CHAPTER 18

ALCOHOL, PHENOLS AND ETHERS

After completing this lesson, you will be able to:

- Describe the preparation of alcohols by reduction of aldehydes,
- Explain reactivity of alcohols.
- Describe the chemistry of alcohols by preparation of ethers and esters, oxidation cleavage of 1,2 Discuss thiols RSH.
- Explain the nomenclature, structure and acidity of phenols.
- Describe the preparation of phenols from benzene sulphuric acid, chlorobenzene acidic oxidation of cumene and hydrolysis of diazonium salts.
- Discuss the reactivity of phenol and their chemistry by electrophonic aromatic substitution, 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:

CH_3 CH_3

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$CH_3 - CH_2 - OH$ $CH - OH$ $CH_3 - C - OH$

Ethyl Alcohol / Isopropyl alcohol / Ter-butyl alcohol

CH_3 CH_3

Q2. Give Nomenclature 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.

$CH_2 - CH_2$ OH OH OH

| |

OH OH

$CH_2 - CH - CH_2$ 1,2 – ethanediol or Ethane – 1,2- diol (glycol)

| | | 1, 2, 3 – propane triol (glycerol)

(common name are given in brackets)

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

CH_3- CH CH - CH_2OH 2-butene-1.01

Q3. a) Why alcohols readily dissolve in water?

b) M.P. and B.P of alcohols is somewhat high, why?

Answer

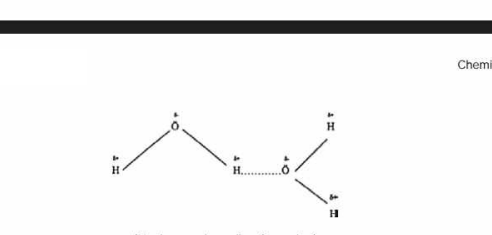
They are readily soluble in water. The solubility of alcohols is due to hydrogen bonding which is significant in lower alcohols but deceases in higher alcohol.

R R R R

| | | |

O – H O – H O – H O – H

(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

I) 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:

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

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

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 H2SO4 to form alkyl hydrogen sulphate

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

Ethyl hydrogen sulphate

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

$$CH_3CH_2OSO_3H + HOH \rightarrow CH_3CH_2OH + H_2SO_4$$

2) 1Hydrolysis of Alkyl halides

$$-\overset{|}{\underset{|}{C}}-X \xrightarrow{H_2O \text{ or } HO^-} -\overset{|}{\underset{|}{C}}-OH$$

Elaboration

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

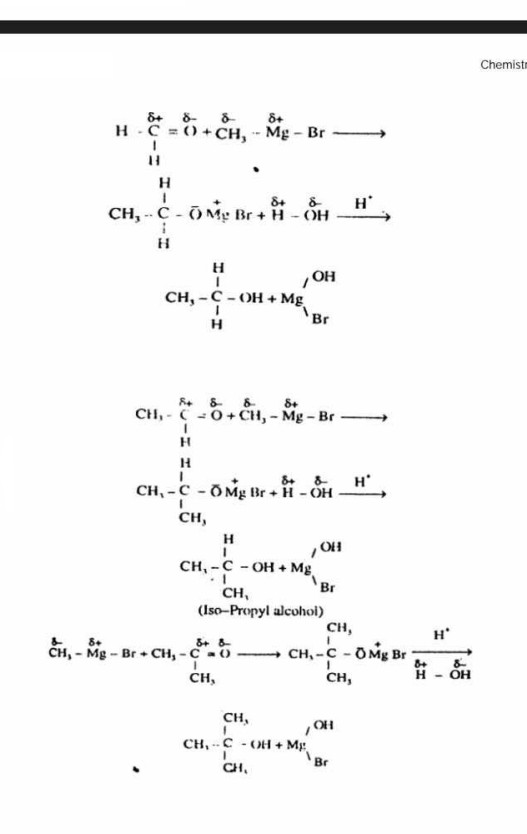
3) Reactions of RLi or RMgX with Aldehydes and Ketones

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:

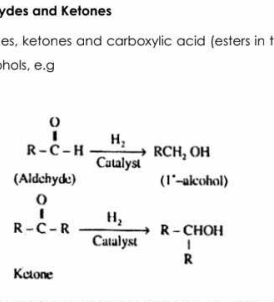
b) Secondary Alcohols: All other aldehydes give secondary alcohols, e.g.,

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



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



LiAlH₄ 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.

H O OC_2H_5

\ || /

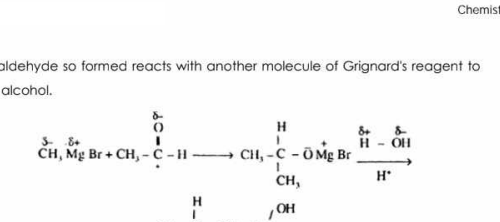
CH_3 Mg Br + C = O ⟶ CH_3 – C – H + Mg

| \

OC_2H_5 Br

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.

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$2C_6H_5$ - Mg Br + C_6H_5 – C = OC_2H_5 ⟶ $(C_6H_5)_3$ C – OH

(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 LiAlH₄ and NOT by the less reactive NaBH₄
- Each reaction requires that 2 hydrides be added to the carbonyl of acids or esters

[redacted]

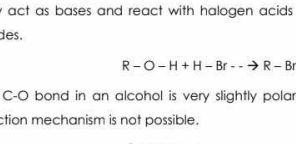
Reactions of Alcohols

Reaction with HX to give Alkyl Halides

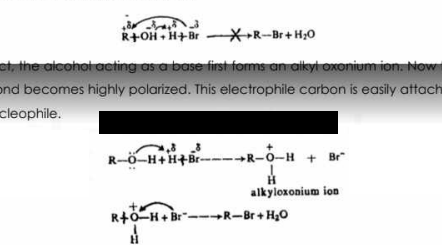
Due to the presence of unshared electron pairs on the oxygen atom of alcohols, they act as bases and react with halogen acids to form their respective alkyl halides.

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

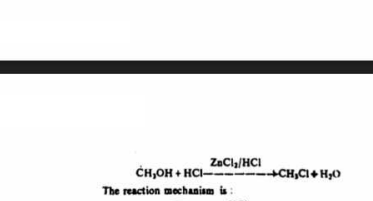
The C-O bond in an alcohol is very slightly polarized. Therefore, the following reaction mechanism is not possible.



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. [redacted]



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 ZnCl₂ in concentrated HCl is used as a catalyst.



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 ZnC12 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.

