are condensed to get liquid methanol.

REACTION:-

$$CO + 2H_2 \xrightarrow[450 - 500^\circ C,\ 200\ atm]{(ZnO + Cr_2O_3)} CH_3OH$$

DIAGRAM:-



FLOW SHEET DIAGRAM FOR PREPARATION OF METHANOL.

(ii)- PREPARATION OF ETHANOL (GRAIN ALCOHOL)

Ethanol is prepared by the process of FERMENTATION.

FERMENTATION. is a biochemical process. Process is carried out with the help of enzymes secreated by yeast and other micro organisms

Ethanol is prepared by the fermentation of molasses, starch grains or fruit-juices.

(a)- By Fermentation of Molasses.

Molasses is the residue left after crystallization of sugar from cane sugar juice. It undergoes fermentation in presence of enzymes present in yeast to give ethanol.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{YEAST}]{\text{INVERTASE}} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow[\text{YEAST}]{\text{ZYMASE}} 2C_2H_5OH + CO_2$$

(b)- From Fermentation of Starch.

Starch present in potatoes, barley or any other cereals on fermentation produces ethanol. Process involves many steps but important steps are given below.

STEP-I FORMATION OF MALTOSE FROM STARCH.

Starch is converted into MALTOSE by action of enzyme DIASTASE.

$$C_{600}H_{1000}O_{500} + 50H_2O \xrightarrow[\text{YEAST}]{\text{DIASTASE}} 50\,C_{12}H_{22}O_{11}$$ (MALTOSE or SUCROSE)

STEP-II. FORMATION OF GLUCOSE.

Malt sugar or maltose is converted into glucose on hydrolysis.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{(INVERTASE) IN YEAST}]{\text{MALTASE}} 2C_6H_{12}O_6$$ (GLUCOSE OR FRUCTOSE)

STEP-III Formation of Alcohol.

A group of 14-enzymes present in living cells of yeast plant is called ZYMASE. It converts glucose into CO_2 and ethanol mixture. This mixture contain only 15% ethyl alcohol.

$$C_6H_{12}O_6 \xrightarrow[\text{IN YEAST}]{\text{ZYMASE}} 2C_2H_5OH + 2CO_2.$$

RECTIFIED SPRIT :-

The alcohol obtained by fermentation is distilled again and again to obtain 95% alcohol. It is called RECTIFIED SPIRIT.

ABSOLUTE ALCOHOL :-

The alcohol obtained by redistillation of rectified spirits in presence of $CaCl_2$ is called ABSOLUTE ALCOHOL.

DENATURING OF ALCOHOL :-

Ethanol is denatured to avoid its use for drinking. It is denatured by addition of 10% methanol. Such alcohol is called Methylated Spirit.
Pdine or Pyridine can also be used to denature alcohol.

REACTIONS OF ALCOHOLS :-

Alcohols undergo two types of reactions.

i - Reactions in which C-O bond breaks.
ii - Reactions in which O-H bond breaks.

Breaking of bond depends upon nature of attacking reagent.

ii - Reactions in which C-O bond breaks.

C-O bond breaks when nucleophile attacks on an alcohol. eg. Reaction can be written as.

$$CH_3CH_2OH \xrightarrow{\text{Nucleophile}} CH_3\overset{\oplus}{C}H_2 + \overset{\ominus}{O}H$$

Order of reactivity of an alcohols when C-O bond breaks is as follows.

tertiary alcohol > secondary alc. > Primary alco

EXAMPLES :-

1. $C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$.

2. $C_2H_5-\underset{CH_3}{\underset{|}{CH}}-OH + HCl \xrightarrow{ZnCl_2} C_2H_5-\underset{CH_3}{\underset{|}{CH}}-Cl + H_2O$.

3. $C_2H_5OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$.

ii - Reactions in which O-H bond breaks.

O-H bond breaks when electrophile attacks on an alcohol. Generally reaction can be written as.

$$CH_3CH_2-\overset{-\delta}{O}-\overset{+\delta}{H} \xrightarrow{\text{electrophile}} CH_3CH_2-O^{\ominus} + H^{\oplus}$$

Order of reactivity of alcohols when O-H bond breaks is as.

