CHAPTER
18

ALCOHOL, PHENOLS AND ETHERS

After completing this lesson, you will be able to:

- Explain nomenclature, structure and acidity of alcohols as exemplified by ethanol.
- Describe the preparation of alcohols by reduction of aldehydes,.
- Explain reactivity of alcohols.
- Describe the chemistry of alcohols by preparation of ethers and esters, oxidative cleavage of 1,2 –diols.
- Discuss thiols RSH.
- Explain the nomenclature, structure and acidity of phenols.
- Describe the preparation of phenols from benzene sulphonic acid, chlorobenzene, acidic oxidation of cumene and hydrolysis of diamzonium salts.
- Discuss the reactivity of phenol and their chemistry by electrophonic aromatic substitution, reaction with Na metal and oxidation.
- Differentiate between alcohols and phenol
- Describe isomerism in alcohols and phenols.
- Identify ethers from their formula.

Q1. What are alcohols? How are they classified?

Answer

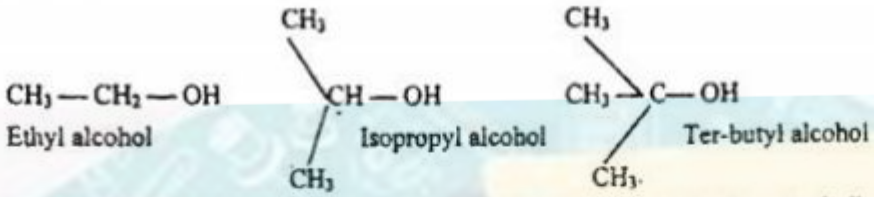
The aliphatic organic compounds containing hydroxyl group –OH, as functional group are called alcohols. Alcohols containing one –OH group are called monohydric alcohols and those containing two or more hydroxyl groups are known as polyhydric alcohol.

Classification of Monohydric Alcohols:

Monohydric alcohols are classified into the following three families:

(i) Primary alcohols (ii) Secondary alcohols and (iii) Tertiary alcohols

Examples:



Q2. Give Nomenculture of Alcohols.

Answer

1) Common System of Naming

In common system alcohols are named by adding the word alcohol after the name of the alkyl group to which the –OH group is attached e.g.

CH_3OH	$C_6H_5CH_2OH$
Methyl alcohol	Benzyl alcohol

2) IUPAC System

According to this system

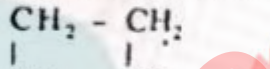
i) The longest chain of carbon atoms containing the hydroxyl group is selected as the parent hydrocarbon.

ii) The ending e of the parent hydrocarbon is replaced by alcohol.

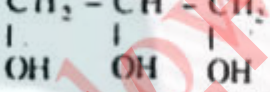
iii) The position of –OH group is indicated by placing the number of carbon to which –OH is attached before the name of alcohol.

iv) The carbon chain bearing –OH group is numbered, beginning from that end which would assign the lowest possible number to carbon atom linked to the –OH group.

v) The presence of more than on -OH groups is indicated by suffixes –diol, -triol, etc. and repeating the number of carbon atoms o which –OH groups are attached e.g.



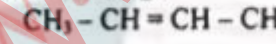
1, 2–ethanediol or
Ethane–1, 2–diol
(glycol)



1, 2, 3–propane triol
(glycerol)

(Common names are given in brackets)

vi) In unsaturated alcohol, the hydroxyl group gets the lower number rather than unsaturation, e.g.,

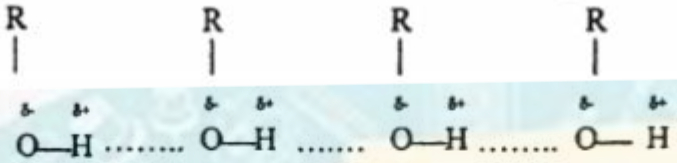


2-butene-1-ol

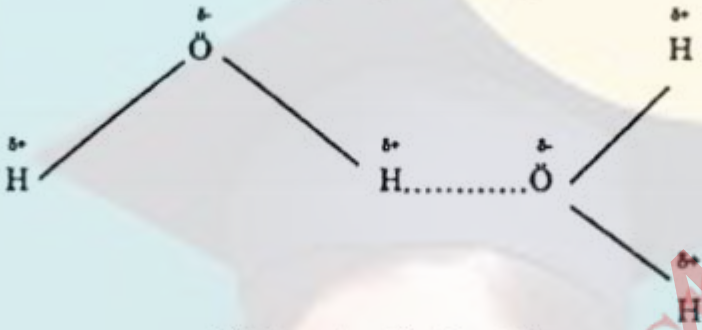
Q3. a) Why alcohols readily dissolve in water?
b) M.P. and B.P of alcohols is somewhat high, why?

Answer

They are readily soluble in water. The solubility of alcohols is due to hydrogen bonding which is significant in lower alcohols but deceases in higher alcohol.



(Hydrogen bonding in alcohol)



(Hydrogen bonding in water)

b) Melting and boiling points of alcohols are higher than corresponding alkanes. This is due to hydrogen bonding which is present in alcohols but absent in alkanes.

Q4. Alcohols are slightly acidic why?

Answer

1) Due to the electronegativity of the O atoms, alcohols are slightly acidic
2) The anion derived by the deprotonation of an alcohol is the **alkoxide**.
3) Alkoxides are important bases in organic chemistry.
4) Alcohols react with Na (or K) like water to give the alkoxide:

$$2\,R\text{-}O\text{-}H + 2\,Na \longrightarrow 2\,NaOR + H_2$$

$$2\,H\text{-}O\text{-}H + 2\,Na \longrightarrow 2\,NaOH + H_2$$

Q5. Give different Methods of preparation of alcohols.

Answer

1) Hydration of Alkenes

a) Hydration of alkenes is carried out in the following two steps:

b) Preparation of alkyl hydrogen sulphate

a) Hydrolysis of alkyl hydrogen sulphate

b) Alkenes are dissolved in concentrated H_2SO_4 to form alkyl hydrogen sulphate

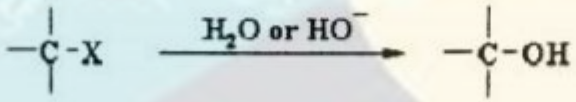
$$CH_2{=}CH_2 + HOH \rightarrow CH_3\text{-}CH_2OSO_3H$$

Ethyl hydrogen sulphate

b) On dilution with water followed by heating alkyl hydrogen sulphates are hydrolyzed to alcohols.

$$CH_3CH_2OSO_3H + H\text{-}OH \rightarrow CH_3CH_2OH + H_2SO_4$$

2) 1Hydrolysis of Alkyl halides



Elaboration

- Alkyl halides can be converted to alcohols using water or hydroxide as the nucleophile.
- Mechanism is a simple nucleophilic substitution

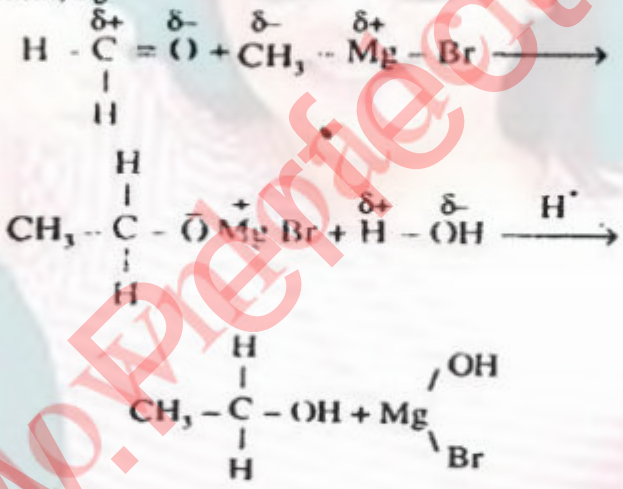
3) Reactions of RLi or RMgX with Aldehydes and Ketones

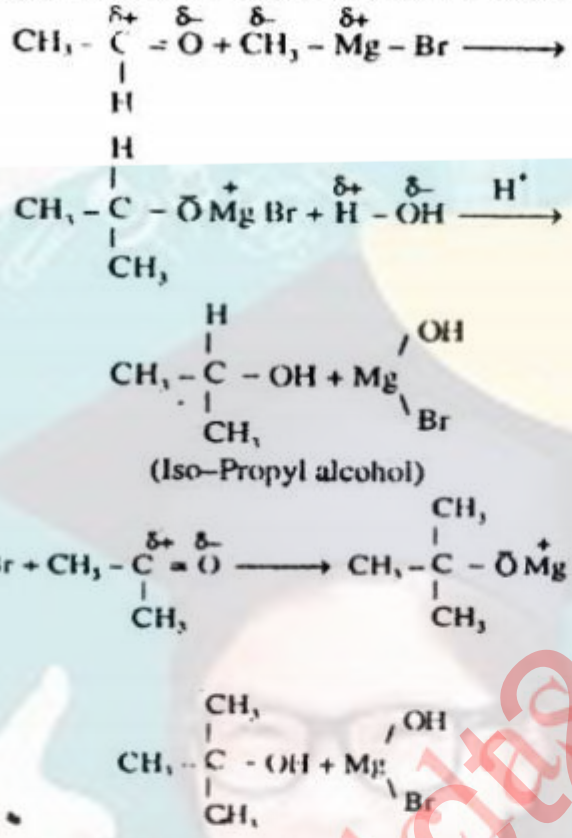
Primary, secondary and tertiary alcohols can be prepared by the use of Grignard's reagent. The Grignard reagent adds to a carbonyl molecule and the resulting compounds forms alcohol on hydrolysis.

a) Primary alcohol: Form aldehyde gives primary alcohol with Grignard's reagent:

b) Secondary Alcohols: All other aldehydes give secondary alcohols, e.g.,

c) Tertiary Alcohols: Ketones form tertiary alcohols with Grignard's reagent under similar conditions, e.g.



