

Alcohols, Phenols, and Ethers.

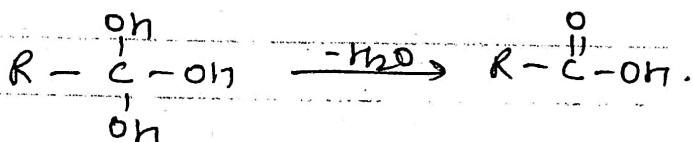
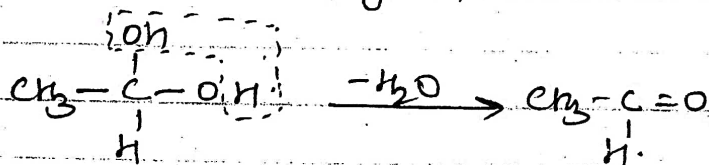
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Alcohols are the compounds that have one or more hydroxyl (-OH) group bonded to aliphatic carbon atoms while phenols are the compounds which have one or more -OH group bonded to the aryl carbon atoms. These are obtained by replacing one or more hydrogen atoms of aliphatic or aromatic hydrocarbons by hydroxyl (-OH) group.

The alcohols are represented by the general formula R-OH.

The alcohols are further classified as mono, di, tri hydric alcohols depending upon one, two, three -OH group present in their molecule.

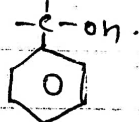
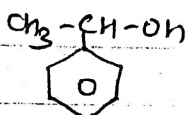
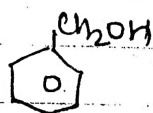
Note - More than one -OH group cannot be present on the same carbon atom. In such a case the compound will be extremely unstable and will readily lose a water molecule to form more stable aldehyde, ketone or carboxylic acid.



- Like alcohols phenols may also be classified as mono, di, tri or polyhydric.

If the -OH group is not directly linked with benzene ring and is present in the alkyl side chain, then the compound is not a phenol. It is called aromatic alcohol because it resembles aliphatic alcohols in its characteristics.

ex.



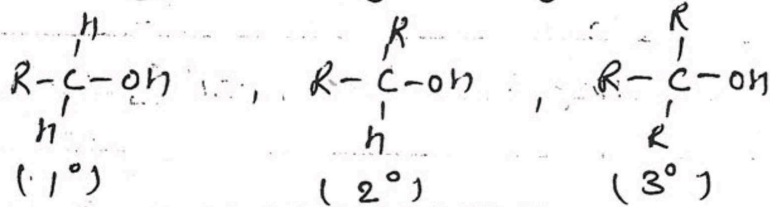
- classification of alcohols -

monohydric alcohols may be classified on the basis of

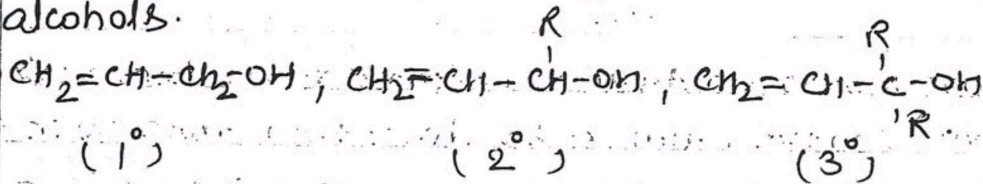
hybridisation of the Carbon atom to which the hydroxyl group is attached.

1. Compound Containing sp^3 Carbon bond with -OH.

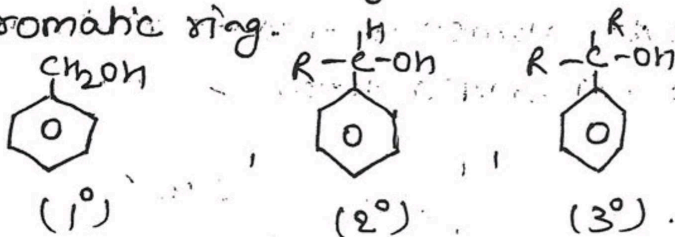
(a) Primary, Secondary, tertiary alcohol.



(b) Allylic alcohols - In these alcohols, the hydroxyl group is attached to a sp^3 Carbon next to Carbon-Carbon double. These alcohols can be classified as $1^\circ, 2^\circ, 3^\circ$ allylic alcohols.



(c) Benzylic alcohols - In these alcohols, the -OH group is attached to a sp^3 hybridised Carbon atom next to an aromatic ring.

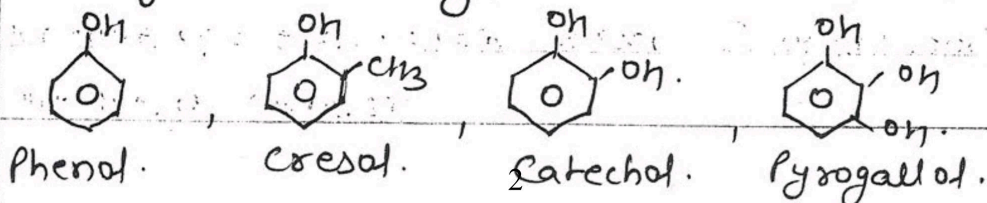


2. Compound Containing C_{sp^2} -OH Bond.

(a) Vinylic alcohols - These contain -OH group attached to a Carbon atom of a Carbon-Carbon double bond. These alcohols are called vinyl alcohols.

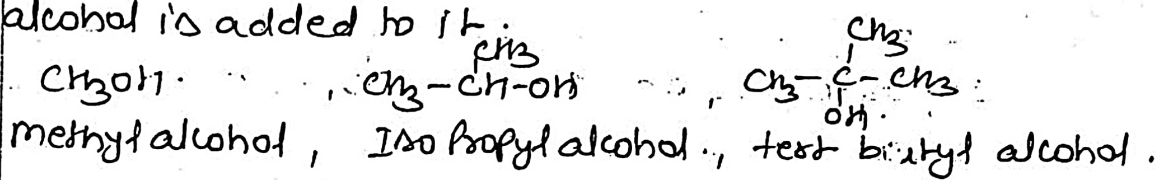


(b) Phenols - These contain -OH group attached to a Carbon atom of benzene ring.



- Nomenclature -

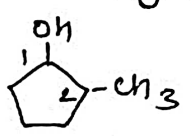
(a) Monohydric alcohols - According to Common System, alcohols are named as alkyl alcohol in which the alkyl group attached to the -OH group is named and the word alcohol is added to it.



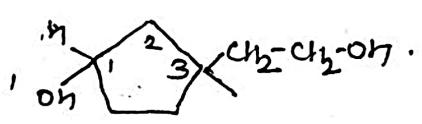
- According to IUPAC, alcohols are named by replacing 'e' in the name of parent alkane by 'ol'.

Rules.

- (1) The longest continuous chain containing the Carbon bonded to OH group is selected as the parent chain.
- (2) The Carbon atom in the chain are numbered in such a way that the Carbon atom carrying the -OH group get lowest.
- (3) The position of the substituents is indicated by suitable numbers.
- (4) Cyclic alcohols are named by using the prefix cyclo and considering the -OH group attached to C-1.

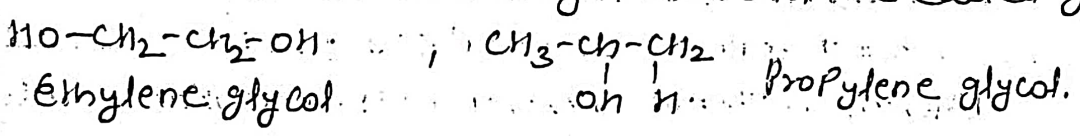


2-methylcyclopentanol

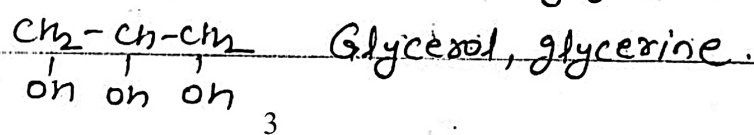


trans-3-(2-hydroxyethyl)cyclopentanol.

(b) Polyhydric alcohols - These contain two or more -OH group in their molecules. The dihydric alcohol are called glycols.



- The trihydric alcohols do not have any general rule for naming.

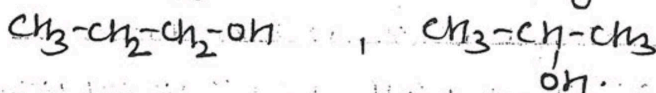


- Isomerism in Alcohols.

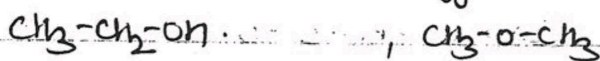
- (1) Chain isomerism - Alcohols containing four or more carbon atoms exhibit chain isomerism in which the isomers differ in the chain of carbon atoms attached to the -OH group.