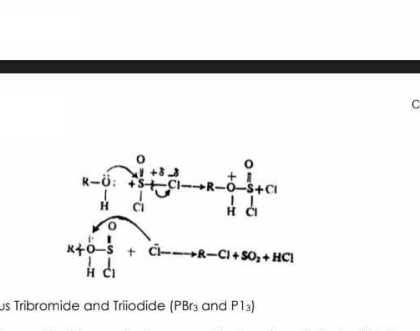
iii) Primary alcohol forms an insoluble prim-alkyl chloride on heating.

Q7. Give reaction of alcohol with SOC12, PX3 to give Alkyl Halides.

Answer

i) Thionyl chloride (SOC1₂)

Alcohols react with thionyl chloride to give alkyl chlorides.



ii) Phosphorus Tribromide and Triiodide (PBr₃ and P1₃)

Alkyl bromides and iodides are best prepared by treating alcohols with PBr₃ and P1₃.

$$3ROH + PBr_3 \dashrightarrow 3RBr + H_3PO_4$$

Similarly,

$$3ROH + PI_3 \dashrightarrow 3RI + H_3PO_4$$

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

Answer

Synthesis of Ethers via Acid-catalyzed Condensation of Alcohols

$$2-\overset{|}{\underset{|}{C}}-OH \xrightarrow[\text{heat}]{H+} -\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-H_2O$$

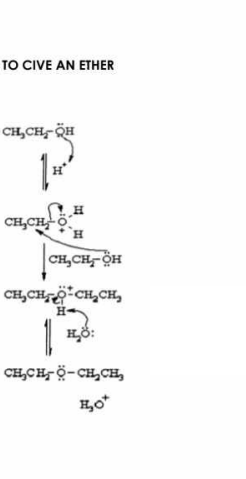
Elaboration

- Reagents typically H₂SO₄ 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 CIVE 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 CH.3CÆ½— O nucleophile and attacks to displace the good leaving group, a 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 along with 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.

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

Glycerin reacts with a mixture of concentrated HNO₃ and H₂SO₄ to give an ester called Nitroglycerine or Glyceryl trinitrate.

CH_2OH CH_2ONO_2

| H_2SO_4 |

$CHOH + 3HNO_3$ $CHONO_2 + 3H_2O$

| |

CH_2OH $CH_2ONO_2 + 3H_2C$

Glycerin nitroglycerine

Nitroglycerine is highly explosive liquid. It is mixed with fine sand and molded 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 KMn04 or K2Cr207 + H2SO4 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.

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

acetaldehyde (21°C)

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

acetic acid

ii) Secondary Alcohol:

A seconaary alconol is oxidized under similar condition to give a ketone which is not further oxidized.

$$\underset{\underset{CH_3}{|}}{CH_3 - CH_2OH} \xrightarrow[50^\circ C]{K_2Cr_2O_7 + H_2SO_4} \underset{\underset{CH_3}{|}}{CH_3 - C = O}$$

iii) Tertiary Alcohol:

CH_3 CH_3

| H_2SO_4 |

$CH_3 - CH_2 - C - OH$ ⟶ $CH_3 - CH = C + H_2O$

| |

CH_3 CH_3

A tertiary alcohol is not oxidized by alkaline KMn04. When heated with a mixture of K₂Cr₂O₇ and H₂SO₄, it is first dehydrated to an alkene in the presence of acid. Then alkene is oxidized to a ketone and a carboxylic acid by K₂Cr₂O₇ and H₂SO₄.

CH_3 CH_3

| $K_2Cr_2O_7 + H_2SO_4$ |

$CH_3 - CH = C$ ⟶ $CH_3 - COOH + C = U$

| 50°C acetic acid |

CH_3 CH_3

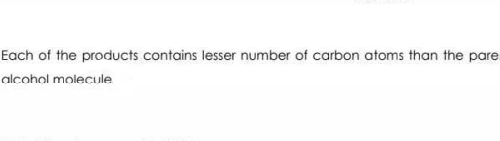
acetone

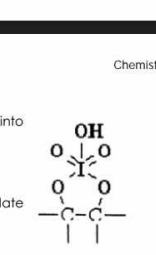
Each of the products contains lesser number of carbon atoms than the parent alcohol molecule.

Q10. Give cleavage of 1,2-Diols.

Answer

Oxidative Cleavage of Diols





I) 1,2- or vicinal diols are cleaved by periodic acid, HIO₄, 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 l ,2-diols.

5) The products are determined by the substituents on the diol.

Q11.What are Thiols or Thio alcohols?

Answer

This 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 a 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

Introductio:.

First prepared by	Runge
Melting point of	41°C
Boiling point of	

"Aromatic compounds containing one or more OH groups, directly attached with carbon of benzene ring, are called phenols". The simplest example phenol is also known as carbolic acid, i.e., C₆H₅OH. It was first obtained from coal tar 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, C₆H₅-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

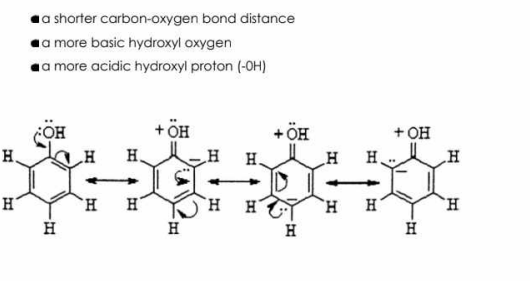
I) The alcohol functional group consists of an O atom bonded to sp²-hybridized aromatic C atom and a H atom via bonds.

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 result is, compared to simple alcohols:

- a shorter carbon-oxygen bond distance
- a more basic hydroxyl oxygen
- a more acidic hydroxyl proton (-0H)



Physical Properties of Phenol

I) Phenol is a colorless, crystalline, poisonous solid with characteristic phenolic odor having melting point 41 °C and boiling point 182ºC.

2) It is sparingly soluble in water forming pink solution at room temprature but completely soluble above 68.5ºC.

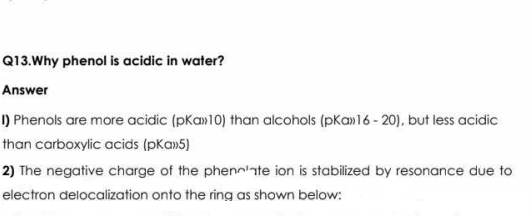
3) It is poisonous and causes blisters on the skin.

Q13.Why phenol is acidic in water?

Answer

I) Phenols are more acidic (pKa≈10) than alcohols (pKa≈16 - 20), but less acidic than carboxylic acids (pKa≈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.