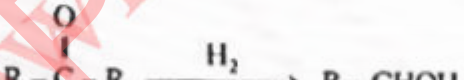


(Iso–Propyl alcohol)

4) Reduction of Aldehydes and Ketones

Reduction of aldehydes, ketones and carboxylic acid (esters in the presence of Ni, Pd or Pt) gives alcohols, e.g.,

(Aldehyde) (1°–alcohol)



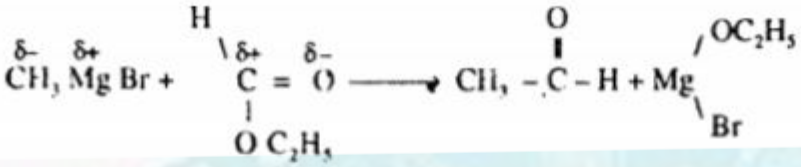
Ketone

$LiAlH_4$ besides reducing aldehydes, ketones and ester, also reduces carboxylic acids, e.g.,

$$RCOOH + LiAlH_4 \rightarrow RCH_2OH$$

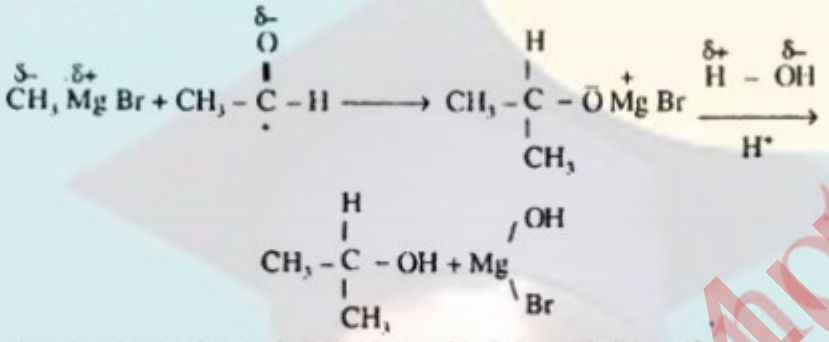
5) Reaction of RLi or RMgX with Esters

Esters react with Grignard reagents to form alcohols,

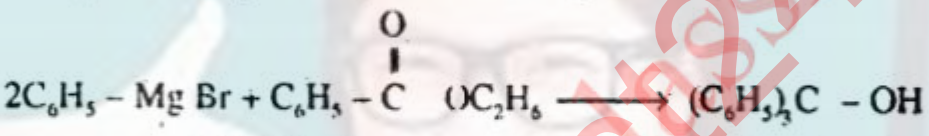


Ethyl formate

The aldehyde so formed reacts with another molecule of Grignard's reagent to give alcohol.

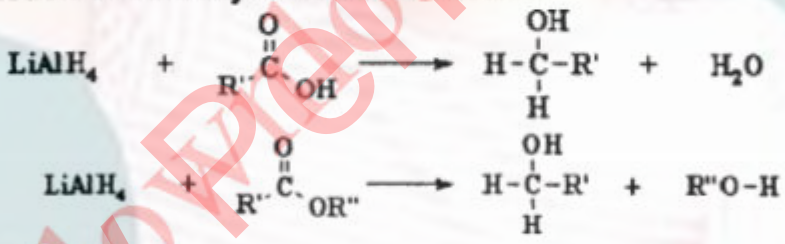


Similarly other esters give tertiary alcohols with Grignard's Reagents.



(Ethyl benzoate) Triphenyl methyl alcohol

6) Reduction of Carboxylic Acids and Esters



Elaboration

- Carboxylic acids and esters are less reactive to **Nu** than aldehydes or ketones
- As a result they can only be reduced by $LiAlH_4$ and **NOT** by the less reactive $NaBH_4$
- Each reaction requires that 2 hydrides be added to the carbonyl of acids or esters

Reactions of Alcohols

Reaction with HX to give Alkyl Halides

Due to the presence of unshared electron pairs on the oxygen atom of alcohols, they act as bases and react with halogen acids to form their respective alkyl halides.

$$R-O-H + H-Br \longrightarrow R-Br + H_2O$$

The C-O bond in an alcohol is very slightly polarized. Therefore the following reaction mechanism is not possible.

$$R\overset{+\delta}{-}OH + H\overset{-\delta}{-}Br \xrightarrow{\times} R-Br + H_2O$$

In fact, the alcohol acting as a base first forms an alkyl oxonium ion. Now the C-O bond becomes highly polarized. This electrophile carbon is easily attached by a nucleophile.

$$R-\ddot{O}-H + H\overset{-\delta}{-}Br \longrightarrow R-\overset{+}{O}(H)-H + Br^-$$

alkyloxonium ion

$$R-\overset{+}{O}(H)-H + Br^- \longrightarrow R-Br + H_2O$$

The orders of reactivity of halogen acids and alcohols are HI > HBr > HCl and ter-alcohol>sec-alcohol>prim-alcohol. HCl and prim-alcohol are the least reactive amongst halogen acids and alcohols respectively. Therefore they react only in the presence of a catalyst. A solution of $ZnCl_2$ in concentrated HCl is used as a catalyst.

$$CH_3OH + HCl \xrightarrow{ZnCl_2/HCl} CH_3Cl + H_2O$$

The reaction mechanism is :

$$R-\ddot{O}-H + ZnCl_2 \xrightarrow{HCl} R-\overset{+}{O}(H)-\bar{Z}nCl_2$$

oxonium ion

$$R-\overset{+}{O}(H)-\bar{Z}nCl_2 \longrightarrow R^+ + H\bar{O}-ZnCl_2$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$R^+ + Cl^- \longrightarrow RCl$$

$$H\ddot{O}ZnCl_2 + H^+ \longrightarrow H_2O + ZnCl_2$$

Q6. Give lucas test to distinguish prim sec. And ter. Alcohols.

Answer

The difference of chemical reactivity of alcohols with halogen acids is sued of their identification. For this purpose alcohol is treated with a solution of ZnCl2 in concentrated HCl.

i) Tertiary alcohol immediately forms an insoluble layer of a ter-alkyl chloride.

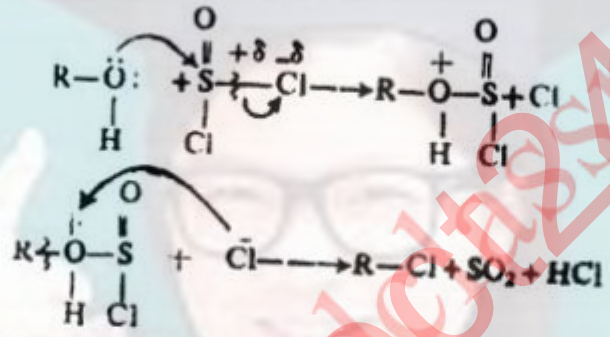
ii) Secondary alcohol forms an insoluble sec-alkyl chloride in 5-10 minutes.

iii) Primary alcohol forms an insoluble prim-alkyl chloride on heating.

Q7. Give reaction of alcohol with $SOCl_2$, PX_3 to give Alkyl Halides.

Answer

i) Thionylchloride ($SOCl_2$)
Alcohols react with thionylchloride to give alkyl chlorides.



ii) Phosphorus Tribromide and Triiodide (PBr_3 and PI_3)
Alkyl bromides and iodides are best prepared by treating alcohols with PBr_3 and PI_3.

$$3ROH + PBr_3 \longrightarrow 3RBr + H_3PO_3$$

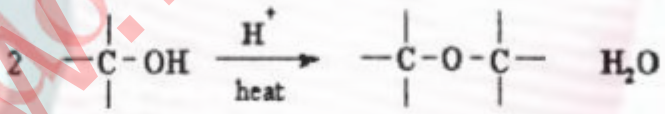
Similarly,

$$3ROH + PI_3 \longrightarrow 3RI + H_3PO_3$$

Q7.Give acid catalyzed dehydration of alcohols, to prep ethers.

Answer

Synthesis of Ethers via Acid-catalyzed Condensation of Alcohols



Elaboration

- Reagents typically H_2SO_4 and heat.
- In general, typically limited to **symmetrical** ethers of **primary** alcohols.
- The method is not suitable for unsymmetrical ethers.
- The substitution involves the O nucleophile of one alcohol attacking the electrophilic C

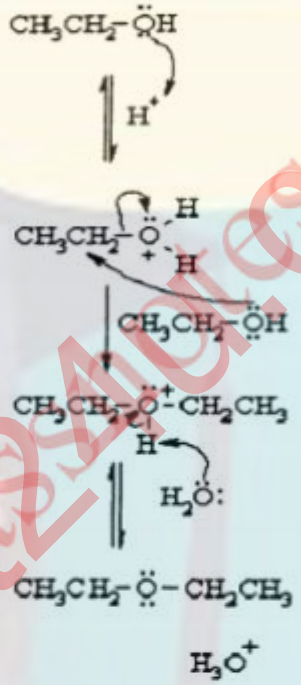
in the other displacing a water molecule.

MECHANISM FOR ALCOHOL CONDENSATION TO GIVE AN ETHER

Step 1:
An acid/base reaction. Protonation of the alcoholic oxygen to make a better leaving group. This step is very fast and reversible. The lone pairs on the oxygen make it a Lewis base.

Step 2:
The O of the second alcohol molecule functions as the nucleophile and attacks to displace the good *leaving group*, a neutral water molecule, by cleaving the C-O bond. This creates an oxonium ion intermediate.

Step 3:
Another acid / base reaction. The proton is removed by a suitable base (here a water molecule, ROH is another alternative) to give the ether product.



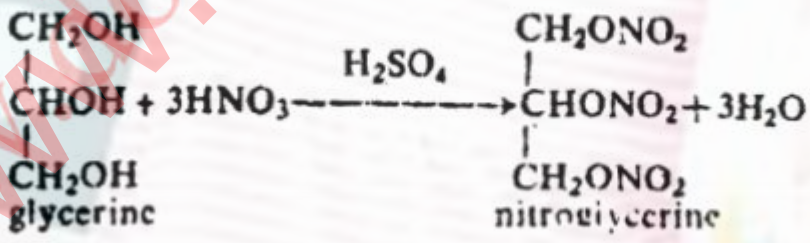
Q8. Give preparation of esters alongwith mechanism.

Answer

Alcohols react with organic as well as inorganic acid to form their respective esters. Thus alkyl halides are also esters of halogen acids.

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

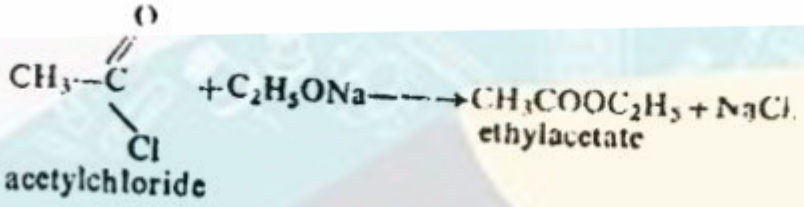
Glycerine reacts with a mixture of concentrated HNO_3 and H_2SO_4 to give an ester called Nitroglecerine or Glyceryltrinitrate.



Nitroglycerine is highly explosive liquid. It is mixed with fine sand and moulded into

sticks called Dynamite.

Esters are also formed by treating acid chlorides with sodium alkoxides.



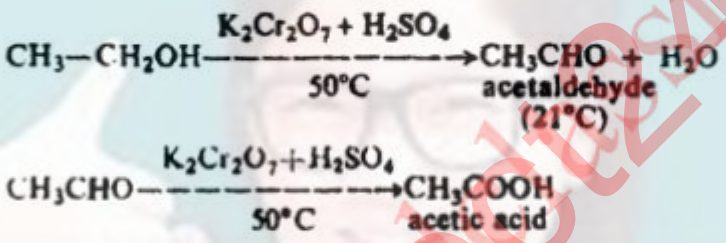
Q9. Give oxidation of prim, sec. and tert alcohols.