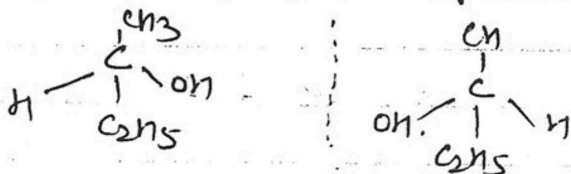
- (2) Position isomerism - The alcohols containing three or more carbon atoms exhibit position isomerism in which the isomers differ in the position of -OH group.



- (3) Functional Isomerism - Monohydric alcohols containing two or more carbon atoms exhibit functional isomerism in which the isomers differ in the functional group.



- (4) Optical isomerism - Monohydric alcohols containing chiral carbon atoms exhibit optical isomerism.



Note: The bond angle C-O-H in methanol is slightly less than the $(109^\circ, 28')$. This is due to larger repulsion between the lone pair of oxygen.

- (1) The bond angle C-O-H in Phenol is 109° . The C-O bond length (136 pm) in Phenol is slightly less than that in methanol. This is due to partial double bond character of C-O bond because of the conjugation of lone pair of electron of oxygen with the aromatic ring.

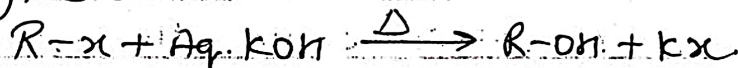
(iii) Phenol has smaller dipole moment than methanol. This is due to the reason that C-O bond in Phenol is less polar due to electron withdrawing effect of benzene ring. On the other hand C-O bond in methanol is more polar due to electron donating effect of CH₃ group.

Due to dipolar nature, alcohols and Phenols form intermolecular hydrogen bond.

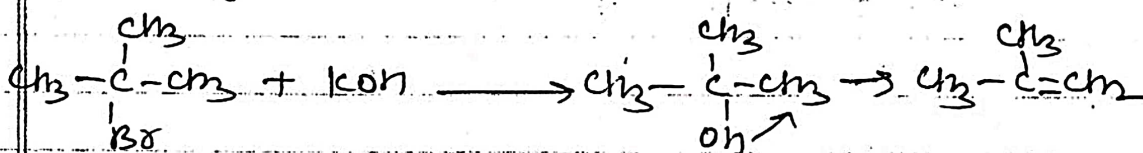
Method of Preparation of Alcohols

I Preparation from haloalkanes -

Haloalkanes when boil with Aq. KOH, NaOH or moist AgOH give alcohol.



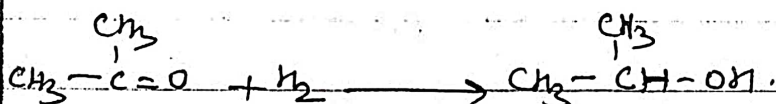
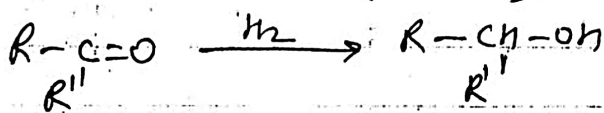
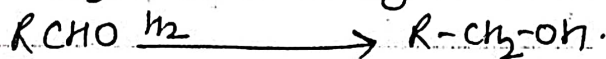
Primary haloalkanes give good yield of alcohols. However tertiary haloalkanes in this reaction give mainly alkenes due to dehydrohalogenation. Secondary haloalkanes give a mixture of alcohol and alkene.



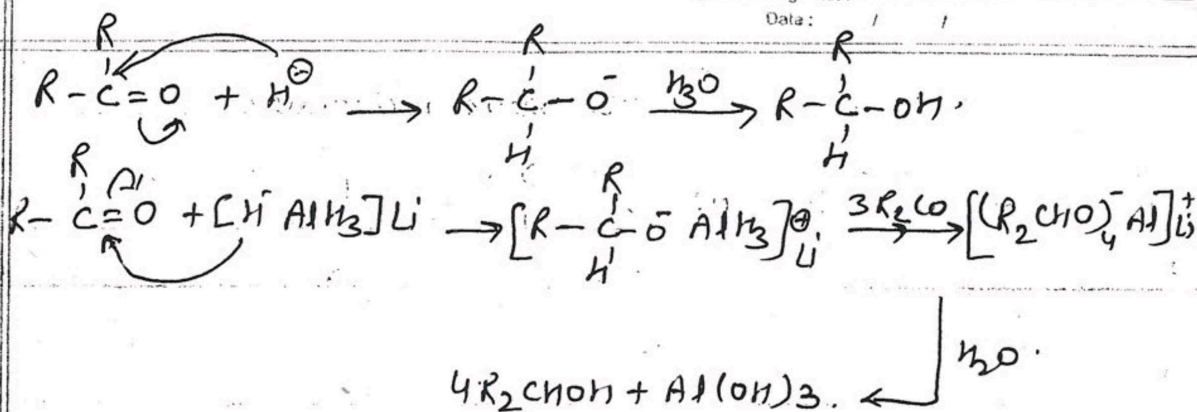
2. By reduction of aldehydes and ketones -

The reduction is carried out by common reducing agent such as (i) hydrogen in presence of Ni, Pd, Pt (ii) Sodium in the presence of ethyl alcohol (iii) LiAlH₄ or NaBH₄.

During Reduction aldehyde gives Primary alcohols and ketones give Secondary alcohol.



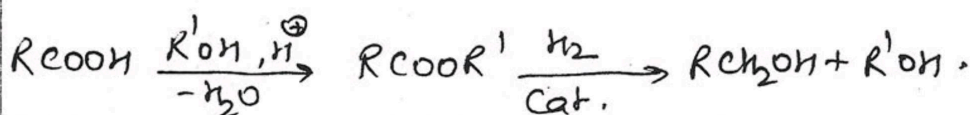
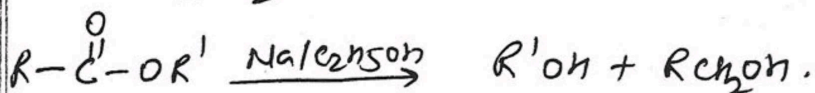
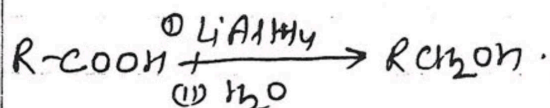
mech.



LiAlH₄ reacts violently with water and therefore the reaction with LiAlH₄ must be carried out in anhydrous condition. Usually ethyl acetate is added after the reaction is over to decompose excess of LiAlH₄ and then water is added to decompose aluminium complex.

(3) By reduction of Carboxylic acid and esters:

Carboxylic acids are reduced to primary alcohols in the presence of strong reducing agents.



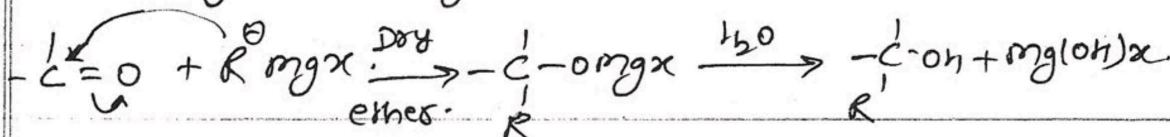
Acid.

ester.

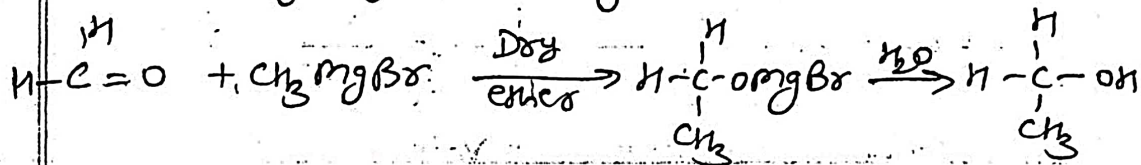
Tertiary alcohols cannot be obtained by reduction of Carbonyl Compound.

Reduction of aldehydes, ketones, and esters with sodium and alcohol is commonly known as Bouveault Blanc reduction.

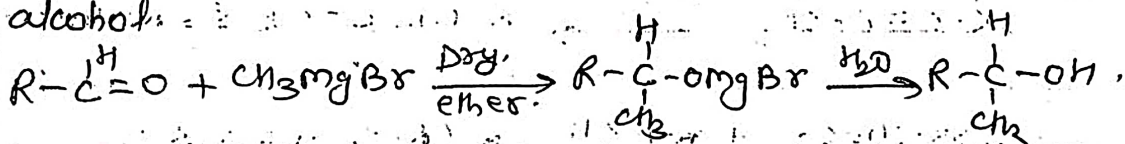
4 From Grignard's reagent.