CH_3OH > Primary alcohol > Secondary alcohol > Tertiary alcohol.

EXAMPLES:-

1. $2C_2H_5OH + 2Na \longrightarrow 2C_2H_5\bar{O}\overset{+}{N}a + H_2$.

2. $C_2H_5\bar{O}\overset{+}{N}a + CH_3COCl \longrightarrow C_2H_5COCH_3$.

2. $C_2H_5OH + \overset{-\delta}{CH_3}\overset{+\delta}{Mg}\bar{I} \longrightarrow CH_4 + Mg\begin{matrix} I \\ OC_2H_5 \end{matrix}$.

OXIDATION OF ALCOHOLS.

Alcohols on oxidation are converted into aldehydes & ketones. oxidizing agent, mostly used, is $K_2Cr_2O_7 + H_2SO_4$.

$$\begin{matrix} CH_3 \\ HC_3 \end{matrix}\!\!>\!CH-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=O + H_2O.$$

$$CH_3CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O$$

(Acetaldehyde)

Acetaldehyde formed is further oxidized to ACETIC ACID in vigorous conditions

$$CH_3CHO + [O] \longrightarrow CH_3COOH \quad \text{(acetic acid)}$$

In contrast to methanol where formic acid is further oxidized to CO_2 and H_2O. Acetic acid is not further oxidized to CO_2 and H_2O.

Tertiary alcohols do not undergo oxidation. In presence of $K_2Cr_2O_7 + H_2SO_4$ these undergo elimination to give alkenes.

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + (O) \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_2=\underset{CH_3}{C}-CH_3 + H_2O$$

LABORATORY METHODS OF PREPARATION OF ETHANOL:-
In laboratory. Ethanol can be prepared by following methods.

HYDRATION OF ALKENES:- Ethene on addition of water produces ethanol. The catalyst used is 10% H_2SO_4 and $HgSO_4$

$$H-\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}-H + \overset{+\delta}{H}\overset{-\delta}{OH} \xrightarrow[100^\circ C]{10\%\ H_2SO_4,\ HgSO_4} H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-H$$

FROM ALKYL HALIDE:- Ethyl bromide on treatment with (i) aqueous KOH can be converted into ethanol.

$$CH_3CH_2\overset{-\delta}{Br} + \overset{+\delta}{K}\overset{-\delta}{OH} \longrightarrow CH_3CH_2OH + KBr$$

(ii) ALKYL HALIDES on treatment with silver oxide in presence of moisture produces ethanol

$$CH_3CH_2Br + Ag_2O + H_2O \xrightarrow{aq.} 2CH_3CH_2OH + 2AgBr$$

FROM GRIGNARD REAGENT:- Methyl magnesium bromide (G.R.) on treatment with formaldehyde followed by hydrolysis produces Ethanol (1°-Alcohol)

$$\underset{-\delta\ +\delta\ -\delta}{CH_3MgBr} + H-\overset{\delta+}{\underset{H}{\overset{O}{C}}}-H \longrightarrow H-\underset{H}{\overset{OMgBr}{C}}-H \xrightarrow[H^+]{\overset{+\delta}{H}\overset{-\delta}{OH}} H-\underset{H}{\overset{OH}{C}}-H + Mg\overset{OH}{Br}$$

REDUCTION OF ALDEHYDE:- Acetaldehyde is reduced to ethanol in presence of metal catalyst

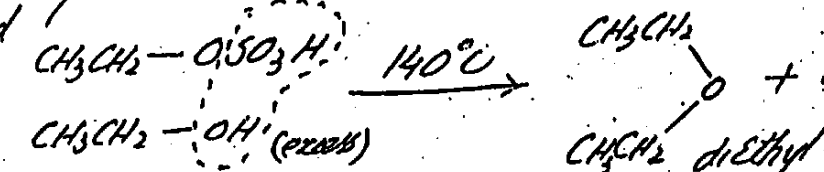
$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow{Pd} CH_3-\underset{H}{\overset{OH}{C}}-H$$