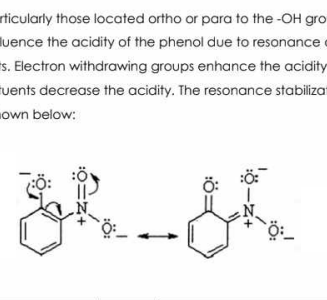
Mixing an ether solution, of either phenol and alcohol or phenol and carboxylic acid, with dilute base (sodium hydroxide and sodium bicarbonate, respectively), results in the stronger acid being converted to its alkali salt, which is then extracted to the aqueous phase and can be separated from the organic 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 on acidity of phenols?

Answer

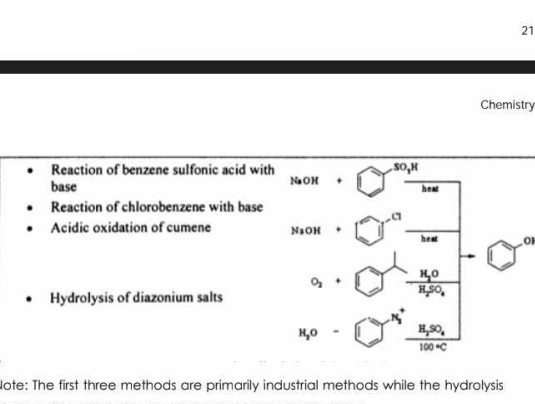
Substituents, particularly those located ortho or para to the -OH group, can dramatically influence the acidity of the phenol due to resonance and / or inductive effects. Electron withdrawing groups enhance the acidity; electron donating substituents decrease the acidity. The resonance stabilization of o-nitrophenol is shown below:



Compound	pKa	Compound	pKa
Phenol	10.0		
0-Methoxyphenol	10.0	p-Methoxyphenol	10.2
0-Methylphenol	10.3	p-Methylphenol	10.3
0-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

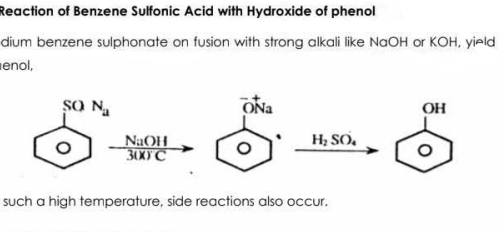
Note: The first three methods are primarily industrial methods while the hydrolysis of diazonium salts is the most important laboratory method.

Give reaction of benzene sulfonic acid with hydroxide of phenol.

Answer

I) Reaction of Benzene Sulfonic Acid with Hydroxide of Phenol

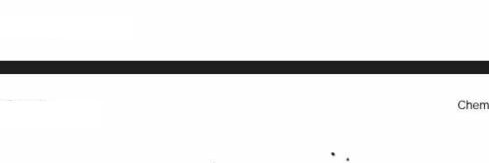
Sodium benzene sulphonate on fusion with strong alkali like NaOH or KOH, yield phenol.



At such a high temperature, side reactions also occur.

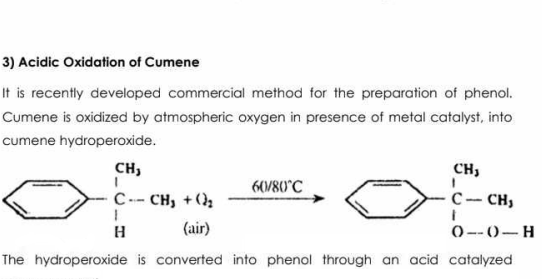
2) Base Hydrolysis of Chlorobenzene

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

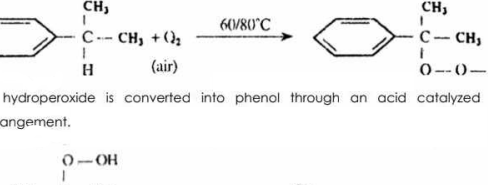


3) Acidic Oxidation of Cumene

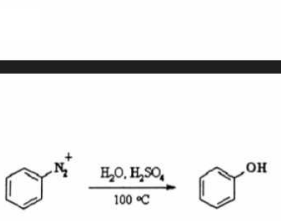
It is recently developed commercial method for the preparation of phenol. Cumene is oxidized by atmospheric oxygen in presence of metal catalyst, into cumene hydroperoxide.



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



4) Preparation of Phenols from Aryl Diazonium Salts



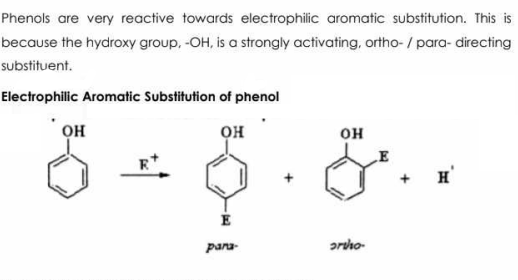
Elaboration

- Aryl diazonium salts can be converted into phenols using H20 / H2S04 / heat
- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid, I-N02

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 substituted

- 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

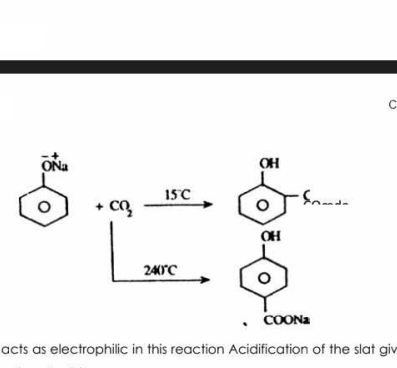
Reaction	Phenol	Benzene
Nitration	dil. HNO₃ in H₂O or CH₃CO₂H	HNO₃ / H₂SO₄
Sulfonation	conc. H₂SO₄	H₂SO₄ or SO₃/ H₂SO₄
Halogenation	X₂	X₂/ Fe or FeX₃
Alkylation	ROH / or RCl / AlCl₃	RCl / AlCl₃
Acylation	RCOCl / AlCl₃	RCOCl / AlCl₃
Nitrosation	aq. NaNO₂ / H⁺	

Different Reactions of Phenols

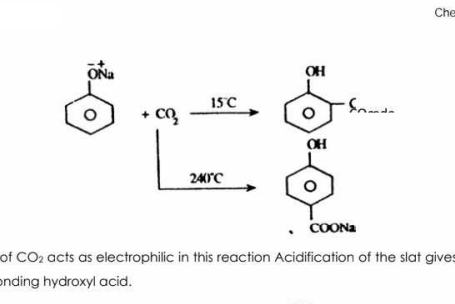
1) Reaction with Sodium Metal

Carboxylation of Phenols (Kolbe-Schmitt reaction)

"The reaction of sodium salt of phenol with CO₂ is called Kolbe reaction. It is carbonation of phenol. At low temperature sodium salicylate (sodium-o-hydroxy benzoate), whereas at higher temperature 0-product isomerizes to p-isomer.