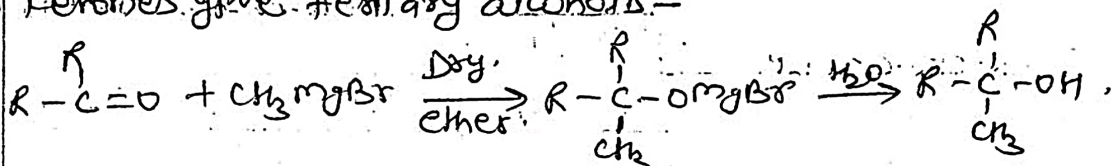
(a) Formaldehyde give primary alcohol



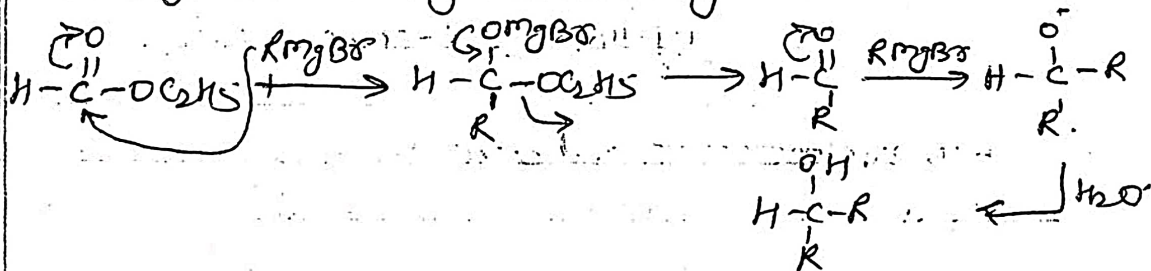
(b) All aldehyde other than formaldehyde give secondary alcohol.



(c) Ketones give tertiary alcohols.



(d) Esters give secondary and tertiary alcohol.

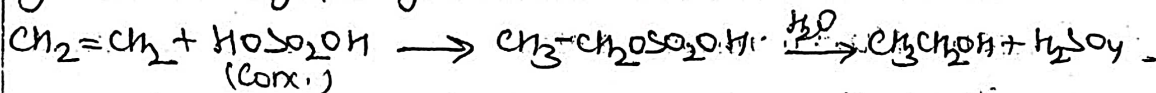


5. By hydrolysis of esters - Alcohols are generally prepared by hydrolysis of esters with aq. alkalis.

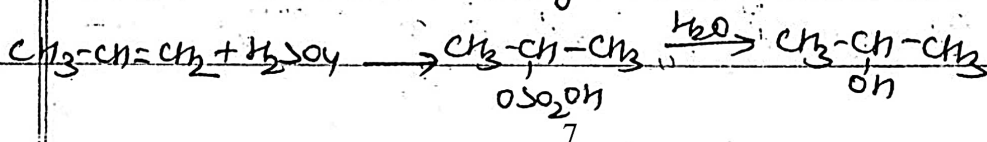


6. From alkenes -

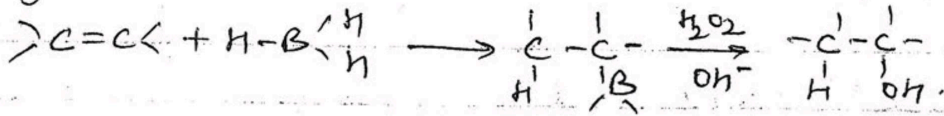
(a) By acid catalysed hydration.



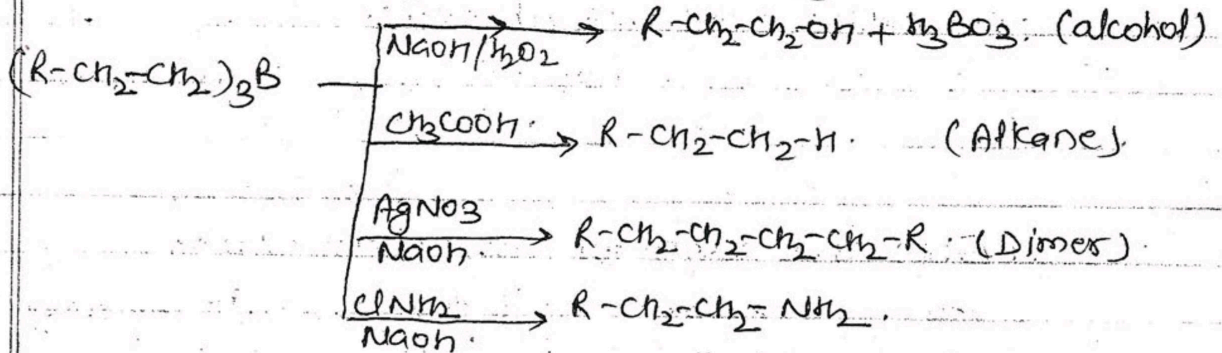
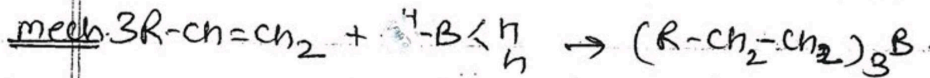
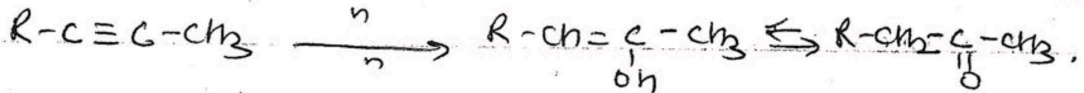
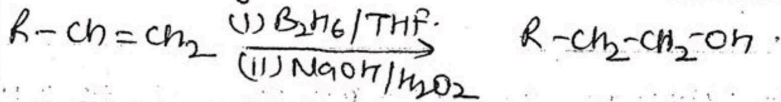
In case of unsymmetrical alkene the addition of H_2SO_4 take place in the accordance of Markovnikov's rule.



(b) Hydroboration oxidation reduction.

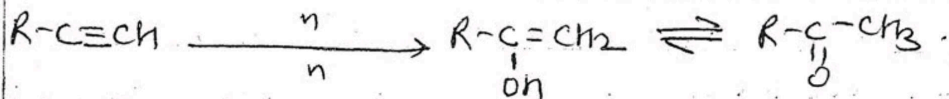
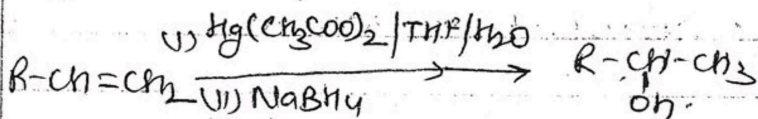


This reaction follows anti markovnikov's rule

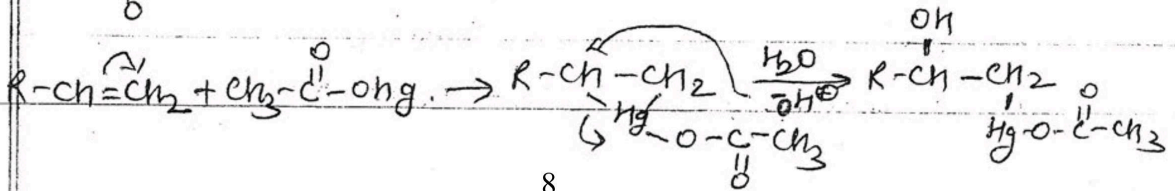
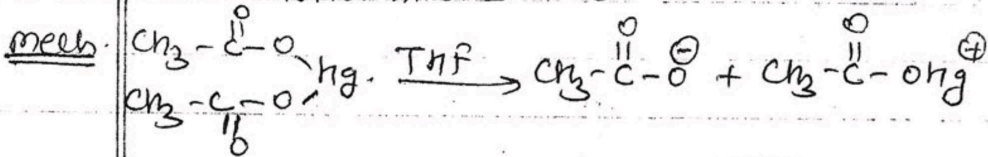


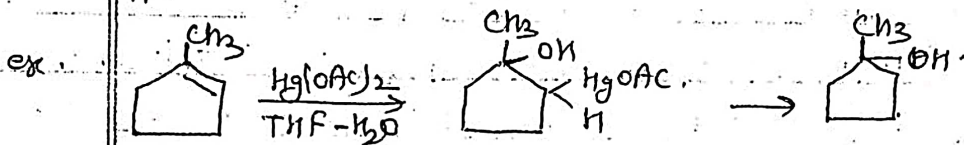
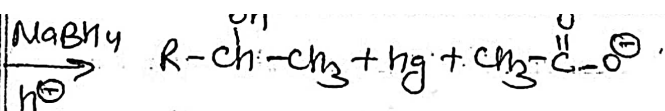
- It is regioselective and stereospecific and stereoselective.
- Overall this reaction is stereospecifically syn addition reaction.