WRITE A NOTE ON DEHYDRATION OF ALCOHOL:-
Removal of water from alcohol is called dehydration. Dehydrating agent can be H_2SO_4, Al_2O_3 (400°C) or P_2O_5 (warm). Dehydration with H_2SO_4 can produce ether (at 140°C) or Ethene (at 180°). The mechanism is shown below.

$$CH_3CH_2-\ddot{O}H + H\ddot{O}SO_3H \xrightarrow{100^\circ C} CH_3CH_2OSO_3H + H_2O$$

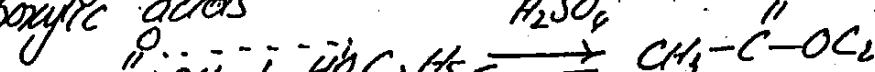
In the first step ethyl sulphonic acid is produced. This intermediate may react with another molecule of ethanol at low temp (140°C) or may produce alkene at 180°C and low conc. of alcohol, as shown below

At low temperature and excess of alcohol diethyl ether is obtained



ESTERIFICATION

The reaction between an alcohol and carboxylic acid or acid halide or acid anhydride produces an ester. This is called esterification. The esters have a general formula $R-\overset{O}{\overset{\|}{C}}-OR$. These are defined as compounds obtained by elimination of H_2O between an alcohol and carboxylic acids

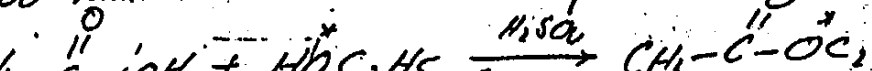


Ethylacetate.

It has been confirmed by using radioactive oxygen that during ester formation $-OH$ from acid and "H" from alcohol combine to form water.

When carboxylic acid with $-OH$ groups having radioactive oxygen is used, water produced is radioactive, but ester is not radioactive

When alcohol with radioactive oxygen is used, water produced is not radioactive while ester produced is radioactive



It confirms that during esterification $-OH$ of acid and "H" of alcohol combine to form H_2O.

The esterification is a reversible reaction. In order to avoid reversibility of reaction water absorbant H_2SO_4 is used. The use of acidhalide is more suitable for esterification.

CONVERTION INTO ALKYL HALIDE:- Ethanol is converted into alkyl halide on treatment with HCl in presence of $ZnCl_2$ or PCl_3 + PCl_5 or $SOCl_2$

$$CH_3CH_2OH + HCl \xrightarrow[2\text{-}3\ \text{HOUR HEAT}]{ZnCl_2} CH_3CH_2Cl + H_2O$$

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

$$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$$

DISTINGUISH BETWEEN METHANOL AND ETHANOL:-
Ethyl alcohol can easily be distinguished by iodoform test. In this test ethanol is made alkaline with NaOH and treated with iodine crystals. A yellow crystalline solid iodoform is produced

$$CH_3CH_2OH + 6I_2 + 6NaOH \longrightarrow \underset{\text{yellow crystals}}{CHI_3} + 5NaI + 5H_2O + HCOONa$$

Methanol does not give this test.

IDENTIFICATION OF ALCOHOLIC GROUP:- Alcohols liberate hydrogen gas with sodium metal.

$$2RCH + 2Na \longrightarrow RONa + H_2\uparrow$$

USES OF ETHANOL:-

(i) It is used as solvent in gums and Resins
(ii) It is used as motor fuel in some countries like Brazil
(iii) It is used as solvent and extractant
(iv) It is used for synthesis of plastics, cellulose, rubber, etc
(v) It is used as antifreeze.
(vi) It is used to preserve biological specimen.
(vii) It is used in almost every medicines.

USES OF METHANOL:- The most important uses of methanol are given below.

(i) FORMALIN:- It is used to produce formaline and formaldehyde
(ii) DRUGS, DYES and PERFUMES:- Methanol is used to prepare drugs, dyes and perfumes.
(iii) AS SOLVENT Methanol is used as an important solvent in varnishes.
(iv) ANTIFREEZE It is used as antifreeze.
(v) DENATURING OF ALCOHOL Methanol is used as denaturant when added to Ethanol in small quantity, it makes ethanol unfit for drinking, this is called Methylated Spirit. 10% Methanol is added to Ethanol make it unfit for drinking.