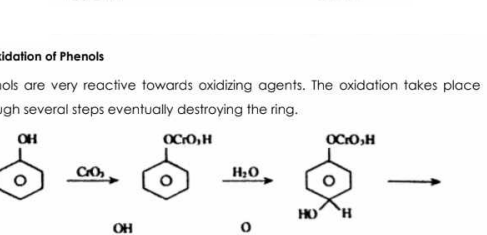


Carbon of CO₂ acts as electrophilic in this reaction Acidification of the slat gives corresponding hydroxyl acid.



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

I) 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 o . 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 °c.

9) Phenols are more acidic (pKa≈lO) than alcohols (pKa≈16 - 20).

10) It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5 °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.,

H

|

$CH_3 - O - CH_3$; $C_6H_5 - O - CH$; $C_2H_5 - O - C - CH_3$

|

CH_3

(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.

$CH_3 - O\ C2H_5$ $CH_3 - CH_2 - CH - CH_3$

|

$O - CH_3$

Q18.Give preparation of ethers.

Answer

By heating excess of alcohol with concentrated H2SO4 at 140ºC, dehydration to ethers occurs.

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

Primary alcohols react through SN2-mehcanism

$CH_3\ CH_2\ OH + CH_3\ CH_2 - OSO_3\ H \rightarrow$

$$\underset{\underset{H}{|}}{CH_3 - CH_2 - O - C_2H_5} \xrightarrow{-H^+} CH_3\ CH_2 - O - C_2H_5$$

Secondary alcohols react by SNI-mechanism

$CH_3\ CH_2\ OH + CH_3\ CH_2 - OSO_3\ H \rightarrow$

$CH_3 - CH_2 - O - C_2H_5 \xrightarrow{-H^+} CH_3\ CH_2 - O - C_2H_5$

|

H

$CH_3\ CH_2\ OH + CH_3\ CH_2 - OSO_3\ H \rightarrow$

$$\underset{\underset{H}{|}}{CH_3 - CH_2 - O - C_2H_5} \xrightarrow{-H^+} CH_3\ CH_2 - O - C_2H_5$$

Di – isopropyl ether

Two different primary alcohols give three ethers when treated with H2SO4.

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

Ter-butyl and ethyl alcohol give one ether.

Q19.Give physical properties of ethers.

Answer

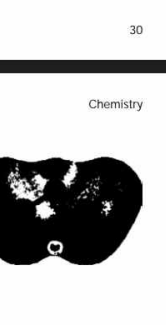
I) Ethers are colorless, low boiling, highly inflammable compounds.

2) Their chemical inactivity and their ability to dissolve fats, oil, gum and many other organic compounds 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 bluer 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 NH3, 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.

R R

\ \

O + H – Br → O⁺ - H + Br

/ /

R R

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 pair, which accepts a proton of H-I to form oxonium in, which reacts with I to form R-OH and RI.

R R

\ \

O + H – I → O⁺ - H + I

/ /

R R

R

\

O⁺ - H – I → ROH + RI

/

R

Diethyl ether reacts with HI to form C2H5-OH and C2H51.

C_2H_5

\

O + H – I → $C_2H_5 - OH + C_2H_5 - I$

/

C_2H_5

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 hundreds 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 microorganisms. 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 part 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 Anesthetic

Before the advent of an anesthetics, 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. Anesthetics enable surgery to develop from crude carpentry to its present sophisticated forms.

Three of the most important early anesthetics were nitrous oxide) dinitrogen oxide, N20), ether (ethoxyethane, CH3CH20CH2CH3) and chloroform (trichloroethane, CHC13). Nitrous oxide is non-toxic and non-flammable, but it only produces light anesthesia. Chloroform produces deep anesthesia 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) C2H5Cl

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 Lewis 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

5) Ethanol is denatured by adding:

a)Methanol b) Carbolic acid

c) Acetone d) Propanol

6) When phenol reacts with CH3COCl the product formed is?

a) Ether b) Alcohol

c) Aldehyde d) Ester

7) Williamson synthesis of ethers is superior to alcohols because it makes:

a)Symmetrical ethers

b)Asymmetrical ethers

c)Ether at room temperature

d)Both symmetrical and asymmetrical ethers

8) A methyl phenol is also called:

a) A Cresol b) Benzyl alcohol

c) Alcohol d) Formaldehyde

9) Which one of the following compounds does not contain carboxylic group?

a) Acetic acid b) Formic acid

c) Benzoic acid d) Picric acid

10) Hydrogen boding is maximum in:

a) Diethyl ether b) Methanol

c) Ethyl alcohol d) Triethyl amine

11) Which of the following compound has no attraction at all with water?

a) C_6H_6 b) C_2H_5OH

c) $CH_3CH_2CH_2OH$ d) $CH_3 - O - CH_3$

12) Phenols are more acidic than alcohols which statement is correct?

a) Phenol turns blue litmus paper red

b) Alcohol liberates C02 with carbonate solution

c) Phenoxide ion is stabilized due to resonance

d) Alxoxide ion is stabilized due to resonance

13) Carbolic acid is treated with dilute nitric and at 25ºC, the product is:

a) O — nitrophenol b) P —nitrophenol

c) m- nitrophenol d) Both a and b

14) Oxonium ion is formed when:

a) Ethanol reacts with Na metal

b) Phenol reacts NaOH solution

c) Ether is treated with HI

d) Ethanol is treated with aq NaOH and iodine

15) 2,4,6 — Trinitrophenol is commercially called as:

a) TNT b) Picric acid

c) Carbolic acid d) Fumeric acid

Answers

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

Q2. Give short answers of the following questions.

Q1. What are alcohols? How are they classified?

Answer

Aliphatic organic compounds having —OH groups are called as alcohols.

There are two types.

I) Monohydric alcohols **2)** Polyhydric alcohols

Examples of Monohydric alcohols:

$CH_3 - CH_2 - OH$ (methy Alcohol) $CH_3-CH_2-CH_2-OH$ (ethyl alcohol)

$\underset{OH}{CH_2} - \underset{OH}{CH_2}$ Glycol (A Dihydric alchol) $\underset{OH}{CH_2} - \underset{OH}{CH_2} - \underset{OH}{CH_2}$ Glycerol (A trihydric alchol)

Q2. How are monohydric alcohols classified?

Answer

Classification of Monohydric alcohols

Monohydric alcohols are of three types.