Answer

Alcohols are easily oxidized by alkaline $KMnO_4$ or $K_2Cr_2O_7 + H_2SO_4$ solutions to give different products.

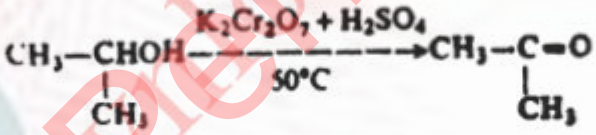
I) Primary Alcohol:

A primary alcohol is first oxidized to an aldehyde, which is further oxidized to a carboxylic acid.



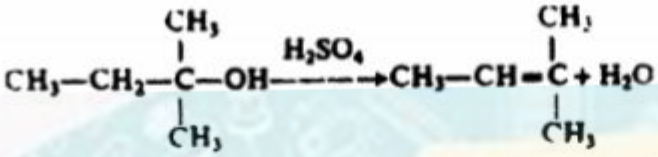
ii) Secondary Alcohol:

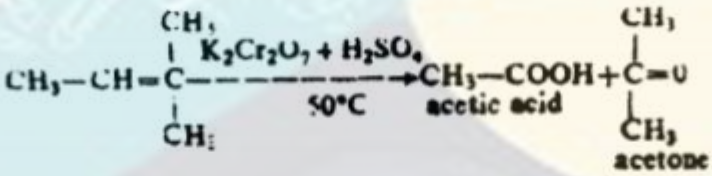
A secondary alcohol is oxidized under similar condition to give a ketone which is not further oxidized.



iii) Tertiary Alcohol:

A tertiary alcohol is not oxidized by alkaline $KMnO_4$. When heated with a mixture of $K_2Cr_2O_7$ and H_2SO_4, it is first dehydrated to an alkene in the presence of acid. Then alkene is oxidized to a ketone and a carboxylic acid by $K_2Cr_2O_7$ and H_2SO_4.



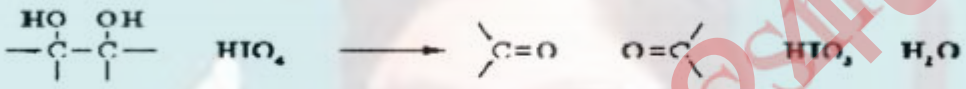


Each of the products contains lesser number of carbon atoms than the parent alcohol molecule.

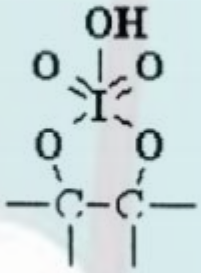
Q10. Give cleavage of 1,2-Diols.

Answer

Oxidative Cleavage of Diols



1) 1,2- or vicinal diols are cleaved by periodic acid, HIO_4, into two carbonyl compounds.
2) The reaction is selective for 1,2-diols.
3) The reaction occurs via the formation of a cyclic periodate ester (see right).
4) This can be used as a functional group test for 1,2-diols.
5) The products are determined by the substituents on the diol.



Q11. What are Thiols or Thio alcohols?

Answer

Thiols are sulphur analogues of alcohols.

Nomenclature of Thiols

Thiols are the sulfur analogues of alcohols. These are names by adding the suffix – Thiol to the name of corresponding alkanes. e.g.

Physical Properties of Thiols

- Hydrogen bonding is *much* weaker than that in alcohols.
- Lower boiling points than similar alcohols.

Structure of Thiols

- Generally similar to alcohols, but bonds to S are longer and weaker than those to O.
- The thiol functional group consists of an S atom bonded to a C atom and a H atom via σ bonds.
- The S-H bonds is *less* polar than that in alcohols since S is less electronegative than O.

Reactivity of Thiols

- Thiols are much more acidic than similar alcohols, *e.g.* RSH (pKa = 10) versus ROH (pKa = 16 to 19)
- Thiols are also much more nucleophilic than similar alcohols, in fact RSH is about as nucleophilic as RO^-
- Thiols are readily oxidized but to **S-O** systems rather than **C=S** systems.

  Thiols are commonly oxidized to disulfides, **R-S-S-R**, a biologically important reaction.

Q12. What are Phenols? Give them nomenclature structure of properties.

Answer

Introduction

First prepared by	Runge
Melting pint of phenol	41°C
Boiling point of phenol	182°C
Simplest example phenol	Carbolic acid (C_6H_5OH)

"Aromatic compounds containing one or more OH groups, directly attached with carbon of benzene ring, are called phenols". The simplest example phenol is alos known as carbolic acid, i.e., C_6H_5OH. It was first obtained form coalter by Runge in 1834.

Phenol is derived from the old name for benzene (phene), to include the suffix that indicates it possesses a hydroxyl group (ol).

Caution: The word phenol (C6H5-OH) is often confused with phenyl (C6H5-). Phenols can be obtained via **substitution** reactions, with the hydrolysis of diazonium salts being the most important laboratory method. Phenols are acidic and are important intermediates in the preparation of aryl ethers, **C_6H_5-OR**

Nomenclature

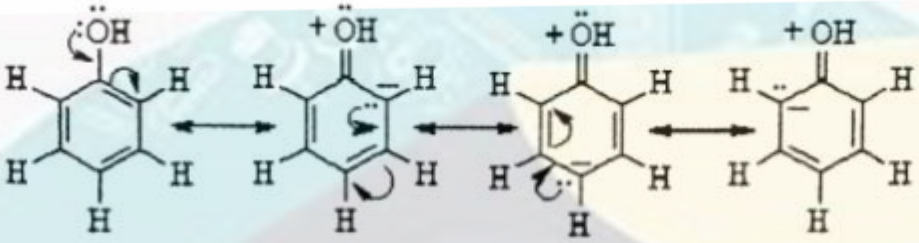
In common system alcohols are named by adding the word 'alcohol' after the name of the alkyl group to which the –OH group is attached, e.g.,

CH_3OH	$C_6H_5CH_2OH$
Methyl Alcohol	Benzyl Alcohol

Structure

1) The alcohol functional group consists of an O atom bonded to an sp^2-hybridized aromatic C atom and a H atom via σ bonds.
2) Both the C-O and the O-H bonds are polar due to the high electronegativity of the O atom.
3) Conjugation exists between an unshared electron pair on the oxygen and the aromatic ring.
4) This results is, compared to simple alcohols:

- a shorter carbon-oxygen bond distance
- a more basic hydroxyl oxygen
- a more acidic hydroxyl proton (-OH)



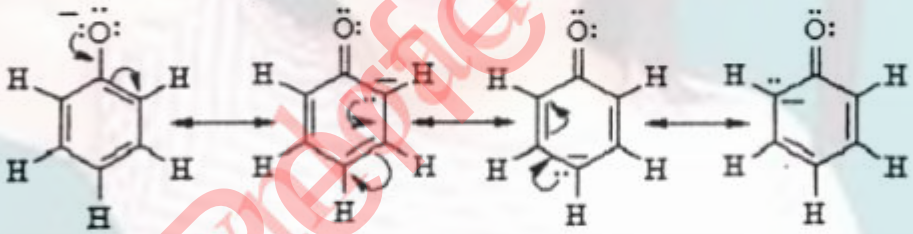
Physical Properties of Phenol

1) Phenol is a colorless, crystalline, poisonous solid with characteristic phenolic odor having melting paint 41°C and boiling point 182°C.
2) It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C.
3) It is poisonous and causes blisters on the skin.

Q13. Why Rhenol is acidic in water?

Answer

1) Phenols are more acidic (pK_a»10) than alcohols (pK_a»16 - 20), but less acidic than carboxylic acids (pK_a»5)
2) The negative charge of the phenolate ion is stabilized by resonance due to electron delocalization onto the ring as shown below:



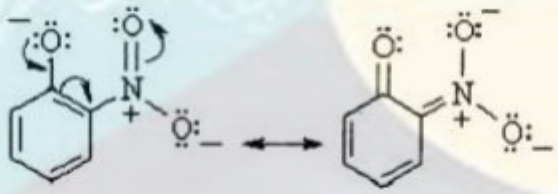
3) The acidity difference means that it is possible to separate phenols from alcohols and/or carboxylic acids.
   - Mixing an ether solution, of either phenol and alcohol or phenol and carboxylic acid, with dilute base (sodium hydroxide and sodium bicarbonate, respectively), results in the stronger acid being converted to its alkali salt, which is then extracted to the aqueous phase and can be separated from the organic phase.
4) Nucleophilic substitution reactions of phenols are generally carried out under basic conditions as the **phenolate ion** is a better nucleophile.

Q14. What is substituent effects on acidity of phenols?

Answer

Substituents, particularly those located *ortho* or *para* to the -OH group, can

dramatically influence the acidity of the phenol due to resonance and / or inductive effects. Electron withdrawing groups enhance the acidity; electron donating substituents decrease the acidity. The resonance stabilization of *o*-nitrophenol is shown below:

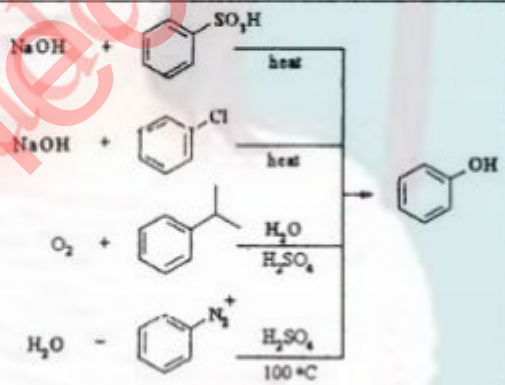


Compound	pKa	Compound	pKa
Phenol	10.0		
o-Methoxyphenol	10.0	p-Methoxyphenol	10.2
o-Methylphenol	10.3	p-Methylphenol	10.3
o-Chlorophenol	8.6	p-Chlorophenol	9.4

Q15. Give different methods of preparations of Phenols.

Answer

- Reaction of benzene sulfonic acid with base
- Reaction of chlorobenzene with base
- Acidic oxidation of cumene
- Hydrolysis of diazonium salts



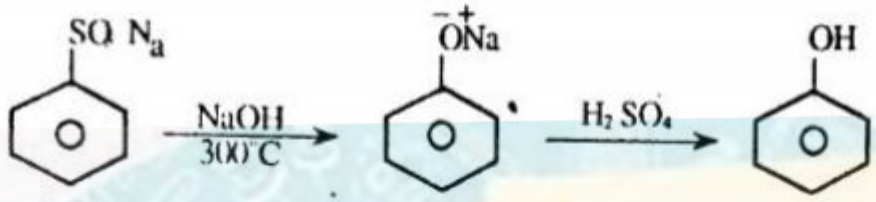
Note: The first three methods are primarily industrial methods while the hydrolysis of diazonium salts is the most important laboratory method.