Q:- WHAT ARE ETHERS? DISCUSS THEIR METHODS OF PREPARATION.

Compounds having R–O–R functional group are called Ethers. For example

$CH_3CH_2-O-CH_2CH_3$, $CH_3-O-CH_2CH_3$

di Ethyl ether — Ethyl methyl ether.

METHODS OF PREPARATION:- Ethers can be prepared by following methods.

(1) WILLIAMSON'S SYNTHESIS:- The most important method of preparation of ethers is williamson's synthesis. It involves following steps.

(i) FORMATION OF ALKOXIDE.

Alcohol is treated with sodium metal to form alkoxide

$$CH_3CH_2OH + Na \longrightarrow CH_3CH_2\bar{O}\overset{+}{N}a + \tfrac{1}{2}H_2$$

Sodium ethoxide.

(ii) REACTION OF ALKOXIDE WITH ALKYL HALIDE.

Sodium alkoxide ($R\bar{O}\overset{+}{N}a$) is a strong nucleophile (nucleus loving) and reacts with an alkyl halide by S_N2 reaction mechanism.

$$CH_3CH_2\bar{O}\overset{+}{N}a + CH_3CH_2\overset{\delta+}{B}r^{\delta-} \xrightarrow{S_N2} CH_3CH_2OCH_2CH_3 + NaBr$$

diEthylether.

The general reaction could be written as follow

$$ROH + Na \xrightarrow{-H_2} R\bar{O}\overset{+}{N}a \quad \text{Sodium alkoxide}$$

$$R\bar{O}\overset{+}{N}a + \overset{\delta+}{R}\!-\!\overset{\delta-}{X} \xrightarrow[S_N2]{} ROR + NaX$$

Ether

FROM SILVER OXIDE AND ALKYL HALIDE.

The alkyl halides react with silver oxide under anhydrous conditions (absence of moisture) to form ether.

$$CH_3CH_2Cl + Ag_2O + ClCH_2CH_3 \longrightarrow CH_3CH_2-O-CH_2CH_3 + 2AgCl$$

diEthyl ether.

FROM ALCOHOLS:- Alcohols on treatment with concentrated sulphanic acid at 140°C produce ethers

$$2\,CH_3CH_2OH \xrightarrow[140^\circ C]{H_2SO_4\ conc.} CH_3CH_2OCH_2CH_3 + H_2O$$

The reaction mechanism is

$$CH_3CH_2\ddot{O}H + H\overset{\oplus}{O}SO_3H \longrightarrow CH_3CH_2\overset{+}{O}(H)-H + HSO_4^{\ominus}$$

$$CH_3CH_2-\overset{\oplus}{O}(H)-H \longrightarrow CH_3\overset{\oplus}{C}H_2 + H_2O$$

$$CH_3\overset{\oplus}{C}H_2 + HSO_4^{\ominus} \longrightarrow CH_3CH_2OSO_3H$$

$$CH_3CH_2OSO_3H \xrightarrow{140^\circ C} CH_3CH_2OCH_2CH_3 + H_2SO_4$$

DISCUSS CHEMICAL REACTIVITY OF ETHERS?

Ethers are quite inert (less reactive) They show very ~~stand~~ few chemical reactions. They are used as good solvents and dissolve many oils, gums and fats. They are used as inert solvent in G.R synthesis. The important physical characteristics of ethers are ~~given~~ shown below.

(1) Colourless solvents with very low Boiling points
(2) These are highly inflamable.
(3) Resistant to oxidation by oxidizing agents.
(4) These are highly stable compounds.
(5) These are soluble in H_2SO_4 due to presence of oxygen which can take part in hydrogen bonding. Due to solubility in H_2SO_4 ethers can be distinguished from alkanes which are insoluble in H_2SO_4.

REACTION OF ETHERS WITH HALOGEN ACIDS

Ethers react with acids forming alcohol and alkyl halides. The reaction involves following steps.