I) Primary alcohols

2) Secondary alcohols

3) Tertiary alcohols

Examples

$CH_3 - CH_2 - OH$ Methyl alcohol (Prim alcohol)

$CH_3 - \underset{CH_3}{CH} - OH$ isoprophylalcohol (Sec alcohol)

$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - OH$ nesbutylalcohol (tetritory alcohol)

Q3. Compare the acidity of primary secondary and tertiary alcohols.

Answer

Acidity of Alcohols

I) Due to high 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 an organic chemistry.

4) Alcohols react with Na (or K) like water to give the alkoxide.

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

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

Q4. 2 — butane is the major product when n—butyl alcohol is heated with conc.

H₂SO₄. Explain.

Answer

n — butyl alcohol on reaction with H ion of H2S04 produce primary carbonium ion. This primary carbonium ion is converted into secondary carbonium ion by shifting p — hydrogen atom, as secondary carbonium ion is more stable than the primary carbonium ion that is why 2 — butane is the major product.

$$H_2SO_4 \longrightarrow \overset{\oplus}{H} + HS\overset{\ominus}{O_4}$$

$$CH_3-CH_2-CH_2-\underset{OH}{CH_2} + \overset{\oplus}{H} \longrightarrow CH_3-CH_2-CH_2-\overset{\oplus}{CH_2} + H_2O$$

$$\underset{\text{(prim carbonium ion)}}{CH_3-CH_2-CH_2-\overset{\oplus}{CH_2}} \longrightarrow \underset{\text{(sec carbonium ion)}}{CH_3-CH_2-\overset{\oplus}{CH}-CH_3}$$

$$H_2\overset{\ominus}{SO_4} + CH_3-CH-\overset{\oplus}{CH}-CH_3 \longrightarrow \underset{\text{(regenerated)}}{CH_3-CH=CH-CH_3+H_2SO_4}$$

Q5. Give the mechanism of dehydration of alcohols.

Answer

Alcohols on heating at 1800C in presence of H2S04 produce alkenes the reaction takes place as per following mechanism:

i) $H_2SO_4 \longrightarrow \overset{\oplus}{H} + HS\overset{\ominus}{O_4}$

ii) $CH_3-CH_2-\underset{H}{O} + \overset{\oplus}{H} \xrightarrow{180^\circ C} CH_3-CH_2-\underset{H}{\overset{\oplus}{O}}-H$

iii) $H_2\overset{\ominus}{SO_4} + \overset{\delta+H}{CH_2}-CH_2-\underset{H}{\overset{\oplus}{O}}-H \xrightarrow{180^\circ C}$

$$\underset{\text{(regenerated)}}{CH_2 = CH_2 + H_2O + H_2SO_4}$$

Q6. How will you obtain benzene from alcohol?

Answer

Conversion of phenol into Benzene

OH + zn $\xrightarrow{\Delta}$ + zn O

Q7. Alcohols phenols both have OH group but phenols are more acidic than alcohols.

Answer

Phenol after release of H — ion produce phenoxide P as conjugated base which is very stable due to resonance.

Whereas alcohols don't give very stable conjugated base.

Q8. How will you differentiate between an alcohol and phenol?

Answer

A test to distinguish alcohols and phenol

Acid bromine water gradually to concentrated solution of phenol in a test tube Bromine water first decolorizes and then on adding excess of it, a white or yellowish white ppt. of polybromo derivative is produced which indicates the presence of phenolic group.

Reactions

(Phenol) + $3Br_2$ Reddish Brown → Colourless (Tribromo cycle hexanol)

+ $3Br_2$ → White ppt of Tribromo phenol + 3HBr

Q9. Write the nomenclature of ether by IUPAC system.

Answer

IUPAC system of Nomenclature of Ethers

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

$CH_3 - O - CH_3$ (Dimethyl ether) $C_2H_5 - O - C_2H_5$ (Dimethyl ether)

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

$CH_3 - O - CH_3$ $CH_3 - CH_2 - \underset{O - CH_3}{CH} - CH_3$

Methoxy ethane butane

Q10. Why is phenol more soluble in water than toluene?

Answer

Phenol is a polar molecule and forms hydrogen bonds with water molecules as follows:

$$\overset{\delta+\ \delta-}{H-O} \cdots\cdots \overset{\delta+\ \delta-}{H-\underset{H}{O}} \cdots\cdots \overset{\delta+\ \delta-}{H-O} \cdots\cdots \overset{\delta+\ \delta-}{H-\underset{H}{O}}$$

Whereas toluene is non-polar and is insoluble in water.

Q3. Give detailed answers for the following questions

Q1. How will you prepare alcohols on industrial scale?

Answer

Industrially ethanol is prepared by fermentation of molasses, starch grains or fruit juices like sugarcane juice (called molasses by fermentation in presence of enzymes present in yeast.

From Molasses

1) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{(yeast)}]{\text{invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$

2) $C_6H_{12}O_6 \xrightarrow[\text{(yeast)}]{\text{Zymase}} 2C_2H_5OH + CO_2$

From Starch

1) $2(C_6H_{10}O_5) + nH_2O \xrightarrow[\text{(yeast)}]{\text{Diastase}} C_{12}H_{22}O_{11}$

2) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{(yeast)}]{\text{Maltase}} 2C_6H_{12}O_6$

3) $C_6H_{12}O_6 \xrightarrow[\text{(yeast)}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$

Q2. Distinction between ethanol and methanol and ethanol from phenol.

Answer

a) Distinction between ethanol and methanol

Ethanol on heating with 12 and NaOH give yellow precipitates of Iodoform whereas methanol does not give this test.

Reactions

$$I_2 + H_2O \longrightarrow 2HI + (O)$$

$$\underset{\text{(Ethanol)}}{CH_3 - \underset{H}{\overset{H}{C}} - O - H + (O)} \longrightarrow \underset{\text{(acetaldehyde)}}{CH_3 - \overset{O}{\overset{\|}{C}} - H + H_2O}$$

$$3I_2 + H - \underset{H}{\overset{H}{C}} - \overset{O}{\overset{\|}{C}} - H \longrightarrow I - \overset{I}{C} - \overset{O}{\overset{\|}{C}} - H + 3HI$$

$$NaOH + I - \underset{H}{\overset{I}{C}} - \overset{O}{\overset{\|}{C}} - H \longrightarrow \underset{\text{Yellow crystal}}{CHI_3\ \text{(Idoform)}} + \underset{\text{Sod. Format}}{NaO - \overset{O}{\overset{\|}{C}} - H}$$

b) Distinction betwween ethanol and phenol

Ethanol gives iodoform test positive but phenol does not,

Iodoform Test

Ethanol + Solid Iodine + NaoH —> Yellow crystals of Iodoform

(reactions given in part a)

But phenol does not give yellow crystal.