Give reaction of benzene sulfonic acid with hydroxide of phenol.

Answer

1) Reaction of Benzene Sulfonic Acid with Hydroxide of phenol

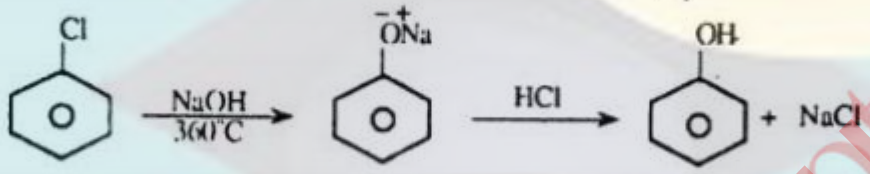
Sodium benzene sulphonate on fusion with strong alkali like NaOH or KOH, yield phenol.



At such a high temperature, side reactions also occur.

2) Base Hydrolysis of Chlorobenzene

Chlorobenzene is hydrolyzed by heating wit NaOH at 360°C and under high pressure.



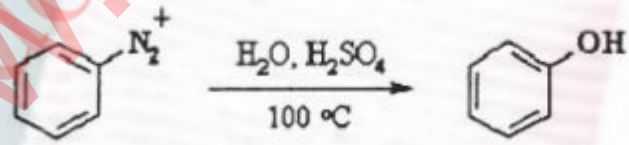
3) Acidic Oxidation of Cumene

It is recently developed commercial method for the preparation of phenol. Cumene is oxidized by atmospheric oxygen in presence of metal catalyst, into cumene hydroperoxide.

The hydroperoxide is converted into phenol through an acid catalyzed rearrangement.

Isopropyl Hydroperoxide (Phenol) Acetone

4) Preparation of Phenols from Aryl Diazonium Salts



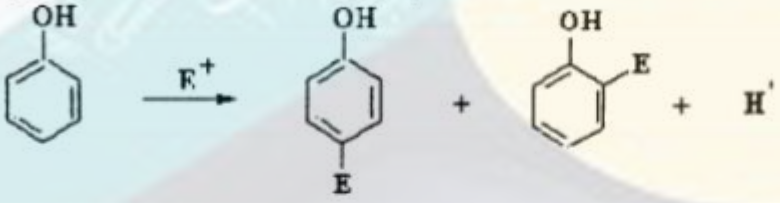
Elaboration

- Aryl diazonium salts can be converted into phenols using H_2O / H_2SO_4 / heat
- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid, HNO_2

Reactions of Phenols

Phenols are very reactive towards electrophilic aromatic substitution. This is because the hydroxy group, **-OH**, is a strongly activating, *ortho-* / *para-* directing substituent.

Electrophilic Aromatic Substitution of phenol



Reaction type: Electrophilic Aromatic Substitution

Elaboration

- *Phenols* are potentially very reactive towards electrophilic aromatic substitution.
- This is because the hydroxy group, **-OH**, is a strongly activating, *ortho-* / *para-* directing substituent
- Substitution typically occurs *para* to the hydroxyl group unless the *para* position is blocked, then *ortho* substitution occurs.
- The strong activation often means that milder reaction conditions than those used for benzene itself can be used (see table below for a comparison)
- Phenols are so activated that polysubstitution can be a problem

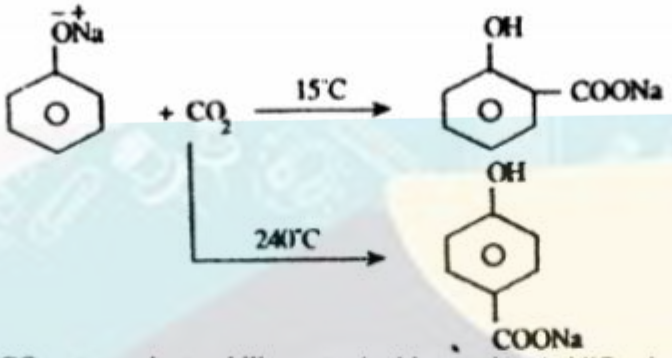
Reaction	Phenol	Benzene
Nitration	dil. HNO_3 in H_2O or CH_3CO_2H	HNO_3 / H_2SO_4
Sulfonation	conc. H_2SO_4	H_2SO_4 or SO_3 / H_2SO_4
Halogenation	X_2	X_2 / Fe or FeX_3
Alkylation	ROH / H^+ or RCl / $AlCl_3$	RCl / $AlCl_3$
Acylation	RCOCl / $AlCl_3$	RCOCl / $AlCl_3$
Nitrosation	aq. $NaNO_2$ / H^+	

Different Reactions of Phenols

1) **Reaction with Sodium Metal**

Carboxylation of Phenols (Kolbe-Schmitt reaction)

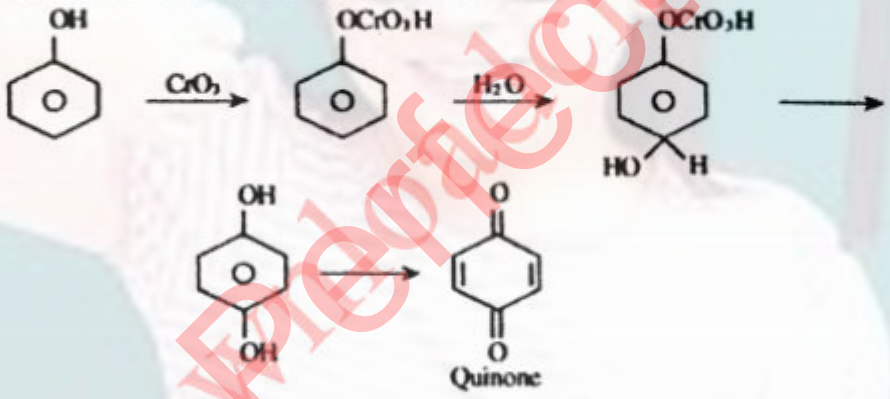
"The reaction of sodium salt of phenol with CO_2 is called Kolbe reaction. It is carbonation of phenol. At low temperature sodium salicylate (sodium-o-hydroxy benzoate), whereas at higher temperature o-product isomerizes to p-isomer,



Carbon of CO_2 acts as electrophilic centre in this reaction Acidification of the slat gives corresponding hydroxyl acid.

2) Oxidation of Phenols

Phenols are very reactive towards oxidizing agents. The oxidation takes place through several steps eventually destroying the ring.



Q16. What are difference between Alcohols and Phenol?

Answer

The main difference between alcohols and phenols are as follow;

Alcohol

1) The compounds in which hydroxyl group is attached to an alkyl group.
2) Alcohols are hydroxyl derivatives of alkanes.
3) The compounds in which one hydrogen of water is replaced by an alkyl group.
4) The general formula of alcohol is R-OH.

5) Alcohols may be monohydric and polyhydric depending on the number -OH groups attached.
6) Lower alcohols are generally colorless liquids.
7) Alcohols have a characteristic sweet smell and bumming taste.
8) They are readily soluble in water but solubility decreases in higher alcohols.
9) Alcohol reacts with other reagents in two ways, either in which C-O bond breaks or in which O-H bond breaks.

Phenol

1) The compounds in which hydroxyl group is attached to an aryl group.
2) Phenols are derivatives of benzene.
3) The compounds in which one hydrogen of water is replaced by an aryl group.
4) The general formula of phenol is  . It is also known as carbolic acid.
5) Phenols are not monohydric or polyhydric.
6) They are colorless, crystalline, deliquescent solids.
7) They have characteristic phenolic odor.
8) Its melting point is 41 ^{0}C.
9) Phenols are more acidic (pK_a»10) than alcohols (pK_a»16 - 20).
10) It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5 ^{0}C.
11) Phenolate ions have resonance structures but alcohols don not have such type structures.

ETHERS

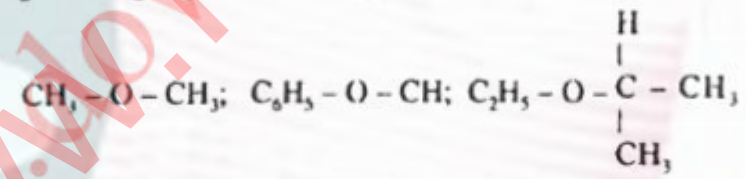
Q17. Give nomenclature of ethers.

Answer

1) Common Names

i) Common System of Naming

In common system of naming simple and mixed (or unsymmetrical) ethers are names by naming the two groups bonded to oxygen followed by the word ether, e.g.,



(Dimethyl ether) (Anisole) Iso propyl ethyl ether

ii) IUPAC System

In IUPAC system of naming simple ethers are named by naming the two groups linked to oxygen atom followed by the word ether, e.g.

CH_3-O-CH_3	C_2H_5-O-C_2H_5
Dimethyl ether	Diethyl ether

Mixed ether are named as alkyl derivatives of hydrocarbons, e.g.

Methoxy ethane

Methoxy butane

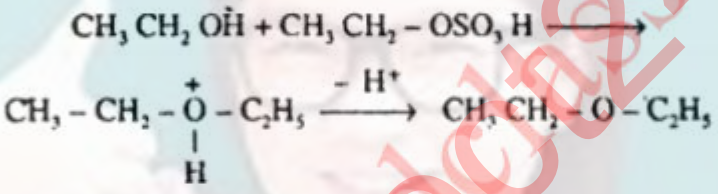
Q18. Give preparation of ethers.

Answer

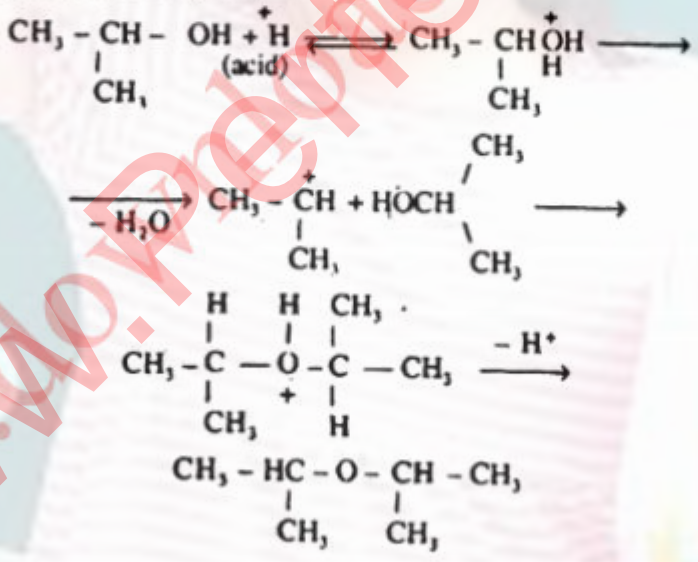
By heating excess of alcohol with concentrated H_2SO_4 at 140°C, dehydration to ethers occurs,

$$2CH_3CH_2OH \xrightarrow[H_2SO_4]{140^\circ C} CH_3-CH_2-O-C_2H_5 + 2H_2O$$

Primary alcohols react through SN_2-mehcanism



Secondary alcohols react by SN_1-mechanism



Di–isopropyl ether

Two different primary alcohols give three ethers when treated with H_2SO_4.

$$CH_3CH_2OH + CH_3OH \rightarrow CH_3O\text{-}CH_3 + C_2H_5\text{-}O\text{-}C_2H_5 + CH_3\text{-}O\text{-}OC_2H_5$$

Ter-butyl and ethyl alcohol give one ether.