(i) FORMATION OF OXONIUM ION

Oxygen has a lone pair of electron. The oxygen is protonated by $H^{\oplus}$ of acid forming Oxonium ion.

$$CH_3CH_2-\ddot{O}-CH_2CH_3 + H\ddot{B}r \longrightarrow CH_3CH_2\overset{\overset{H}{|}}{\underset{\oplus}{O}}CH_2CH_3 + Br^{\ominus}$$

Oxonium ion.

(ii) FORMATION OF ALCOHOL

$$CH_3-CH_2-\overset{\overset{H}{|}}{\underset{\oplus}{O}}-CH_2CH_3 + Br^{\ominus} \longrightarrow CH_3CH_2Br + \overset{H}{|}O-CH_2CH_3$$

Ethanol

The reaction with strong acids like HI is more favourable.

$$CH_3CH_2-\ddot{O}-CH_2CH_3 + HI \longrightarrow CH_3CH_2\overset{\overset{H}{|}}{\underset{\oplus}{O}}CH_2CH_3 + I^{\ominus}$$

$$\downarrow$$

$$CH_3CH_2I + \overset{H}{|}O-CH_2CH_3$$

The general reaction could be written as

$$R-O-\acute{R} + HX \longrightarrow R-\overset{\overset{H}{|}}{\underset{\oplus}{O}}-\acute{R} \xrightarrow{X^{\ominus}} ROH + R'X$$

AND/OR

$$RX + R'OH$$

WHAT TYPE OF ISOMERISM IS PRESENT IN ETHERS

Ethers exhibit a type of isomerism called METAMERISM.

The METAMERS have same chemical formula, same functional group but different alkyl groups attached to same multivalent atom. For example consider

$CH_3CH_2-O-CH_2CH_3$

diEthyl ether.

$CH_3-O-CH_2CH_2CH_3$

Methyl-n-propyl ether.

WRITE SOME IMPORTANT USES OF ETHERS.

Ethers are commonly used in practical life for a number of purposes. The important uses of ethers are

1) AS AN ANESTHETIC: It is most common of all anesthetic used. But there are two main disadvantages in its use

(a) Its boiling point is 35°C, less than body temperature (37°C). Thus it is difficult to use it in hot climate.

(b) Due to high inflamability it can lead to explosions.

2:- ARTIFICIAL SILK COLLODION:- Ether is used in manufacture of artificial silk collodion and SMOKELESS GUN POWDER.

3:- AS SOLVENTS: These are used as solvents in manufacture of gums, resins, fats and waxes.

4:- SYNTHETIC CHEMISTRY Ethers are used as solvents in Synthesis of G.R. and in Wurtz Reaction.

5:- EXTRACTANT: Ether is used as good extractant for extraction of organic compounds.

Bsc

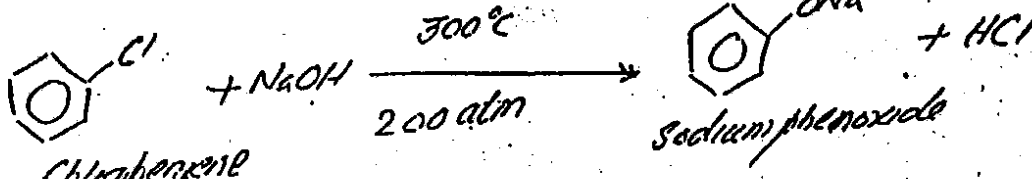
WHAT ARE PHENOLS? DISCUSS ITS METHODS OF PREPARATION. WHY IS IT ACIDIC?

The hydroxal derivatives of benzene are called PHENOLS. i.e If hydrogen of benzene is replaced by hydroxal groups (–OH) the compound is called PHENOL OR CARBOLIC ACID.