Q3. How will you distinguish between primary, secondary and tertiary alcohols? Explain with reactions.

Answer

Please see Answer of Q7. of chapter notes.

Q4. Give IUPAC names and structures of the following compounds.

i) Sec. butyl alcohol **ii)** Lactic acid

iii) Ter. butyl alcohol **iv)** Tartaric acid

Answer

i) $CH_3 - CH_2 - \underset{CH_3}{CH} - OH$ Sec. butyle alcohol 2 – methyl –2 butanol

ii) $CH_3 - \overset{OH}{C} - COOH$ Lactic acid 2 – hydroxyl propanoic acid

iii) $CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - OH$ Ter butyl alcohol 2 – methyl – 2 – propanol

iv) $\overset{(1)}{COOH}$, $H\overset{(2)}{C} - OH$, $H\overset{(3)}{C} - OH$, $\overset{(4)}{COOH}$ Tartaric acid 2,3 - dihydroxy butandioci acid

Q5. Give the reactivity of Ethers.

Answer

Reaction with Haloacids

$$\begin{matrix} R \\ \quad\backslash \\ \quad\quad O^+ \\ \quad / \\ R \end{matrix} \quad - H - I \rightarrow ROH + RI$$

Like;

$$\begin{matrix} C_2H_5 \\ \quad\backslash \\ \quad\quad O^+ \\ \quad / \\ C_2H_5 \end{matrix} \quad - H - I \rightarrow C_2H_5 - OH + C_2H_5 - I$$

Reaction with water

$$\begin{matrix} R \\ \quad\backslash \\ \quad\quad O^+ \\ \quad / \\ R \end{matrix} \quad - H\ OH - I \xrightarrow{H_2SO_4} 2C_2H_5 - OH$$

C_2H_5

$$\begin{matrix} \backslash \\ \quad O^+ \\ / \\ C_2H_5 \end{matrix} \quad + OH \xrightarrow{H_2SO_4} 2C_2H_5 - OH$$

Reaction with PC1₅

$$\begin{matrix} R \\ \quad\backslash \\ \quad\quad O^+ \\ \quad / \\ R \end{matrix} \quad + PCl_5 \longrightarrow 2R - Cl + POCl_3$$

$$\begin{matrix} C_2H_5 \\ \quad\backslash \\ \quad\quad O^+ \\ \quad / \\ C_2H_5 \end{matrix} \quad + PCl5 \longrightarrow 2C_2H_5 - Cl + POCl_3$$

Q6. Give at least methods for the preparation of phenol.

Answer

Please Answers ofQ15 and Q16.

Q7. How does phenol reacts with

i) HNO₃ **ii) H₂SO₄**

iii) H2/Pt **iv) NaOH**

v) Ag₂O

Answer

i) OH + $3HNO_3 \xrightarrow{200^\circ C}$ NO_2 OH NO_2 NO_2 + $3H_2O$

ii) OH + $2HSO_4 \xrightarrow{H_2SO_4}$ OH HSO_3 + OH H_2SO_4 + $2H_2O$

iii) OH + $H_2 \xrightarrow{Pt}$ OH cyclo hexanol

iv) OH + NaOH → ONa + H_2O

v) 2 OH + Ag_2O → 2 OAg + H_2O

Q8. What is oxonium ion? Describe the chemical reactivity of ether.

Answer

An oxygen having positive charge is called as oxonium ion.

e.g.

$$CH3 - \ddot{O} - H + H \longrightarrow \underset{\text{(oxonium ion)}}{CH3 - \underset{H}{O} - H}$$

Reactivity of Ethers

Please see Answer of reactivity of ether Q5 of exercise.

Q9. Explain following terms using ethyl alcohol as on example; Answer

i) Oxidation **ii) Dehydration**

iii) Esterification **iv) Ether formation**

Answer

i) Oxidation

Oxidation of ethyl alcohol procedure octadehyle which on oxidation is converted into acetic acid.

$$CH_3 - \underset{H}{\overset{H}{C}} - O - H + (O) \xrightarrow{KMnO_3} CH_3 - \overset{O}{\overset{\|}{C}} - H + H_2O$$

$$CH3 - \overset{O}{\overset{\|}{C}} - H + (O) \xrightarrow{KMnO_3} CH3 - \overset{O}{\overset{\|}{C}} - OH$$

ii) Dehydration

Removal of hydrogen from a substance is called dehydration Dehydration of ethyl alcohol at different temperature produce different products.

$$2\,CH_3 - CH_2 - OH \xrightarrow[H_2SO_4]{140^0C} C_2H_5 - O - C_2H_5 + H_2O$$

$$CH_3 - \underset{OH}{CH_2} \xrightarrow[H_2SO_4]{180^0C} CH_2 = CH_2 + H_2O$$

iii) Esterification

Formation of an ester from an alcohol is called esterification.

$$CH3 - \overset{O}{\overset{\|}{C}} - \boxed{OH + H}O - C_2H_5 \xrightarrow{H_2SO_4} \underset{\text{Ethyl methyl ester}}{CH3 - \overset{O}{\overset{\|}{C}} - O - C_2H_5 + H_2O}$$

iv) Ether Formation

Ethyl alcohol on heating with H2S04 at 140ºC.

$$CH3 - \overset{O}{\overset{\|}{C}} - \boxed{OH + H}O - C_2H_5 \xrightarrow[140^\circ C]{H_2SO_4} \underset{\text{Ethyl methyl ester}}{CH3 - \overset{O}{\overset{\|}{C}} - O - C_2H_5 + H_2O}$$

Q10. How does ethyl alcohols react with the following reagents?

Answer

i) conc. H2S0⁴ **ii) Na**

iii) PCl, **iv) CH3COOH**

v) SOCl2

Answer

i) Conc. H₂SO₄

$$2\,CH_3 - CH_2 - OH \xrightarrow[H_2SO_4]{140^0C} C_2H_5 - O - C_2H_5 + H_2O$$

$$CH_3 - CH_2 \xrightarrow[H_2SO_4]{180^0C} CH_2 = CH_2 + H_2O$$

$$CH_3 - CH_2 - O H + Na \rightarrow CH_2 - CH_2 - Ona + \tfrac{1}{2} H_2$$

$$C_2H_5 - OH + PCl_5 \rightarrow C_2H_5 - Cl + HCl + POCl_3$$

$$CH3 - \overset{O}{\overset{\|}{C}} - OH + HO - C_2H_5 \xrightarrow{H_2SO_4} \underset{\text{Ethyl acetate (ester)}}{CH3 - \overset{O}{\overset{\|}{C}} - O - C_2H_5 + H_2O}$$

$$C3 - CH2 - OH + Cl - \overset{O}{\overset{\|}{S}} - Cl \longrightarrow C_2H_5 - Cl + HCl + SO_2$$

Q11. How will you distinguish between

i) an alcohol and a phenol

ii) an alcohol and an ether

iii) Methanol and ethanol

iv) A tertiory alcohol and a primary alcohol

v) I — propanol and 2 — propanol

Answer

An alcohol and a phenol

i) Please see Answer of Q2,8 of exercise.

ii) Distinction between alcohol on reaction with Na — metal generate 1-12 gas which burn luminous flame.