Q19. Give physical properties of ethers.

Answer

1) Ethers are colorless, low boiling, highly inflammable compounds.
2) Their chemical inactivity and their ability to dissolve fats, oil, gum and many other organic compound make them very good solvent.
3) Ethers are soluble in concentrated sulphuric acid, a characteristic of oxygen containing compounds. This property is used as a test to distinguish between ethers and saturate hydrocarbons.

Q20. Give chemical reactivity of ethers.

Answer

The image shows the electrostatic potential for dimethyl ether. The more **(red)** an area is, the higher the electron density and the more blue an area is, the lower the electron density.

- The ethereal O atom is a region of high electron density **(red)** due to the lone pairs.
- Ether oxygen atoms are Lewis bases.
- Like an alcohol -OH group, the -OR group is a poor leaving group and needs to be converted to a better leaving group before substitution can occur.

The most important reaction of ethers is their cleavage by strong acids such as HI or HBr.

Q21. How ethers show resistance to oxidation?

Answer

Resistance to Oxidation

Ethers are resistant to attack by the usual chemical oxidizing agents. Moreover, reagent like NH_3, Na, alkali and acids have no action on ethers.

Q22. How ethers react with H-Br?

Answer

Reaction with H-Br

The oxygen atom of an ether molecule possesses unshared electron pair, which, accepts a portion of H-Br to form oxonium ion.

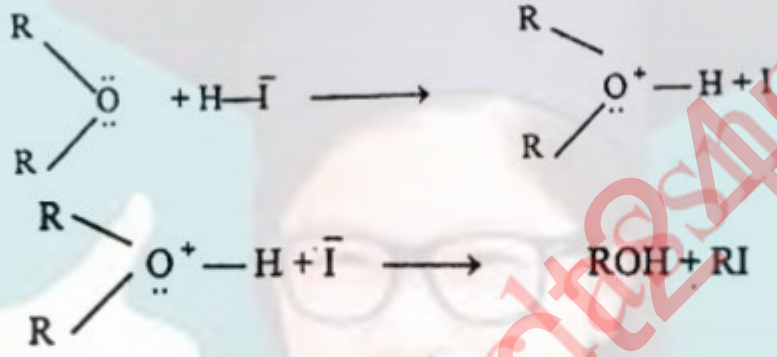
No further reaction takes place.

Q23. How ethers react with H-I?

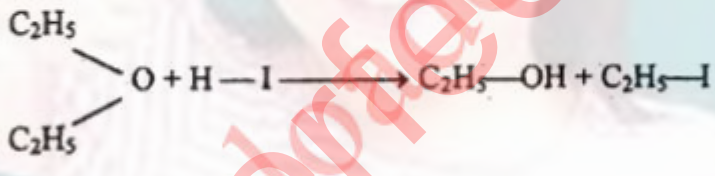
Answer

Reaction with H-I:

The oxygen atom of an ether molecule possesses unshared electron piar, which accepts a proton of H-I to form oxonium in, which reacts with I to form R-OH and RI.



Diethyl ether reacts with HI to form C_2H_5-OH and C_2H_5I.



Q24. What are antiseptics and disinfectants?

Answer

1) Antiseptics and Disinfectants

Antiseptics and disinfectants are an essential part of infection control practices and aid in the prevention of nosocomial infections. They are extensively used in hospitals and other health care settings for a variety of topical and hard surface application. A wide variety of active chemical agents or biocides are found in these products many of which have been used for hundred of years for antisepsis, disinfection and preservation. In general, biocides have a broader spectrum of activity than antibiotics. The widespread use of antiseptic and disinfectant products has promoted some speculation on the development of microbial resistance, in particular cross-resistance to antibiotics. Anti microbial activity of antiseptics and disinfectants can be influenced by many factors e.g. formulation effects, presence of an organic load, temperature, dilution etc.

Antiseptics

An antiseptic is a substance which inhibits the growth and development of micro organisms. For practical purposes, antiseptics are thought of as topical agents for application to skin, mucous membrane and inanimate objects. They can be either bactericidal or bacteriostatic. Their uses include cleansing of skin and wound, surfaces after injury preparation of skin surface prior to injection or surgical procedure and routine disinfection or surgical procedure and routine disinfection of oral cavity as par of oral hygiene.

Disinfectants

Disinfectants were introduced by Listen who introduced carbolic acid (phenol) as the first disinfectant. Today disinfectants are widely used in the health care, food and pharmaceutical sectors to prevent unwanted micro-organisms from cuisine disease. Disinfectants chemicals disrupt significant cellular structures or processes in order to kill or eliminate micro-organism.

2. Ether – An effective Anaesthetic

Before the advent of anaesthetics, surgery was a savage and primitive affair. It was agony for the patient, and surgeons were therefore only prepared to operate if it was absolutely essential, for example the amputation of a damaged limb that would otherwise become gangrenous. Anaesthetics enable surgery to develop from crude carpentry to it present sophisticated forms.

Three of the most important early anaesthetics were nitrous oxide) dinitrogen oxide, N_2O), ether (ethoxyethane, $CH_3CH_2OCH_2CH_3$) and chloroform (trichloromethane, CHCl3). Nitrous oxide is non-toxic and non-flammable, but it only produces light anaesthesia. Chloroform produces deep anaesthesia and is non-flammable, but it is toxic and carries the risk of liver damage.

EXERCISE

Q1: Select the right answer from the choices given with each question.

1) **Which compound shows hydrogen bonding?**
   a) C_2H_6 b) C_2H_5Cl
   c) $CH_3 - O - CH_3$ d) C_2H_5OH

2) **Which compound is called a universal solvent?**
   a) H_2O b) CH_3OH
   c) C_2H_5OH d) $CH_3 - O - CH_3$

3) **According to Levis concept ethers behave as:**
   a) Acid b) Base
   c) Acid as well as base d) None of them

4) **Ethanol can be converted into ethanoic acid by:**
   a) Hydrogenation b) Hydration
   c). Oxidation d) Fermentation

EXERCISE

Q1: Select the right answer from the choices given with each question.

1) **In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms:**
   a) Two
   b) Three
   c) One
   d) Four

2) **SN2 reactions can be best carried out with:**
   a) Primary alkyl halides
   b) Secondary alkyl halides
   c) Tertiary alkyl halides
   d) All the three

3) **For which mechanisms, the first step invalued is the same;**
   a) E_1 and E_2
   b) E_2 and S_N2
   c) E_1 and S_N2
   d) E_1 and S_N1

4) **The rate of E_1 reaction depends upon:**
   a) the concentration of substrate
   b) the concentration of nucleophile
   c) the concentration of substrate as well as nucleophile
   d) none of the above

5) **Alkyl halides are considered to be very reactive compounds towards nucleophile because:**
   a) they have an electrophilic carbon.
   b) they have an electrophilic carbon and a good leaving group.
   c) they have an electrophilic carbon and a bad leaving group.
   d) they have a nucleophile carbon and a good leaving group.

6) Which one of the following is not a nucleophile:
   a) H_2O b) H_2S
   c) BF_3 d) NH_3

7) Double bond is formed as a result of:
   a) Substitution reactions b) Elimination reactions
   c) Addition reactions d) Rearrangement reactions

8) Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen:
   a) R – Br b) R – Cl
   c) R – F d) R – I

9) CH_3CH_2Br on treatment with alc.KOH gives
   a) Propanal b) Propene
   c) Propane d) None

10) Grignord's reagent gives alkane with:
   a) water b) Ethylamine
   c) Ethanol d) All of these

11) Action of alkyl halides with Na metal yield;
   a) Alkones b) Alcohols
   c) Alkenes d) Phenols

12) Alkyl halides react with excess of ammonia to give;
   a) 1° – amine b) 2° – amine
   c) 3° – amine d) all

13) Among the alkyl halides the primary alkyl halides always follow the mechanism.
   a) SN1 b) SN2
   c) SN3 d) SN4

14) Grignord's reagent on treatment with chloramines gives;
   a) Acetamide b) Primary amine
   c) Secondary amine d) Urea

15) Nucleophilic addition of a primary amine gives;
   a) Imine b) Urea
   c) Ammonia d) Nitrobenzene

Answers

1)	c)	2)	c)	3)	d)	4)	a)	5)	b)
6)	c)	7)	b)	8)	d)	9)	b)	10)	d)
11)	a)	12)	c)	13)	b)	14)	b)	15)	a)

Q2. Give short answers of the following questions.

Q1. What are primary, secondary and tertiary alkyl halides?

Answer

Please see Answer of Q no 18 of chapter notes.

Q2. Why alkyl iodides cannot be prepared by directly heating iodine with alkene?

Answer

(i) Iodine on reaction with alkenes produced iodoalkanes which are unstable and decompose again to give I2.

(ii) The second factors is strong wanderwal's among I2 molecules due to strong wanderwal's forces among I2 molecules the reactivity of I2 in alkanes decreases.

(iii) Also the addition of I2 to an alkene produces dihalides and not alkyl halides.

Q3. What are Nucleophilic substitution reactions or SN reactions?

Answer

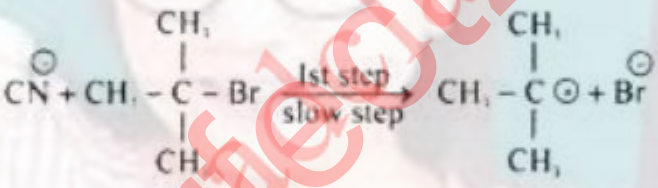
Please see answer of Q6 of chapter notes.

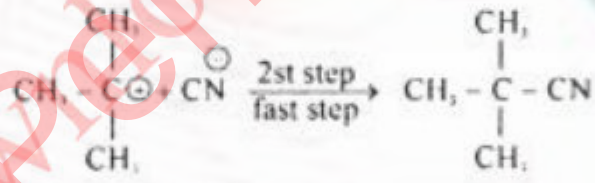
Q4. Tertiary alkyl halides shoe SN1 reactions mostly, why?