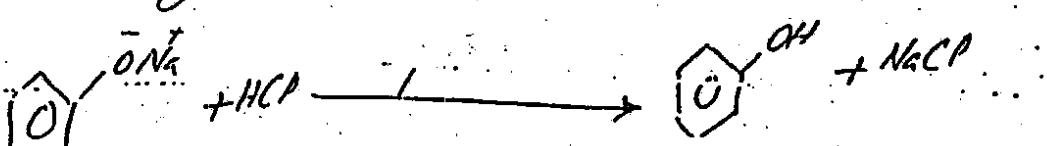
PREPARATION:-

(i) **BY DON PROCESS:-(COMMERCIAL METHOD).**

In this method Chlorobenzene is hydrolyzed with 10% solution of NaOH at high temp and pressure. In first step sodium phenolate is formed. This is salt of phenol. Sodium salt of phenol on treatment with strong acid (HCl) produce phenol.



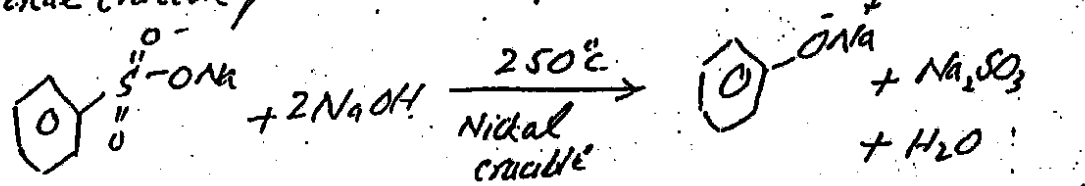
Chlorobenzene — Sodium phenoxide



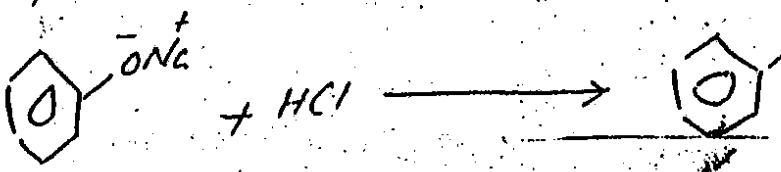
Sodium phenoxide

(iii) **SODIUM BENZENE SULPHONATE:-**

The sodium salt of benzene sulphonic acid (sodium benzene sulphonate) on fusion with NaOH at 250°C in a Nickal crucible produce sodium phenoxide.



Sodium phenoxide on treatment with conc. HCl produce phenol.



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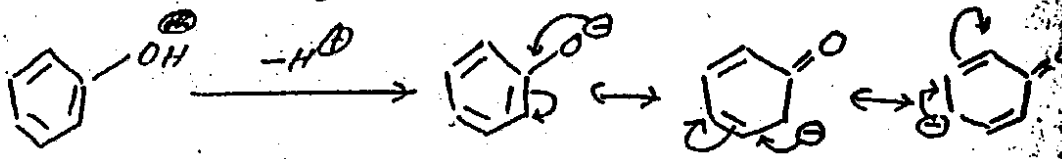
ACIDIC NATURE OF PHENOL:-

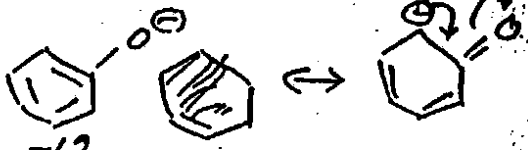
According to Arhenious concept acid is defined as a compound which produce $H^{\oplus}$ ions in aqueous solution.
According to Lowery Bronsted concept acid is a proton donar (H^+ ion donar).

The strength of acid depends upon
(i) ease with which proton is donated.
(ii) Stability of Anion formed by removal of proton.

Phenol is acidic because the phenolate ion is stabilized by resonance as shown below



Thus phenol is acidic due to stability of its Anion
While Alcohols are not acidic

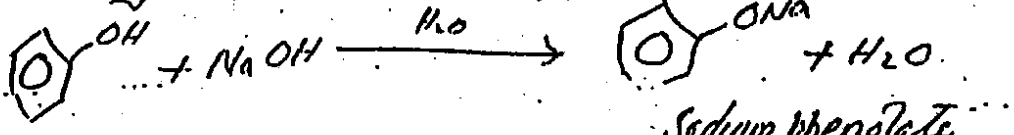


K_a for phenol is $= 1.3 \times 10^{-10}$

Thus very small value of K_a indicates that it is very weak acid. Hence it does not effect litmus paper.