But ethers don't react with Na-metal.

iii) Distinction between ethanol and methanols Please see Answer ofQ3. 2 of exercise.

iv) A tertiary alcohol and a primary alcohol.

Please see Answer ofQ7. of chapter notes.

v) I — propanol and 2 — propanol

Please see Answer of Q7. of chapter notes.

Q12.Give reason for the followings:

i) Ethyl alcohol is a liquid while ethyl chloride is a gas.

ii) Ethanol has higher boiling point than diethyl ether.

iii) Absolute alcohol cannot be prepared by fermentation process.

iv) Ethanol gives different products with Conc, H2S04 under different condition ns.

v) Water has higher boiling point than ethanol.

Answe

i) Ethyl alcohol is liquid due to strong hydrogen bonds which are not present in ethyl chloride i.e.

$$\overset{\delta+\ \delta-}{\underset{C_2H_5}{H - O}} \cdots\cdots \overset{\delta+\ \delta-}{\underset{C_2H_5}{H - O}} \cdots\cdots \overset{\delta+\ \delta-}{\underset{C_2H_5}{H - O}} \cdots\cdots \overset{\delta+\ \delta-}{\underset{C_2H_5}{H - O}} \cdots\cdots$$

ii) In ethanol there are strong hydrogen bonds like:

$$\overset{\delta+\ \delta-}{\underset{C_2H_5}{H - O}} \cdots\cdots \overset{\delta+\ \delta-}{\underset{C_2H_5}{H - O}} \cdots\cdots \overset{\delta+\ \delta-}{\underset{C_2H_5}{H - O}} \cdots\cdots \overset{\delta+\ \delta-}{\underset{C_2H_5}{H - O}} \cdots\cdots$$

Whereas diethyl ether is a neutral molecule having zero dipole moment.

iii) During fermentation there are obtained mixture of compounds whereas absolute alcohol is 100% pure alcohol. The fractional separation of alcohols by distillation of alcohols is not easy due to strong hydrogen bonds among alcohols.

iv) Ethanol on heating with concentrated H_2SO_4 at 140ºC produce an ether. Whereas ethanol on heating with H_2SO_4 at 180ºC produce on alkene.

$$2\,CH_3 - CH_2 - OH \xrightarrow[H_2SO_4]{140^0C} C_2H_5 - O - C_2H_5 + H_2O$$

$$CH_3 - \underset{OH}{CH_2} \xrightarrow[H_2SO_4]{180^0C} CH_2 = CH_2 + H_2O$$

v) I one water molecule may forms two hydrogen bonds whereas one ethanol molecule may form one hydrogen bond that is why boiling point of water is 100ºC and that of ethanol is 78.5 ºC.

$$\underset{H}{\underset{|}{H - \ddot{O}}} \cdots\cdots \overset{\delta+\ \delta-}{\underset{H}{H - O}} \qquad \overset{H}{O - H\delta+} \qquad \underset{C_2H_5}{H - O}$$

Two H - bonds of water molecule

Multiple Choice Questions

1) Primary, Secondary and Tertiary Alcohol can be distinguished by Lucas test. The alcohol which takes 5-10 minutes to react with HCl in presence of ZnC12 is:

a) Prim alcohol
b) Sec. Alcohol
c) Tertiary alcohol
d) None of these

2) A mixture of CH_3COOH, Ethyl alcohol and H_2SO_4 on heating yields:

a) Ethyl Acetate
b) Ether
c) Acetic anhydride
d) Ethene

3) Ethanol on reaction with Conc. H2S04 at 180°C yields:

a) Ethane
b) Ethene
c) C+H,
d) Ethyne

4) Isopropyl bromide on reaction with Na metal yields:

a) Sodium propyl ide
b). propene
c) 2,3-dimethyl butane.
d) Butane

5) Williamson's synthesis yields:

a) An alcohol
b) An amine
c) An Ether
d) An Ester

6) Methanol and Ethanol were heated with Conc.H2S04 at 140°C in a single container made up of gena glass. The products are:

a) Dimethyl Ether
b) Diethyl ether
c) Ether and Methane
d) A mixture of dimethyl ether, diethyl ether and methyl ethyl ether.

7) The Formula of amino methanamide is:

a) (NH2)2CO
b) NH4CONH2
c) NH2CH3
d) (NH2)4C

8) The Formula of anesthetic ether is:

a) (CH3)20
b) (C2H5)20
c) CH30C2H5
d) None of these

9) Methanol on reaction with a mixture of K2Cr207 and H2S04 yields:

a) Acetaldehyde
b) Propanol
c) Methane
d) Formaldehyde.

10) Formaldehyde or reaction with a mixture of NaCN and HCl yields compound "A". When Compound "A" is hydrolyzed, obtained product is:

a) Acetic acid
b) Hydroxy acetic acid
c) Formaldehyde
d) Cyanogen methanol

11) Oxidation of isopropyl alcohol with a mixture of K2Cr207 and Conc.H2S04 yields:

a) Acetaldehyde
b) Propyl aldehyde
c)Butanone
d) Propanone.

12) HOOC – CH_2 - C (OH) (COOH) - CH_2 -COOH is the formula of:

a) Tartaric acid
b) Citric acid
c)Maleic acid
d) Lactic acid

13) When alcohols are protonated, the formed conjugated acid is called:

a) An aldehyde ion
b) hydroxonium ion
c) An oxide ion
d) Hydronium ion

14) Phenol on heating with a mixture of HNO_3 and H_2SO_4 at 35°C yields:

a) o — Nitro phenol
b) p — Nitro phenol
c) o and p — nitro phenols
d) o and p - dinitro phenols

15) Ethyl bromide was shaken with magnesium in ether at 25°C. Products were reacted with acetone followed by reaction with a mixture of HBr and water Final product is:

a) 2 — methyl —2 — butanol
b) 3,3 — dimethyl propanol
c) 2 — ethyl — 2 — propanol
d) None of these is correct

16) Which one of the following is also known as lactic acid?

a) 3— Hydroxy propanoic acid
b) 2— hydro propanoic acid.
c) 2— hydroxy butanoic acid
d) 3—hydroxy butanoic acid

17) The residue obtained after the crystallization of sugar from concentrated sugar cane juice is called?

a) Mother liquor
b) Filtrate
c) Extract
d) Molasses.