7. Oxymercuration and demercuration (OMDM) -



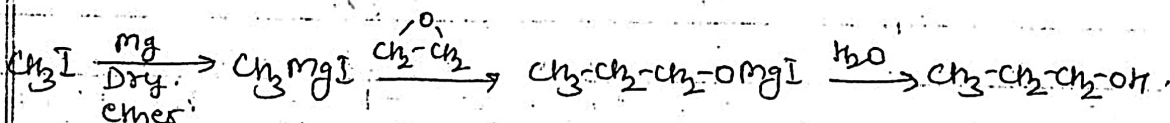
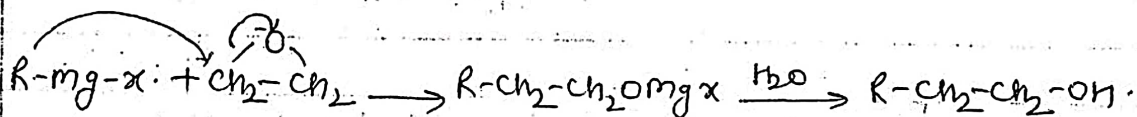
The net reaction involves addition of -H and -OH in accordance with Markovnikov's rule.



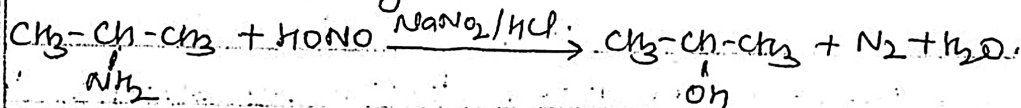


It is non stereospecific, Rearrangement not take place.

II From ethylene oxide or oxirane -



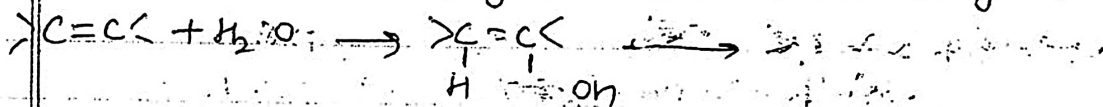
B. From aliphatic primary amines -



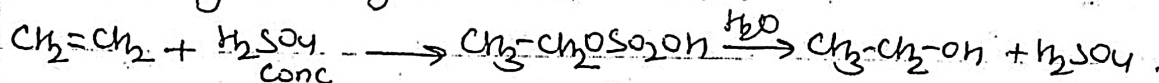
— Industrial preparation —

(1) Hydration of alkenes.

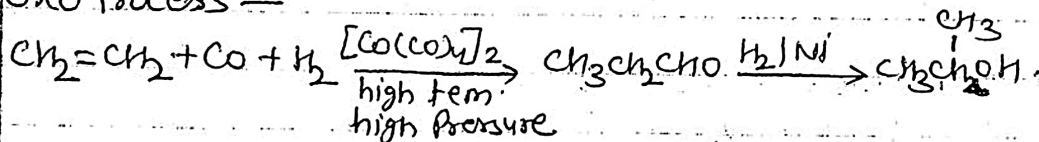
(a) By direct addition of water at low temperature and high pressure in the presence of mineral acids as catalyst.



(b) By indirect method in which alkene are passed through conc. H_2SO_4 to form alkyl hydrogen sulphates which upon hydrolysis with boiling water give alcohol.

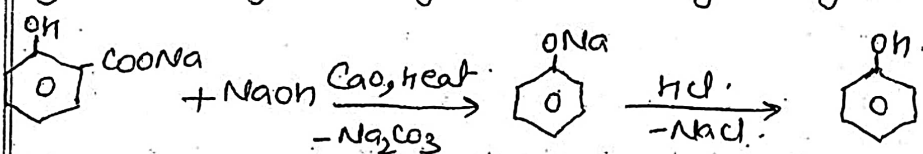


(2) Oxo process -

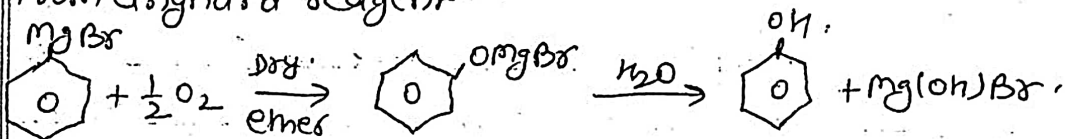


(3) Fermentation of carbohydrates -

3. By decarboxylation of Sodium salt of Salicylic acid -

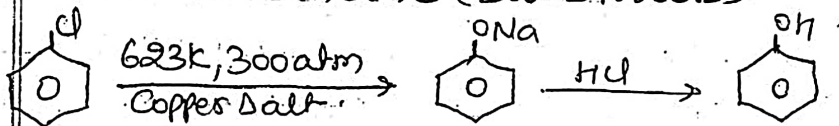


4. From Grignard reagent -

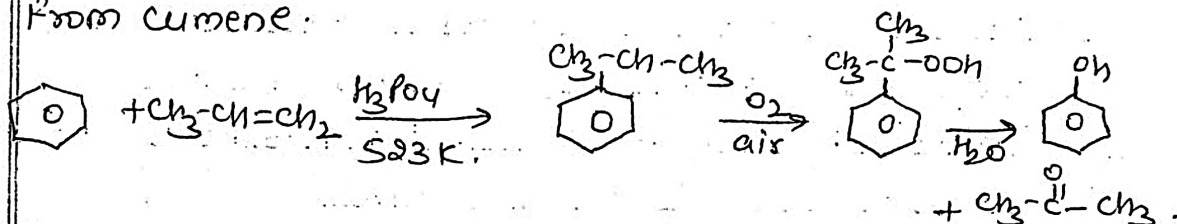


- Commercial Preparation of Phenol.

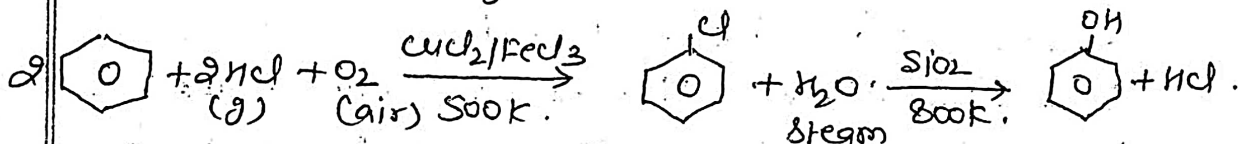
(1) From Chlorobenzene (Dow's Process)



(2) From cumene:



(3) From benzene (Raschig's method)



- Physical Properties.

(i) Physical state - The lower members are colourless liquid having a characteristic smell and burning taste. Higher members have more than 12 carbon are colourless, odourless, wax like solid.

(ii) Associated nature - Alcohols exist as associated molecules having intermolecular hydrogen bond due to large difference in electronegativity of oxygen and hydrogen.

(iii) Boiling point - The lower members have low boiling points but increase in molecular mass the boiling point increases.

alcohols have higher boiling point as compared to other organic compounds of similar molecular masses due to hydrogen bond.

IV Solubility — The lower members of alcohols are highly soluble in water but the solubility decreases with increases in molecular weight.

The solubility of lower alcohols in water is due to the formation of hydrogen bond between alcohol and water molecule. But as the size of alcohol molecule increases the alkyl group become larger and prevent the formation of hydrogen bond.

However amongst isomeric alcohols the solubility increase with branching. This is due to the reason that as the branching increases the surface area of non-polar hydrocarbon part decreases and the solubility increases.

V Density — alcohols are lighter than water although density increases with increase in molecular mass.

VI Intoxicating effect — methanol is poisonous and ethanol has been used for drinking purpose.

— Physical Properties of Phenol.

I State and Smell — Phenols are colourless crystalline solids or liquids. They have characteristic odours.

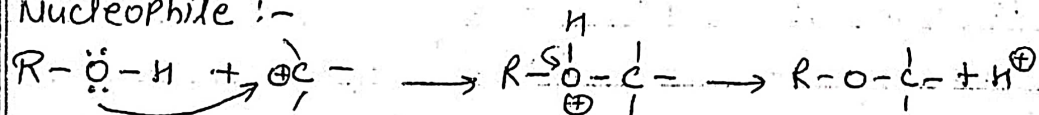
II Solubility — Phenols are sparingly soluble in water and soluble in alcohols, ethers and in NaOH.

III Boiling Points — The boiling points of phenols are higher than the boiling points of aromatic hydrocarbons of comparable molecular mass due to intermolecular hydrogen bonding.

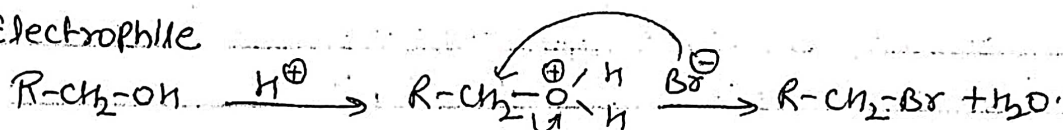
= Chemical Properties of alcohols.

Alcohols are versatile compound. They behave both as nucleophile as well as electrophile.