REACTION WITH NaOH :- (SALT FORMATION).

Acidic nature of phenol is supported by its reaction with sodiumhydroxide (NaOH) to form salt and H_2O



Sodium phenolate

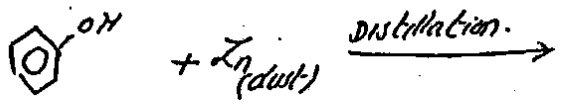
Alcohols does not react with NaOH
Thus they are not acidic.

Relative acid strength of alcohol, phenol, water and carboxylic acid is

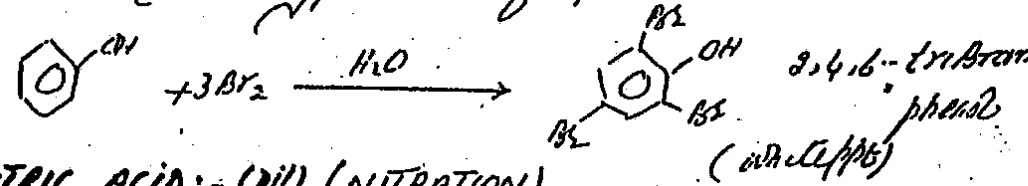
carboxylic acid > Phenol > Water > Alcohol.

SHOW REACTIONS OF PHENOL WITH FOLLOWING REAGENTS. MENTION REACTION CONDITIONS.

(i) ZINC DUST:- Phenol is reduced to benzene on treatment with zinc dust. Phenol is distilled with zinc dust to get benzene.



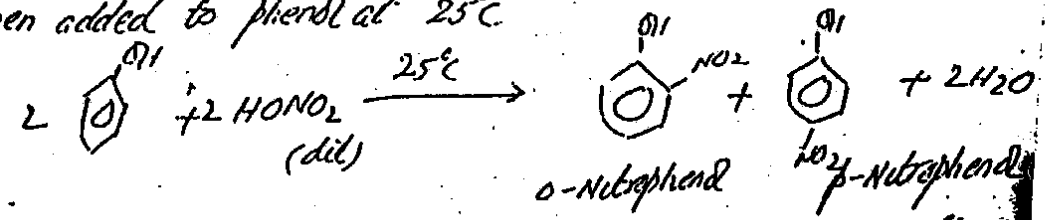
(ii) BROMINE WATER Bromine water produce white precipitate with Phenol. This is typical test for phenol.



2,4,6-tribromo phenol (white ppts)

NITRIC ACID:- (dil) (NITRATION)

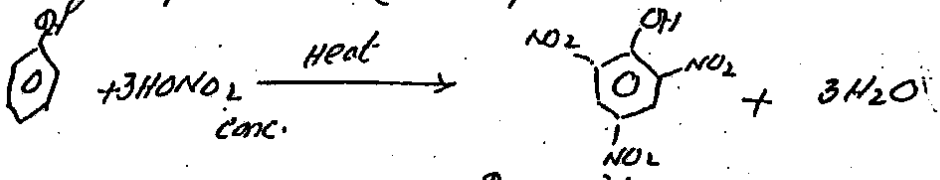
Dilute nitric acid produce o-Nitrophenol and paranitrophenol when added to phenol at 25°C.



o-Nitrophenol p-Nitrophenol

The o-Nitrophenol and p-Nitrophenol are separated by steam distillation.

CONC. NITRIC ACID:- Concentrated nitric acid react with phenol to form picric acid (trinitrophenol).

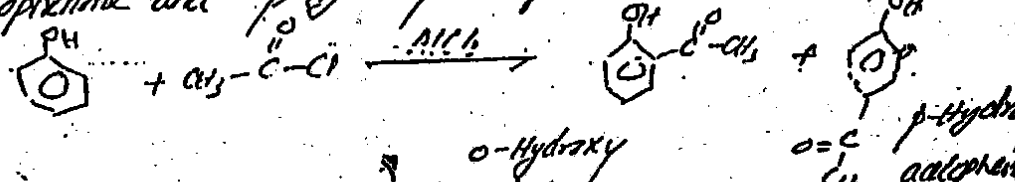


Picric acid.