Answer

Tertiary alkyl halides on reaction with nucleophile are converted into the product. It means in one step there accurs one change so that is why it is called SN1 reaction.

For example





Q5. What are elimination reactions?

Answer

Please see answer of Q13 of chapter notes.

Q6. Which factor decides the reactivity of alkyl halides?

Answer

Please see answer of Q2 of chapter notes.

Q7. What are the diazonium salt?

Answer

Please see answer of Q47 of chapter notes.

Q8. How can nucleophilic addition of a primary amine giving an immine?

Answer

Primary amines on reaction with aldehydes and Ketones on condensation give an imine which is called Schiff base

$$C_2H_5NH_2 + CH_3CHO \xrightarrow{H^+} C_2H_5N = CH - CH_3$$

$$C_6H_5NH_2 + CH_3CHO \xrightarrow{H^+} C_6H_5N = CH - CH_3$$

Q9. Amines are more basic than analogous alcohols, why?

Answer

Please see answer of Q39 of chapter notes.

Q10. How tertiary alcohols are obtained from R–Mg–X?

Answer

Please see answer of Q30 of chapter notes.

Q3. Give detailed answers for the following questions.

Q1. Discuss the reactivity of alkyl halides.

Answer

Please see answer of Q2 of Chapter notes.

Q2. Give three methods for the preparation of alkyl halides?

Answer

Please see answer of Q1 of Chapter notes.

Q3. Explain in detail SN1 and SN2 reactions with mechanism.

Answer

For SN1 reaction Please see answer of Q10 of chapter notes for SN2 reaction please see answer of Q10 of chapter notes.

Q4. What are β– elimination reactions? Explain them with detail.

Answer

Please see answer of Q13 of Chapter notes.

Q5. How will you convert ethyl chloride to the

i) Ethyl cyanide
ii) Ethanol
iii) Propane
iv) N-butane
v) Tetraethyl lead

Answer

(I) Ethyl chloride into Ethyl cyanide:

$$CH_3 - CH_2 - Cl + Nach \longrightarrow CH_3 - CH_2 - CH + Nacl$$

(II) Ethyl chloride into Ethanol:

$$CH_3 - CH_2 - Cl + Koh_{(aq)} \longrightarrow CH_3 - CH_2 - OH + Kcl$$

(III) Ethyl chloride into Propane:

$$CH_3 - CH_2 - \boxed{Cl + 2Na + Cl} - CH_3 \longrightarrow CH_3 - CH_2 - CH_2 + 2NaCl$$

(iv) Ethyl chloride into N-butane

$$CH_3 - CH_2 - Cl + 2Na + Cl - CH_2 - CH_3 \longrightarrow CH_3 - CH_2 - CH_2 - CH_3 + 2NaCl$$

(v) Ethyl chorlde into tetraethyl lead:

$$Na_4 / Pb + 4C_2H_5 - Cl \longrightarrow (C_2H_5)\,Pb + 4NaCl$$

Q6. Discuss the preparation and reactivity of grignard's reagent?

Answer

Please see answer of Q29 of chapter notes.

Q7. What are the amines? Gives its nomenclature.

Answer

Please see answer of Q36 of chapter notes.

Q8. What are the main features which increase the basicity of amine?

Answer

Please see answer of Q44 of chapter notes.

Q9. Amides are reduced by LiAlH4. Give mechanism.

Answer

Please see answer of Q43 of chapter notes.

Q10. What are the diazonium salts? How they can be prepared? Give their reactions.

Answer

Please see answer of Q47 of chapter notes.

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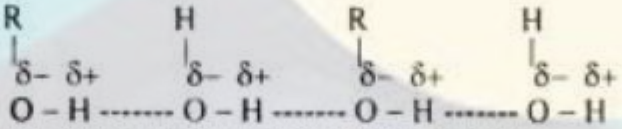
Short Questions and answers.

Q1: Write down the physical properties of alcohol?

Answer

Alcohol upto butanols are generally colourless liquids characteristics sweet smell and burning taste. They are readily soleuses in H_2O. The solubility of alcohol is due to hydrogen bonding which is significant in lower alcohols but discuses in high alcohols.



Bonding which is present in alcohols but absent in alkanes.

Q2: Write down the structure of alcohol?

Answer

The alcohol functional group consist of an O atom bonded to a atom and an H atom via S bonds.

Butt the C-O and O-H bonds are polar due to the high electromegnativity of the O atom.

Q3: Write down the acidity of alcohols?

Answer

Due to the elctromegnativity of the O-atoms alcohols are slightly acidic.

The atom deceived by the deprotonation of an alcohol is the alkonides.

Alkonides are important bases in organic chemistry.

Alcohol react with Na (ork) like H_2O to give the alkonide.

$$2R-O-H+2Na \longrightarrow 2NaOR+H_2$$

$$2H-O-H+2Na \longrightarrow 2NaOH+H_2$$

Q4: Write down the reaction of RLi or RMgx aldehydes and ketones.

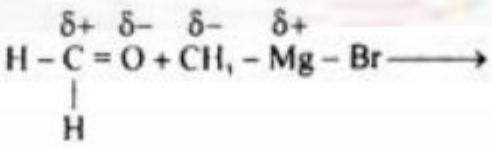
Answer

Primary, secondary and tertiary alcohols can be prepared by the used Grignard reagents. The Grignard reagents acts to a carbonyl molecule and the resulting compound from alcohol on hydrolysis.

a) Primary Alcohol: Form aldehyde gives primary alcohol with Grignard's reagent.

b) Secondary Alcohol: All other aldehyde give secondary alcohols.

c) Tertiary Alcohols: Ketones from tertiary alcohols with Grignard's reagent under similer conditions.



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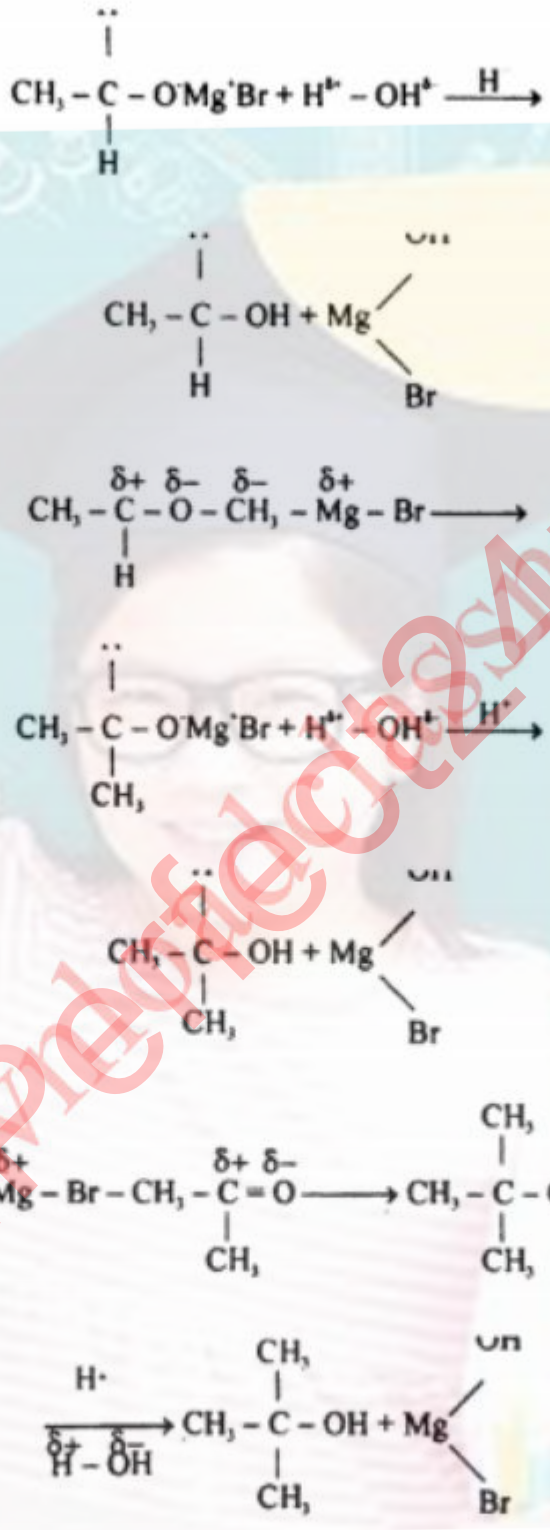
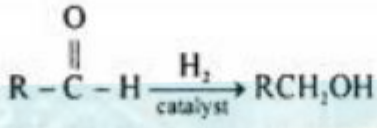


(so prophyl alcohol)

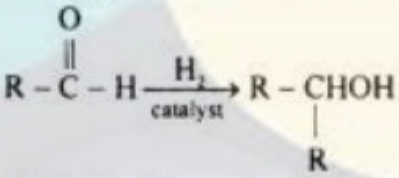
Q5: Write down the reduction of aldehydes and ketones?

Answer

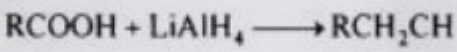
Reduction of aldehydes, ketones and calsonulic acid (estics in the presence of Ni, Pd or Pt) gives alcohol.



(aldehyde) (1-alcohol)



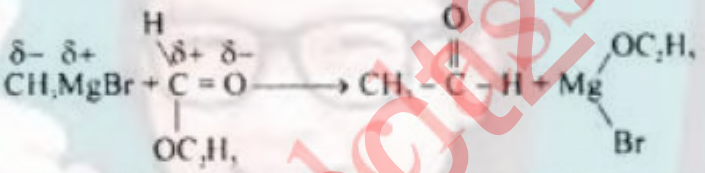
$LiAlH_4$ besides reducing aldehydes, ketones and ester, also reduces calsoxylic acid.



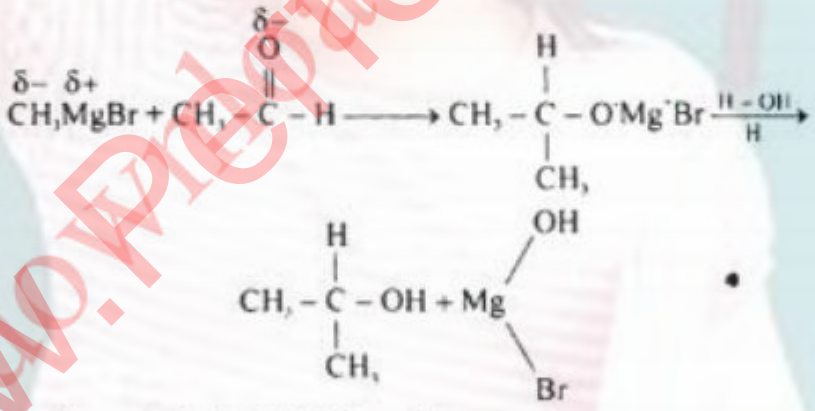
Q6: Write down the reaction of RLi or RMgx with esters?