(a) Nucleophile :-

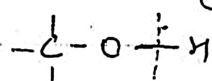


(b) Electrophile

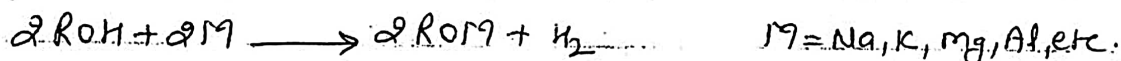


- on the basis of cleavage of different bonds the reaction of alcohols may be divided into.

(A) Reaction involving the cleavage of oxygen-Hydrogen bond.

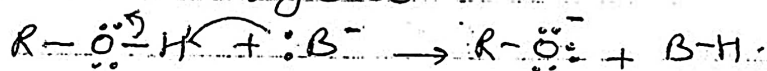


I. Reaction with active metals - Acidic character -

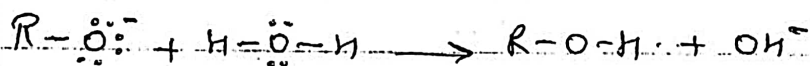


Alcohols are ~~totally~~ weakly acidic in nature and react with metal to liberate hydrogen gas and form metal alkoxide.

The alcohols act as a Bronsted acids because they donate a proton to a strong base.



alcohol. Base Alkoxide



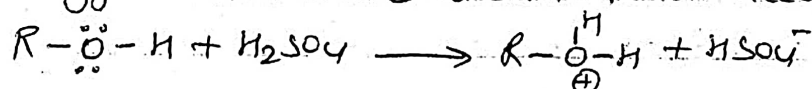
Water is a better proton donor than alcohol or water is a strong acid than alcohol.

Order of Acidic strength $1^\circ > 2^\circ > 3^\circ$ due to inductive effect.

Basic character. $3^\circ > 2^\circ > 1^\circ$

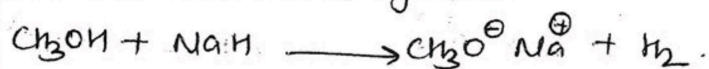
Note

Alcohols act as a Bronsted base due to presence of lone pair on oxygen which make alcohols proton acceptors.

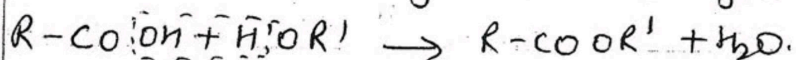


(In the presence of strong acid Alcohol act like a base)

2. Reaction with metal hydride -

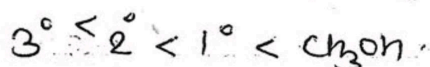


3. Reaction with Carboxylic acid (esterification)

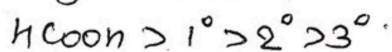


Acid. Alcohol. ester.

In this reaction alcohol act as a ^{Proton donor} also reactivity of alcohol.

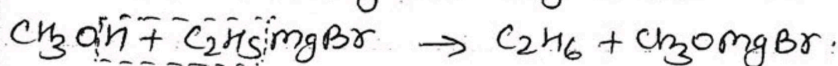


and Carboxylic acid is



this order is due to steric hindrance of bulky group.

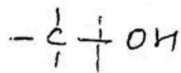
4. Reaction with Grignard reagent.



5. Reaction with acyl chloride or acid anhydride (acylation) -

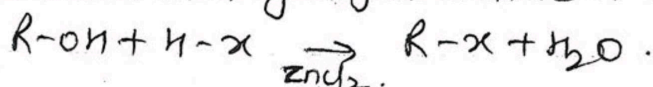


B Reaction involving cleavage of Carbon oxygen bond:



order of reactivity $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{OH}$. due to +I effect of CH_3 .

(U) Reaction with hydrogen halide -



Reactivity of hydrogen halide $\text{HI} > \text{HBr} > \text{HCl}$.

- The reaction of primary and secondary alcohols with HCl gas in the presence of anhydrous $ZnCl_2$ is called Groove method.
- In case of HBr a small amount of Conc. H_2SO_4 is added as a catalyst for primary alcohol. But no catalyst is added for the reaction with 2° and 3° .
- In case of HI, alkyl halide are formed by heating alcohol with HI.

However if reaction between hydrogen iodide and alcohol is carried out in the presence of red phosphorus, alcohol get reduced to hydrocarbon rather than to form alkyl halide.



NOTE - Primary alcohols react by S_N2 mech. whereas 2° and 3° react by S_N1 mech. (rearrangement take place).

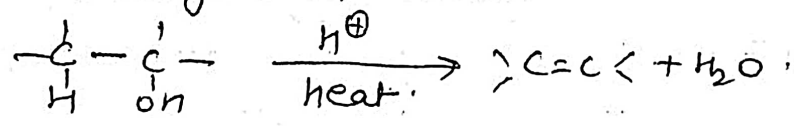
2. Reaction with Phosphorus halide - PCl_3, PCl_5, PBr_3 , or PI_3 .
 $R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$
 $3R-OH + PCl_3 \rightarrow 3R-X + H_3PO_3$ $x = Cl, Br, or I$.
 PBr_3 and PI_3 are generally prepared in site

3. Reaction with thionyl chloride.
 $R-OH + SOCl_2 \xrightarrow{Pyridine} R-Cl + SO_2 \uparrow + HCl \uparrow$

The reaction with thionyl chloride is preferred because the by products formed are gases and can be easily removed.

C. Reaction involving both the cleavage of Alkyl and hydroxyl group.

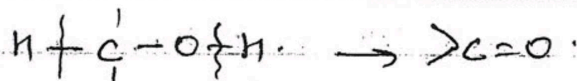
I. Acidic dehydration -



reactivity order $3^\circ > 2^\circ > 1^\circ$ and major product is

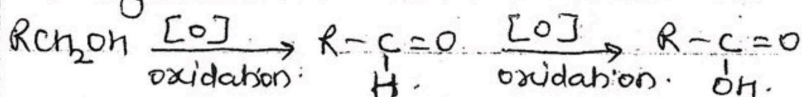
Saytzeff's

2- Oxidation - The oxidation of alcohol involves the formation of Carbon-oxygen double bond with cleavage of O-H and C-H bonds.

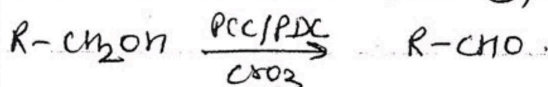


These reaction are also called dehydrogenation. This can be carried out by a number of reagent such as aqueous, alkaline or acidified $KMnO_4$, acidified Na_2CrO_3 , $K_2Cr_2O_7$ or nitric acid, chromic acid etc.

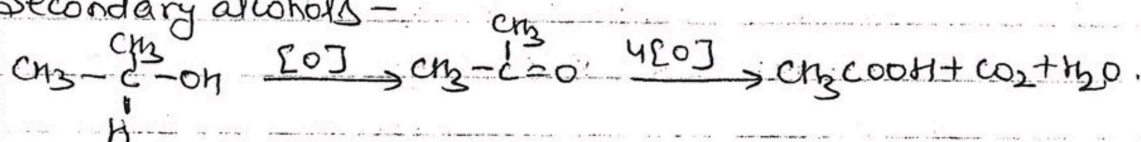
(i) Primary alcohol -



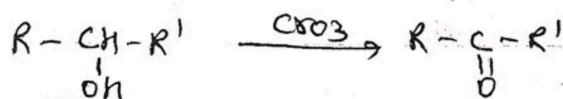
acidified $K_2Cr_2O_7$ convert alcohols directly in Carboxylic acid. To prevent this we use CrO_3 , PCC, PDC.



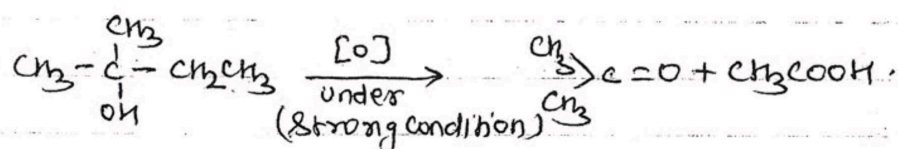
(ii) Secondary alcohols -



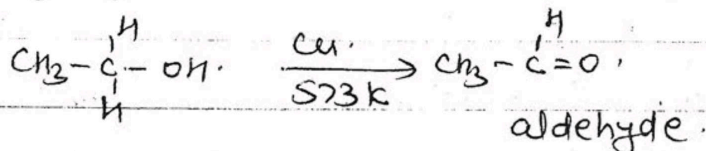
The oxidation can be stopped at ketone by CrO_3 .