Picric acid is an explosive compound. It is also used as dye and an antiseptic.

ACETYL CHLORIDE:- $CH_3-\overset{O}{\overset{\|}{C}}-Cl$ (ACETYLATION).

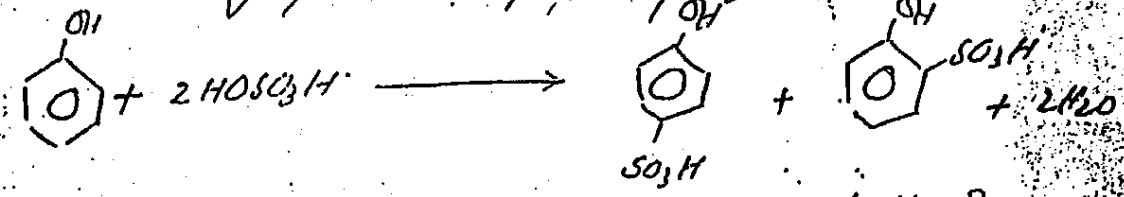
Phenol reacts with acetyl chloride in presence of $AlCl_3$ at relatively lower temperature to form o-Hydroxy acetophenone and p-Hydroxy acetophenone.



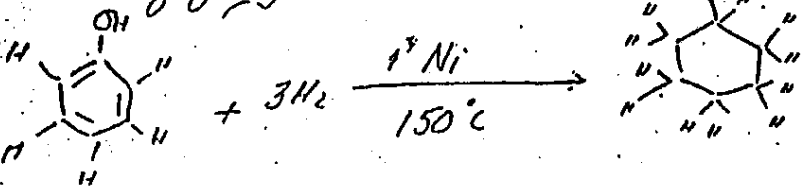
o-Hydroxy acetophenone

p-Hydroxy acetophenone

REACTION WITH SULPHURIC ACID:- (SULPHONATION)
Phenol reacts with concentrated sulphuric acid to form ortho and para isomeric phenol sulphonic acid. The relative % of isomer depend upon temperature.
(i) At 25°C major product is o-Hydroxy benzene sulphonic acid (o-Phenol sulphonic acid).
(ii) At 100°C major product is p-Hydroxybenzenesulphonic acid

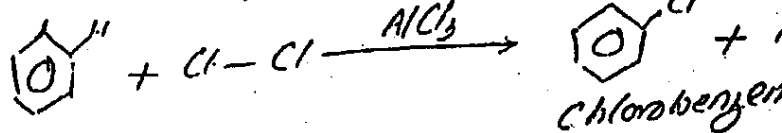


HYDROGENATION:- The addition of hydrogen to phenol is called hydrogenation. Hydrogenation occurs when hydrogen gas is passed through phenol at 150°C in presence of finely divided Nickel



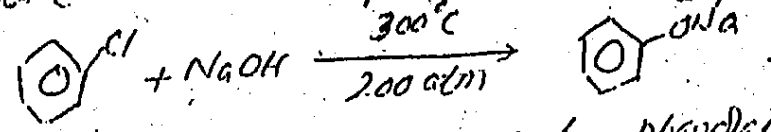
Cyclohexanol.

HOW WILL YOU CONVERT BENZENE TO PHENOL:-
Benzene can be converted into phenol by Dow process. It involves following steps.
(i) FORMATION OF CHLOROBENZENE:- Benzene is treated with chlorine in presence of $AlCl_3$.



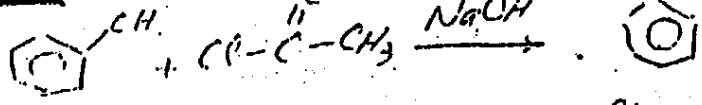
Chlorobenzene

(ii) FORMATION OF SODIUM PHENOLATE:-
Chlorobenzene is treated with NaOH at 300°C and 200 atm pressure to form sod. phenolate



Sodium phenolate

ESTERIFICATION:-



Phenyl Acetate