Ester react with Grignard reagent to form alcohols? Justify it?

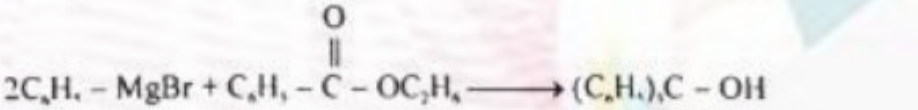
Answer



The aldehyde so formed reacts with another molecule of Grignard's reagent to five alcohol.



Ester give tertiary alcohols with Grignard's reagents.



(Ethyl benzoate) (Triphnyl methyl alcohol)

Q7: Write down the order of reactivity of alcohol with respect to O-H bonds cleavage?

Answer

Alcohol reacts with other reagents due to the breathing of C – O and O – H bonds. Breaking of bonds depends upon the nature of the attaching reagent moleculeophile

attacks the C-O bonds break and if an electrophile attacks the O-H bonds bonds breaks.

$$CH_3 - CH_2OH \xrightarrow{\text{Nucleophile}} CH_3 - CH_2 + OH$$

$$CH_3 - CH_2O - H \xrightarrow{\text{Electrophile}} CH_3CH_2O + H^+$$

The order of reactivity of alcohol with respect to cleavage of C-O bond is

Tertiary alcohol Secondary alcohol primary alcohol

The order of reactivity of alcohol with respect to O-H bonds cleavage.

CH_3OH Tertiary alcohol Secondary alcohol Primary alcohol.

Q8: What is Lucas test?

Answer

The difference of chemical reactivity of alcohol with halogen acid is used for their identification.

For this purpose alcohol is treated with a solution of Znclo is concentrated HCl.

1) Tertiary alcohol immediately forms an insolution layer of a ter-alkyl chloride.

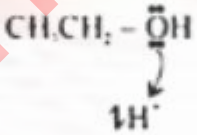
2) Secondary alcohol forms an insolution Sec alkyl chloride in 5-10 minuts.

3) Primary alcohol form an insoluble prim-alkyl chloride on heating.

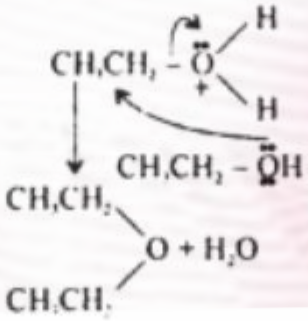
Q9: Write down the mechanisms for alcohol condensation to give an ether?

Answer

Step 1: An acid base reaction protonation of the alcoholic oxygen to make a better leaving group. This step is very fast and recensible. This lone pairs on the oxygen make it a leuis base.



Step 2: The O of the second alcohol molecule functions as the nucleophile and attacks to displace the good leaving group a nutral water molecule by cleaning the C-O bond. This create an oxoniumion intermediate.



Step 3: Another acid/base reaction. The proton is unmount by a situable base to give the ether produced.

Q10: Write down the preparation of eaters?

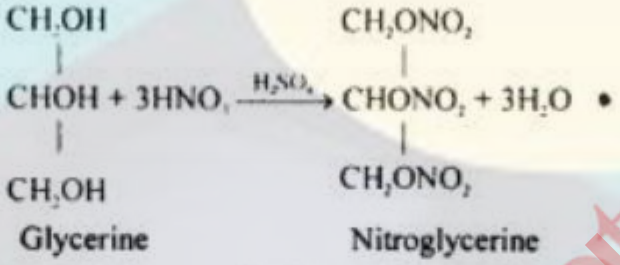
Answer

Alcohol react with organic as well as inorganic acid to form their sespective esters.

This alkyl halides an also esters of halogen acids.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

Glycerine reacts with a mixture on concentrated HNO_3 and H_2SO_4 to give an ester called Nixoglecerine.



Q11: Write the oxidation of primary, alcohols and secondary alcohols?

Answer

Alcohols are easily oxidized by alkaline $KMnO_4$ or $K_2CrO_7 + H_2So_4$ solution to give different products.

i) Primary alcohols:

Primary alcohol is first oxidized to an aldehyde, which is further oxidized to a carboxylic acid.

$$CH_3 - CH_2OH \xrightarrow[50^\circ]{K_2Cr_2O_7 + H_2SO_4} CH_3CHO + H_2O$$

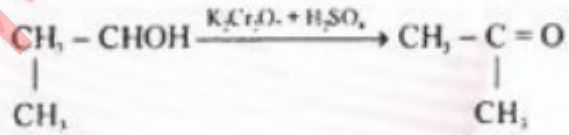
Acctadehyde

$$CH_3CHO \xrightarrow[50^\circ]{K_2Cr_2O_7 + H_2SO_4} CH_3COOH$$

Acetic acid

ii) Secondary alcohol:

A secondary alcohol is oxidized under similar condition to give a atom which is not further oxidized.

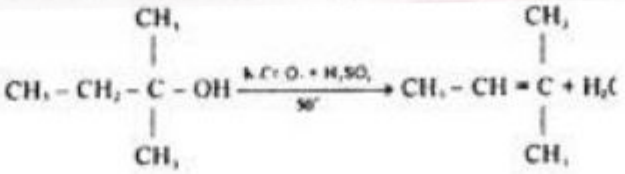


Q12: Write down the oxidation of tertiary alcohol and cleavage of 1, 2 diols?

Answer

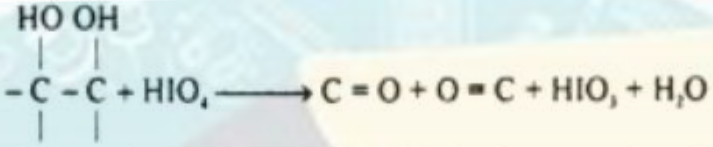
Tertiary alcohol:

Tertiary alcohol is not oxidized by alkaline $KMnO_4$ when heated with a mixture of $K_2Cr_2O_7$ and H_2SO_4. It is first dehydrated to a alkane in the pracence of acid. Then alkane is oxidized to a ketone and a carboxylic acid by $K_2Cr_2O_7$ and H_2SO_4.



Cleavage of 1, 2 Diols.

Oxidation cleavage of Diols.



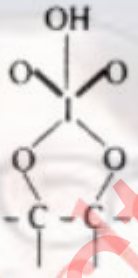
12 or uicinal diols are cleaved by periods and HIO_4 in two carbonyl compounds.

The reaction is selective for 1, 2 diols.

The reaction occurs with the formation of a cyclic periodate ester.

This can be used as a functional group test for 1, 2 diols.

The products are determined by the substituents on the diol.



Q13: Draw and explain the structure of phenols?

Answer

The alcohol functional group consist on an O atom bonded to an sp_2 hybridized aromatic C atom and a H atom via O bonds.

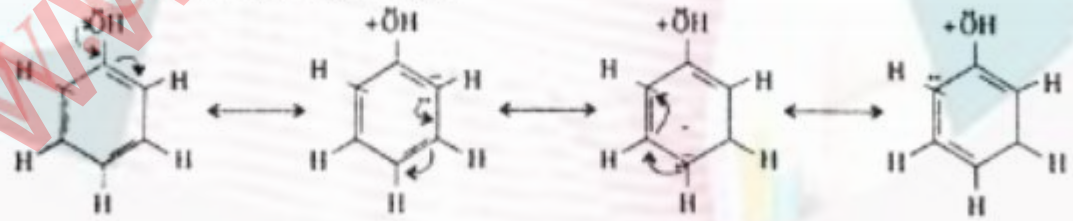
Both the C-O and O-H bonds are polar due to the the high elctronegitivity of the O atom. Conjucation exist between an unshord electron pair on the oxygen and the aromatic ring.

This result is compound to simple alcohol.

→ a shorter carbon oxygen bond distance.

→ a more basic hydroxyl oxygen

→ a more oxidic hydroxyl oxygen.

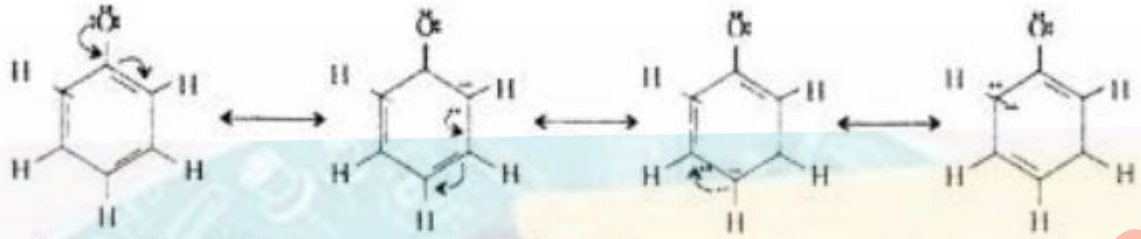


Q14: Write down the acidity of phenols?

Answer

Phenols are more acidic (PKa >>10) than alcohol (PKa>>16-20) but less acidic then carboxylic acids (PKa>>5).

The negative change of the phenolate ion is stabilized by resonance due to electron delocalization onto the ring as shown.



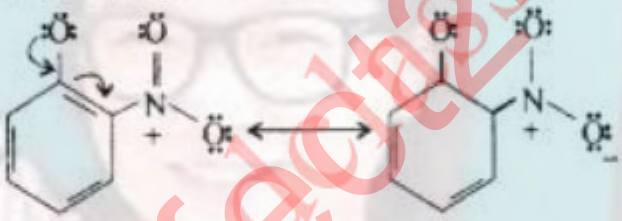
The acidity difference means that it is possible sepacate from alcohols and / or carboxylic acids.

Nucleophilic substitution sections of phenols are generally carried out under basic condition as the phenolate ion is a better nucleophile.

Q15: Substituent effect the acidity of phenols? Justify?

Answer

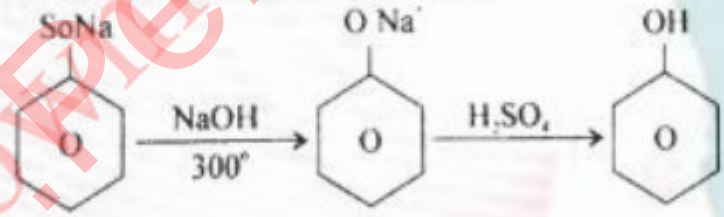
Substituents particularly those located others place to the OH froup can dramatically influence the acidity of the phenol due to resonance and / or inductive effect. Electron withdrawing group enhance the acidity electron donating. Substituents decrease the acidity. The resonance staslization of O-nitrophenol is



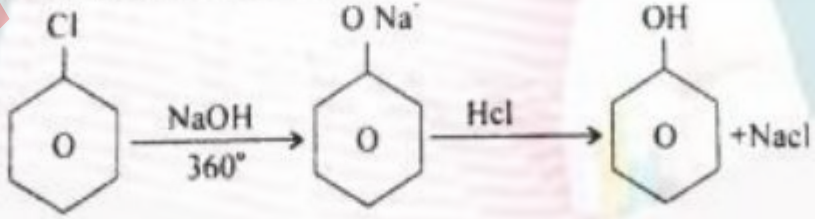
Q16: Write down the reaction for the prepation of phenol?