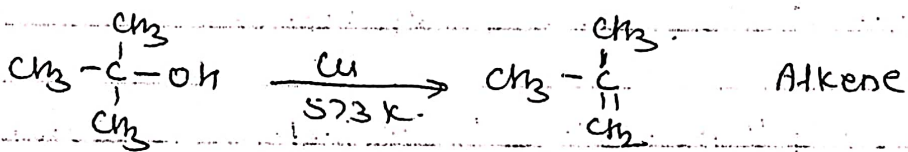
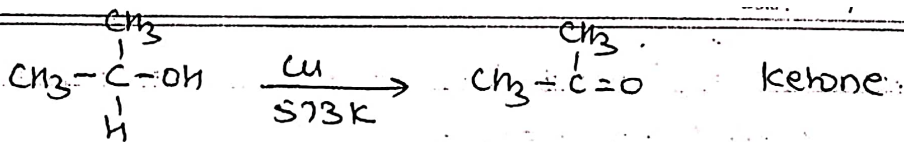


(iii) Tertiary alcohols :-



3. Dehydrogenation -





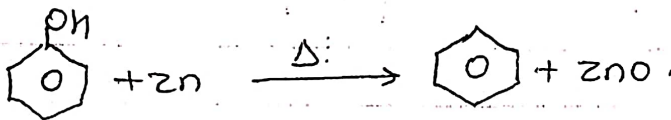
= Chemical Properties of Phenols

A Reactions of Phenolic group (-OH)

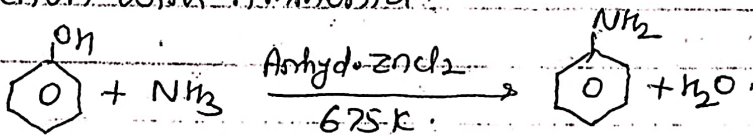
1. Acidic character:-

Phenol are more acidic in nature than alcohol due to resonance, but less acidic than Carboxylic acid.

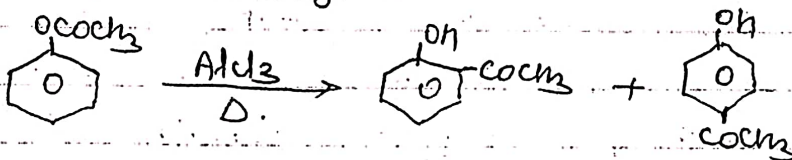
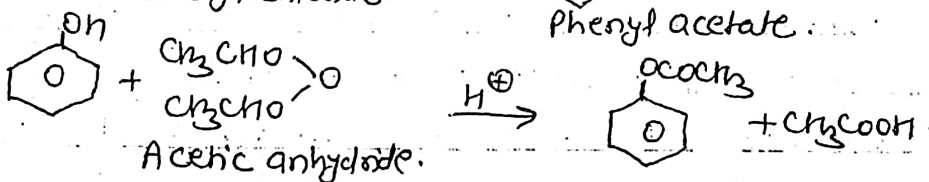
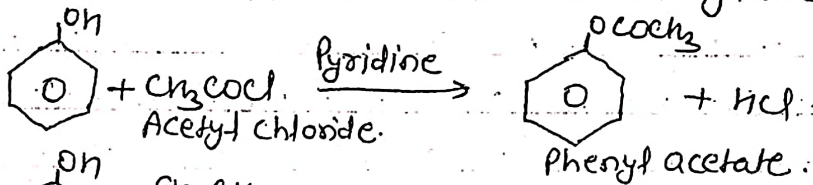
2. Action with zinc dust.



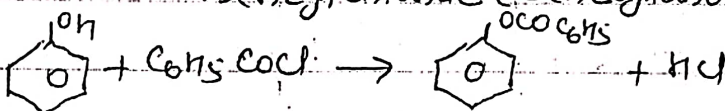
3. Action with Ammonia.



4. Action with acid chlorides and acid anhydrides (acylation).

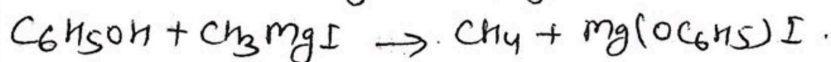


5. Action with benzoyl chloride (benzoylation)

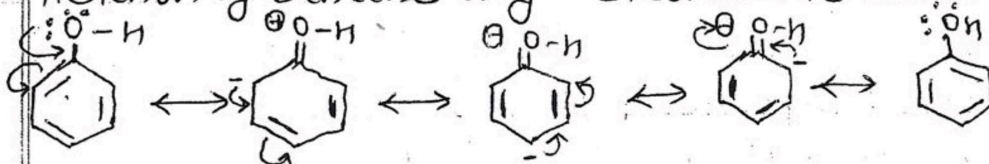


This reaction is called Schotten Baumann reaction.

6. Reaction with Grignard Reagent.

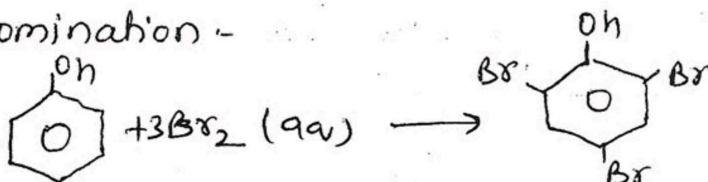


B. Reaction of Benzene ring: Electrophilic Substitution -

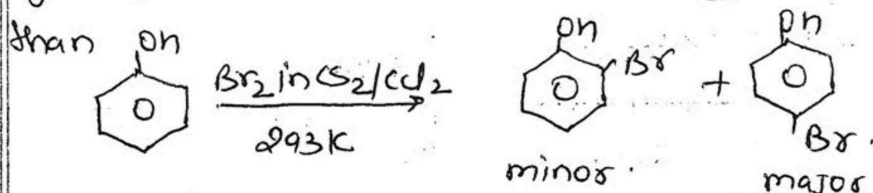


Phenol is ortho-para directing.

(1) Bromination -



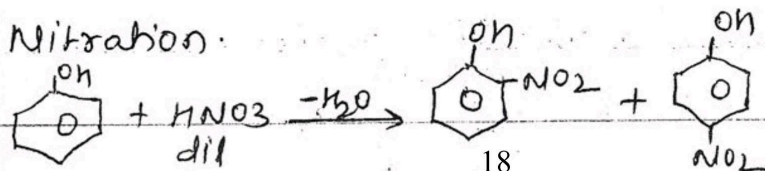
If the reaction is carried out in CS_2 or $CDCl_2$ at low temp.



- In aqueous solution phenol ionise to give phenoxide ion. Due to the presence of negative charge, the oxygen atom of the phenoxide ion donates electrons to the benzene ring to a large extent. As a result the ring gets highly activated leading to the formation of trisubstituted product.

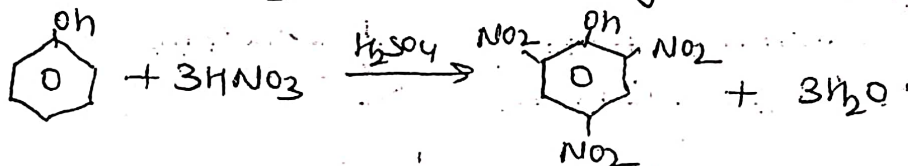
On the other hand in the non polar solvent, the ionisation of phenol does not occur. As a result the -OH group donates electrons to the ring only a small extent and the ring is activated slightly and only mono substituted occur.

2. Nitration.

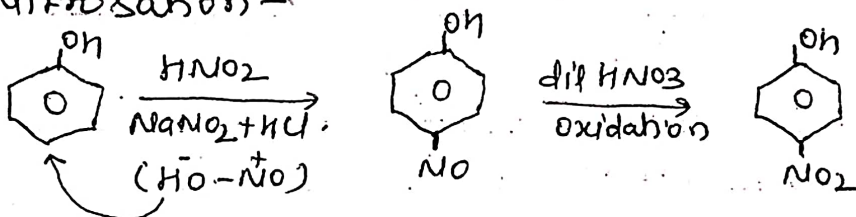


The ortho and Para isomer can be separated by steam distill. o-nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding.