Answer

→ Rex of Benzene sulfonic acid with hydroxides.

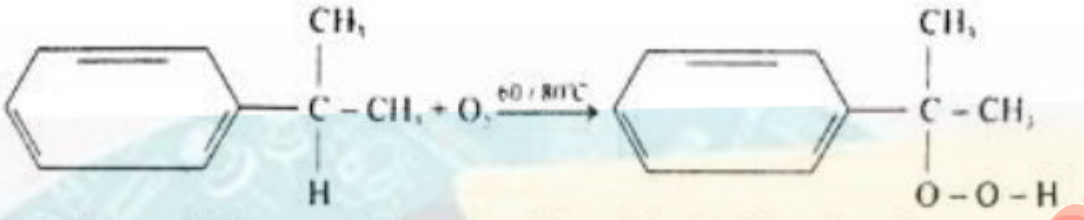


→ Rex of hydrolysis of chlorobenzene.

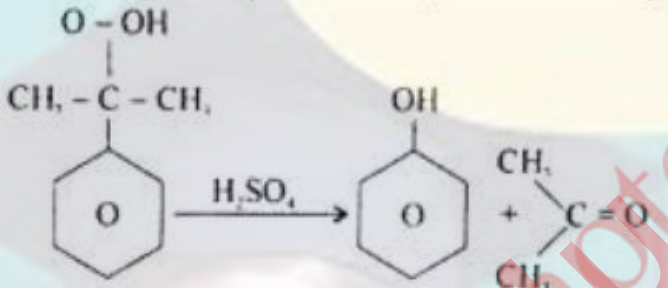


Acidic oxidation of cumene.

It is recently developed commercial method for the preparation of phenol, cumeneis oxidized by atmosphere oxygen is presence of mate catalyst in to cumene hydroproxide.

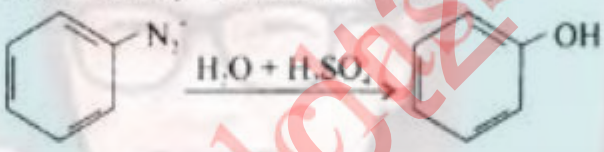


The hydroproxide is coverted into phenol through and acid catalyzed reaceangement.



(Phenol) (Acetone)

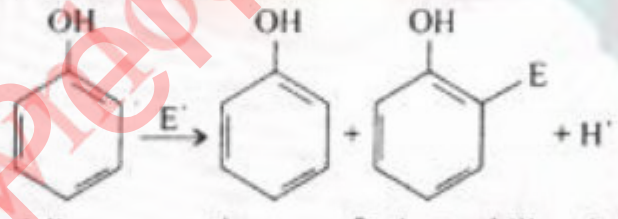
Preparation of phenols from acyl Diazonium salts.



Q17: Write down the reactions of phenols?

Answer

Electrophilic aromatic substitution:



Phenols are potencially very reactive towards electrophilic substitution.

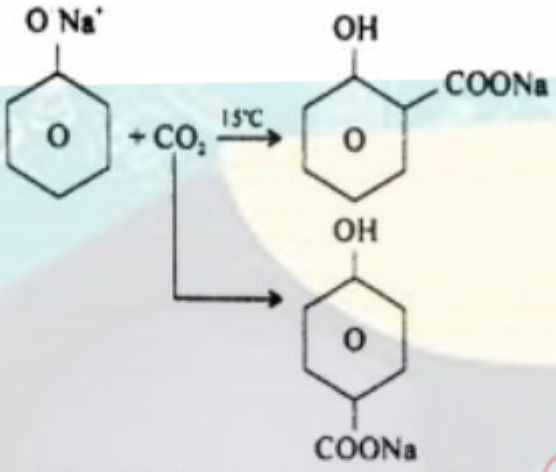
This is because the hydroxyl group OH is activating other, pace, directing substituent.

Substitution typically occurs pace to the hydroxyl group unless the pace position is blocked, then ortho substitution occurs the strong activation often means that melete reaction condition than those used for benzene itself can be used. Phenol are 80 activated that polysubstitution can be a problem.

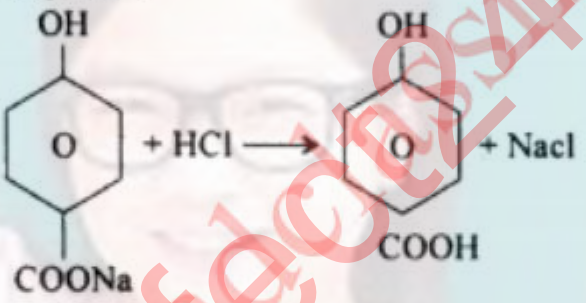
Q18: Write down the reaction of phenol with sodium metal?

Answer

Kolbe Schmitt reaction (carboxylation of phenol)

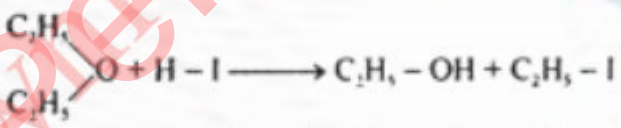


Carbon of CO_2 acts as electrophilic centre in this reaction acidification of the salt gives corresponding hydroxyl acid.

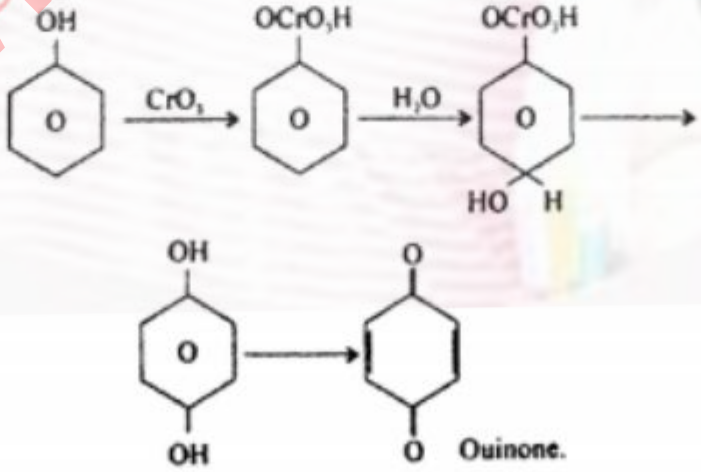


Oxidation of Phenols:

Phenols are very reactive towards diethyl ethers reacts with HI to form C_2H_5–OH and C_2H_5I.



Oxidizing agents. The oxidation takes place through several steps eventually destroying the ring.



Q19: Differentiate between the alcohols and phenols.

Answer

The compound in which hydroxyl group is attached to an alkyl group. Alcohols are hydroxyl derivatives of alkanes. The compounds in which one hidiogen of H_2O is replaced by an alkyl group. The general formula of alcohol is R-OH. Alcohols may be monohydric and polyhydric depending on the number –OH groups attached. However alcohol generally colorless liquids. Alcohol have a characteristic sweet smell and bumming taste. They are readily soluble in H_2O but solusility decreases in higher alcohols. Alcohols react with C-O bond breaks or in which O-H bond breaks.

Phenols:

The compounds in which hydroxyl group is attached to an acyl group. Phenols are decivate or benzene. The compounds in which one hydrogen of H_2O is replaced by an acyl on group. The general formula of phenol is it is also known as calbolic acid.

Phenols are not monohydric or polyhydric. They are colourless, crystalline, deliquescent solids. They have characteristics phenolic order its metting points is 41°C. Phenol are make acidic (Pka>>10) than alcohols (Pka>>16-20). It is aparingly soluble in H_2O forming pink solution at room temperature but completely soluble above 68.5°C. Phenols ion have resonance structure but alcohols do not have such type structure.

Q20: Write down the preparation of ethers?

Answer

By heating axcess of alcohol with concentrated H_2SO_4 at 140°C dehydration to ethers occurs to ethers occurs.

$$2CH_3CH_2OH \xrightarrow[H_2SO_4]{140^\circ C} CH_3-CH_2-O-C_2H_5+2H_2O$$

Primary alcohol reacts through SN_2 machanisms

$$CH_3CH_2OH + CH_3-CH_2-OSO_3H \longrightarrow CH_3-CH_2-\underset{\displaystyle H}{\overset{\displaystyle |}{O}}-C_2H_5$$

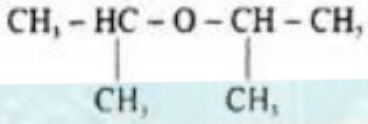
$$\xrightarrow{-H^+} CH_3CH_2-O-C_2H_5$$

Secondary alcohol react by SN_1 machanism.

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-OH + H^+ \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-O_2H \longrightarrow$$

$$\xrightarrow[-H_2O]{} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}+HOCH+H^+ \longrightarrow \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\overset{\displaystyle |}{CH}}}}$$

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\overset{\displaystyle H}{\overset{\displaystyle |}{C}}}}-\overset{+}{O}-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\overset{\displaystyle |}{C}}}}-CH_3 \xrightarrow{-H^+}$$



Di-isopropyl ether.

Two different primary alcohol give three ethers when treated with H_2SO_4

$$CH_3CH_2OH + CH_3OH \longrightarrow CH_3O-CH_3 - C_2H_5 - O - C_2H_5 + CH_3 - O - OC_2H_5$$

Ter-butyl and ethyl alcohol give on ether.

Q21: Write down the physical properties of ethers?

Answer

Ethers are colourless, low boiling, highly frammable compounds.

Their chemical reactivity and their ability to dissolve fats, oil, gum, and many other organic compound make them very good solvent.

Ether are soluble in concentrated sulphuric acid, a characteristics of oxygen containing compounds. This property is used as a test to distinguist between ether and satorate hydrocarbons.

Q22: How ethers show resistance to oxidation?

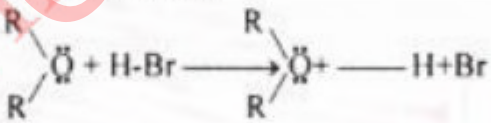
Answer

Ethers are resistance to attack by the usual chemical oxidizing agents. Morever reagent like NH_3 Na, alkali and acids have no action on ethers.

Q23: How ethers react with H-Br?

Answer

The oxygen atom of an ether molecule posseses unshared electron pair which accepts portion of H-Br to form oxonium ions.



No further rex takes place.

Q24: How ether react H-I?

Answer

The oxygen atom of an ether molecules possesses unshared electron pair which accept a proton of H-Ito form oxonium ion which react with I to form R-OH and RI.