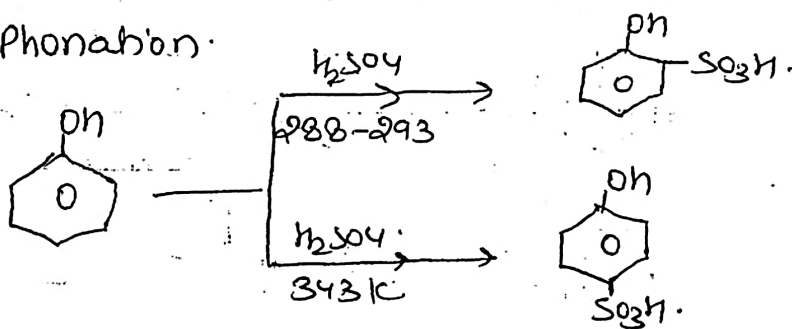
with conc HNO_3 in the presence of conc. H_2SO_4



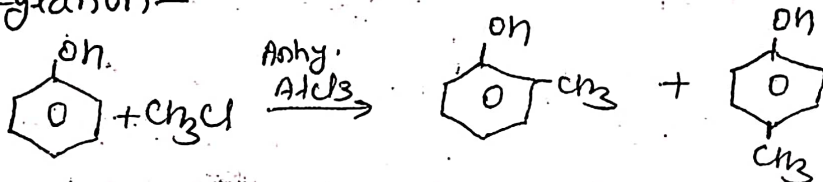
3. Nitrosation -



4. Sulphonation.

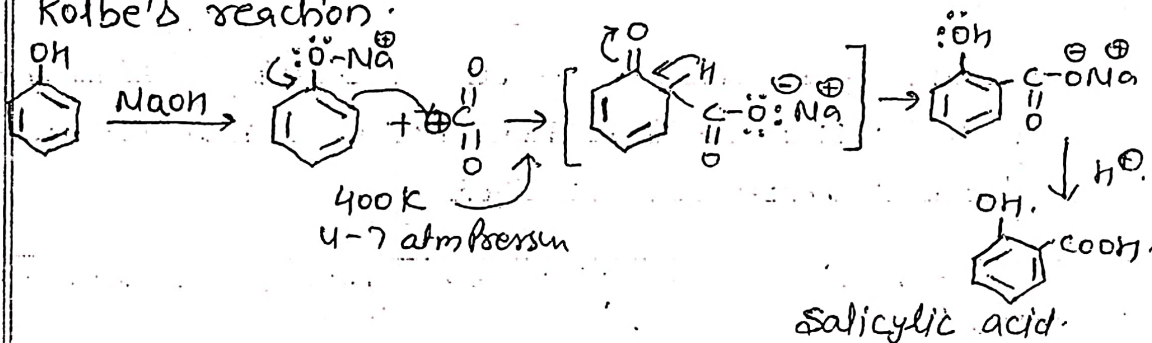


5. Alkylation -



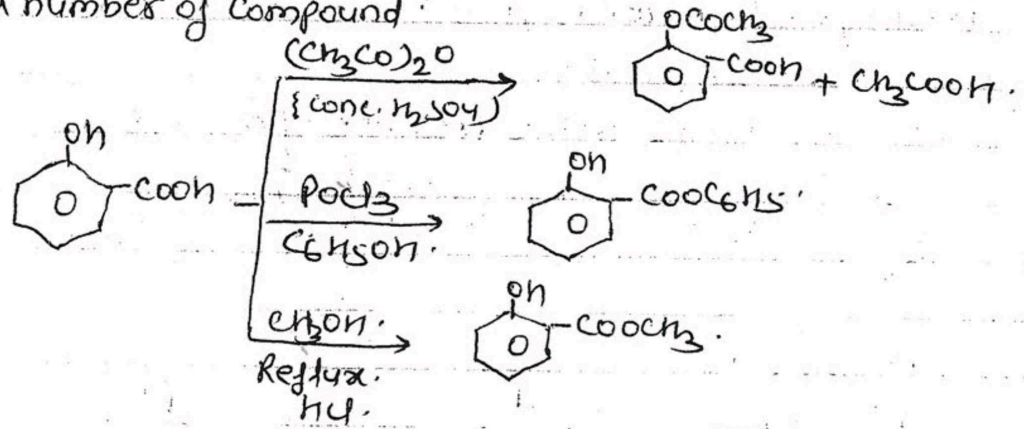
c Special Reaction of Phenol.

⊥ Kolbe's reaction:

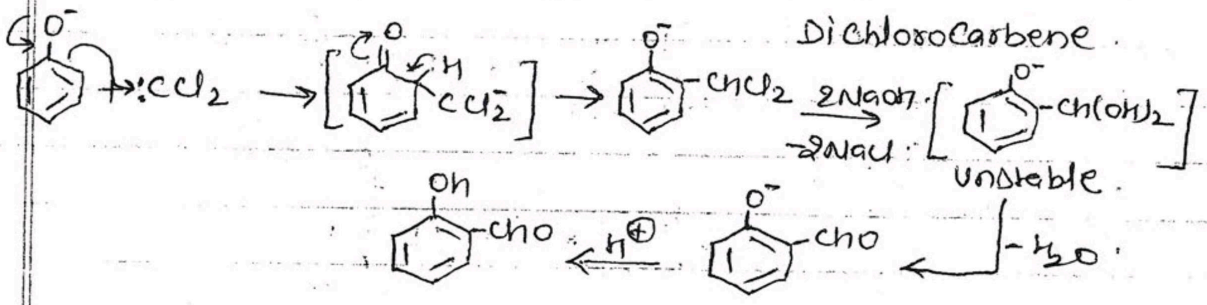
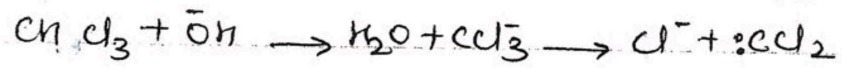


A small amount of para isomer is also obtained and if the temper

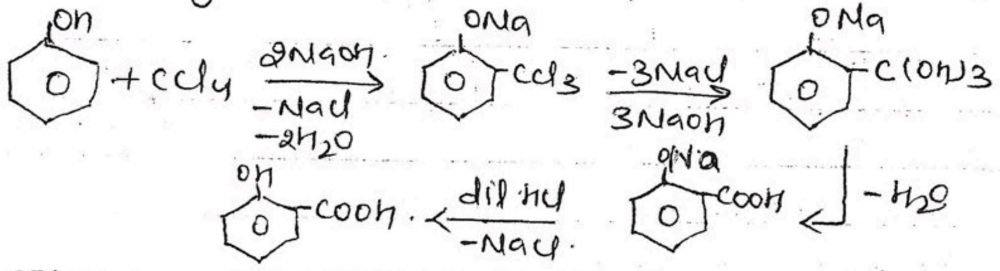
be allowed to rise above 410 K, the para isomer dominates. Salicylic acid is the starting material for the manufacture of a number of compounds:



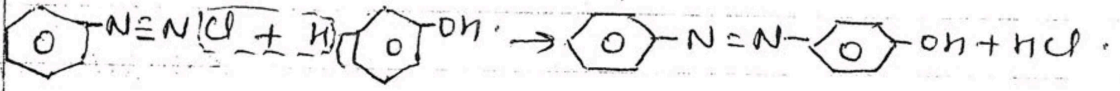
2. Reimer-Tiemann reaction - This reaction involves electrophilic substitution reaction.



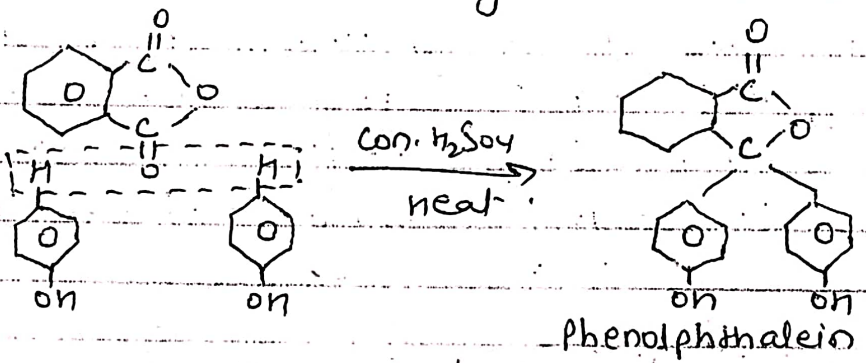
If in case of CHCl_3 we use CCl_4 then:



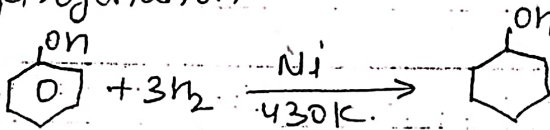
3. Coupling reaction - an ice cold solution of phenol combines with ice cold solution of benzene diazonium chloride to form coloured substance azo-dyes.



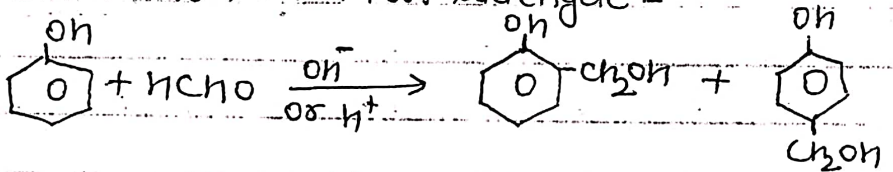
4. Reaction with Phthalic anhydride -



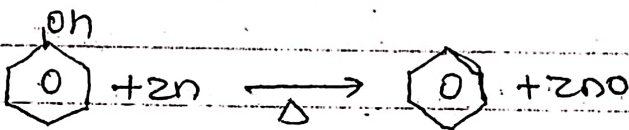
5. Hydrogenation -



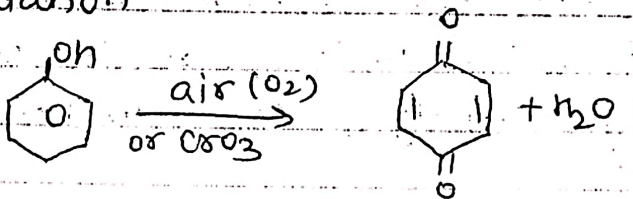
6. Condensation with formaldehyde -



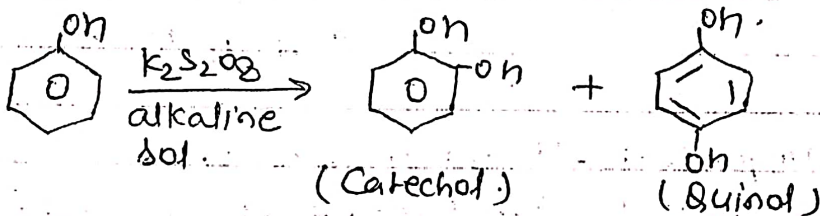
7. Reaction with zinc dust:



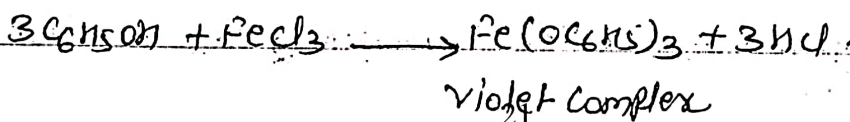
8. Oxidation:



9. Elbs persulphate oxidation:

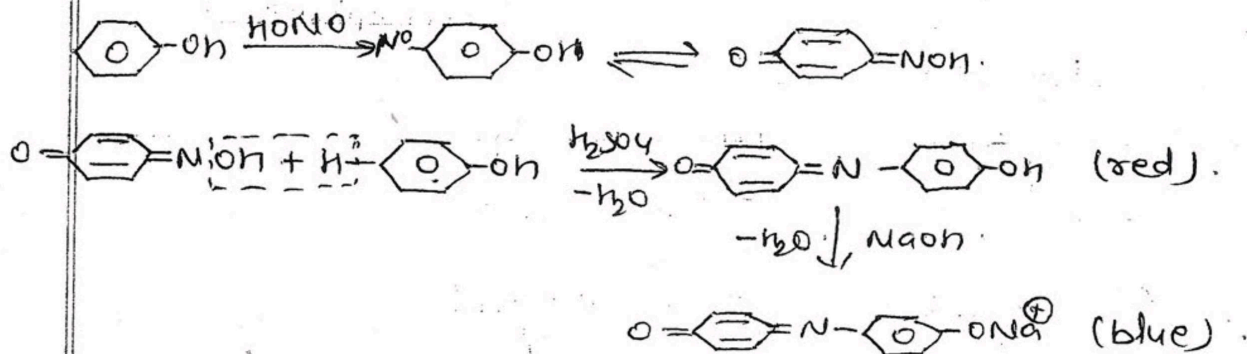


10. Reaction with Ferric chloride:



11. **Liebermann's test -**

Phenols reacts with nitrous acid to give p-nitrosophenol which rearrange to Quinone. In the presence of conc. H_2SO_4 , Quinone Condense with Phenol to give indophenol which is red. with excess NaOH, Sodium Salt of indophenol is obtain which is blue.



This test can be used to distinguish Phenol from alcohol.

1. **Lucas test -**

In this test an alcohol is treated with an equimolar mixture of conc. HCl and anhyd. $ZnCl_2$ (Lucas reagent) is treated. The alcohol get converted into alkyl halide. Since alkyl halides are insoluble in water, their formation is indicated by the appearance of turbidity in the reaction of mixture. Since the order of reactivity of alcohol with halogen is $3^\circ > 2^\circ > 1^\circ$ then:

- $3^\circ \longrightarrow$ produce cloudiness immediately.
- $2^\circ \longrightarrow$ " " within 5 minutes.
- $1^\circ \longrightarrow$ " " only on heating.

2. **Victor-Meyer test -** This test involve

- (i) The given alcohol is treated with red (P) and iodine resulting in the formation of alkyl iodide.
- (ii) The alkyl iodide treated with $AgNO_3$ to form nitroalkane.

(iii) This nitroalkane is treated with (NaNO₂ + dil. H₂SO₄) or HNO₂ and the resulting solution made alkaline.

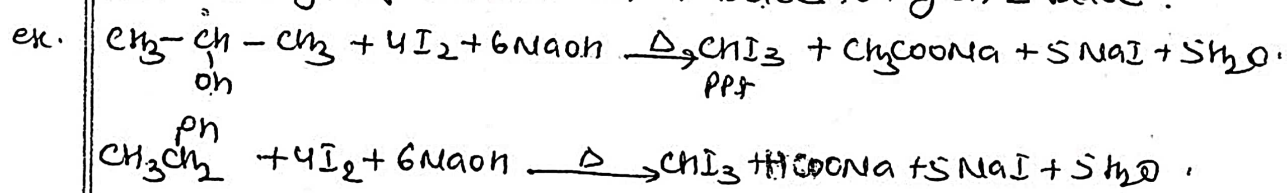
- 1° → blood red colour
- 2° → blue colour
- 3° → colourless

3. Reduction with copper metal at 573 K. (Page No. 16-17)

4. Iodoform test:
All alcohol containing $\text{CH}_3\text{-CH}(\text{OH})\text{-}$ group linked to carbon or hydrogen atom can give this test.

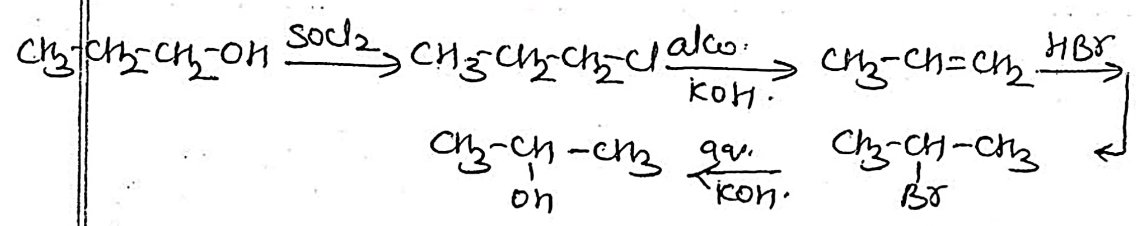
This test is performed by heating the alcohol with aq. NaOH or Na₂CO₃ and iodine solution. On warming the mixture yellow ppt indicates positive test.

If -OH group present on no. 1 than only ethanol give this test otherwise all alcohols not give this test. For positive test -OH group is not on 1 place, only on 2 place.

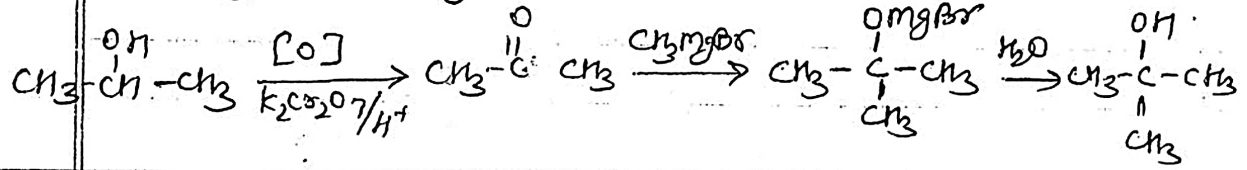


— Interconversion of alcohol

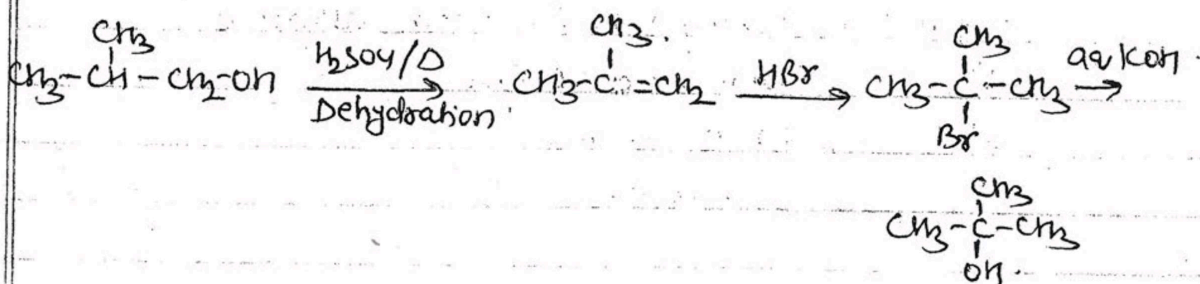
(a) Primary in Secondary.



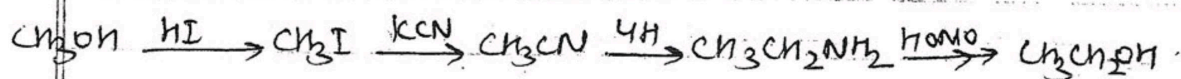
(b.) Secondary in tertiary.



(c) Primary to tertiary alcohol.



(d) Lower alcohol into higher alcohol. (ascent of series)



(e) Higher to lower.