18) The oxidation of isopropyl alcohol will yield:

a) Propane
b) Propanol
c) Propanone
d) Propanoic acid

19) When phenol is heated with nitric acid strongly, the product is:

a) Picric acid.
b) Nitrobenzene
c) 2,4,6-trinitro benzene
d) benzene

20) Methyl alcohol is not used:

a) As a solvent
b) As an anti-freezing agent
c) As a substitute for petrol
d) For denaturing of ethyl alcohol

Answers

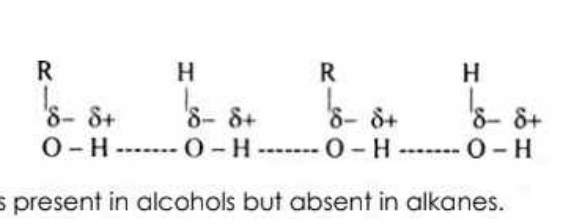
1)	b)	2)	a)	3)	b)	4)	c)	5)	c)
6)	d)	7)	a)	8)	b)	9)	d)	10)	b)
11)	d)	12)	b)	13)	b)	14)	c)	15)	b)
16)	b)	17)	d)	18)	c)	19)	a)	20)	c)

Short Questions and Answers.

Q1: Write down the physical properties of alcohol?

Answer

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



$$\overset{R}{\underset{\delta-\ \delta+}{\mathrm{O-H}}}\text{-------}\overset{H}{\underset{\delta-\ \delta+}{\mathrm{O-H}}}\text{-------}\overset{R}{\underset{\delta-\ \delta+}{\mathrm{O-H}}}\text{-------}\overset{H}{\underset{\delta-\ \delta+}{\mathrm{O-H}}}$$

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 an atom and an H atom via S bonds.

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

Q3: Write down the acidity of alcohols?

Answer

Due to the electronegativity 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.

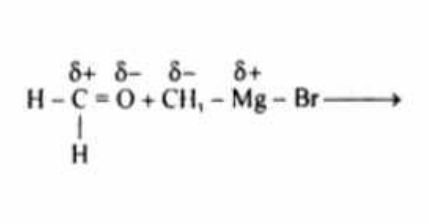
Answer

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.

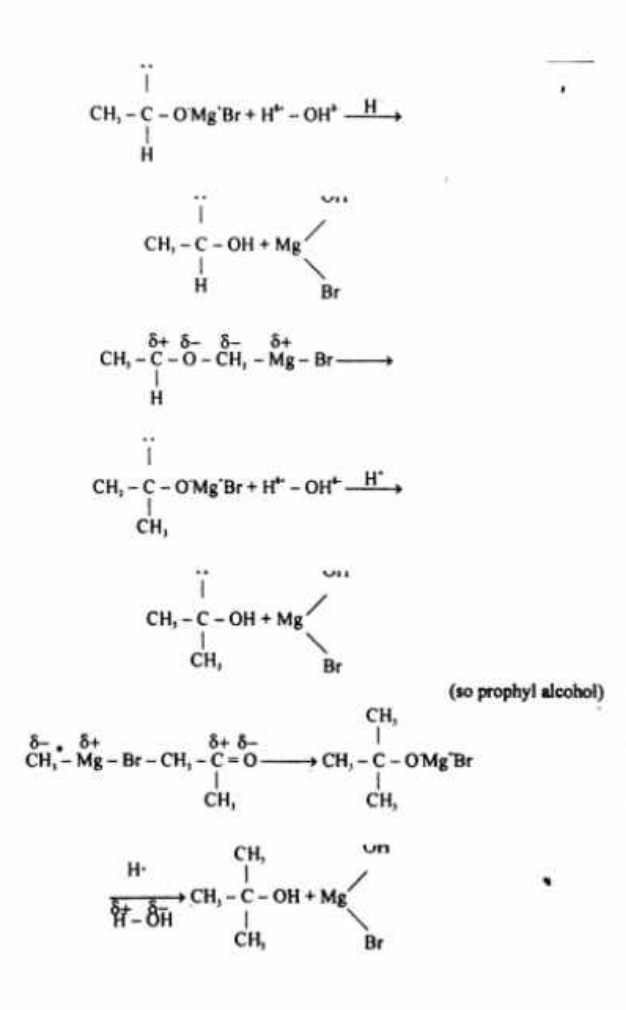
a) Primary Alcohol: Form aldehyde gives primary alcohol with Grignard's reagent.

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

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



$$H-\underset{H}{\overset{\delta+}{C}}=\overset{\delta-}{O}+\overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-Br\longrightarrow$$



Q5: Write down the reduction of aldehydes and ketones?

Answer

Reduction of aldehydes, ketones and calsonulic acid (estics in the presence 0f Ni, Pd or Pt) gives alcohol.

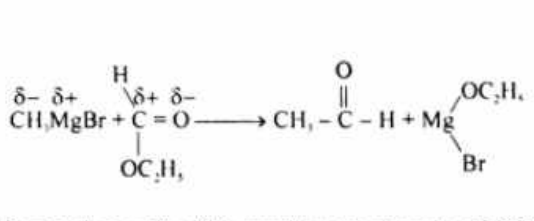
$LiAlH_4$ besides reducing aldehydes, ketones and ester, also reduces calsoxylic acid.

$$RCOOH + LiAlH_4 \longrightarrow RCH_2CH$$

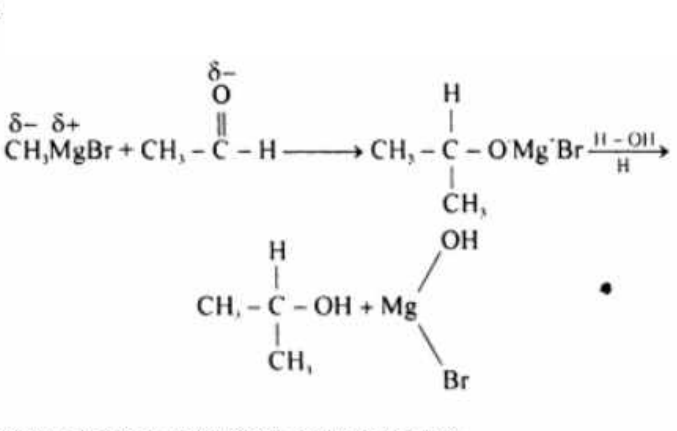
Q6: Write down the reaction of RLi or RMgx with esters?

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

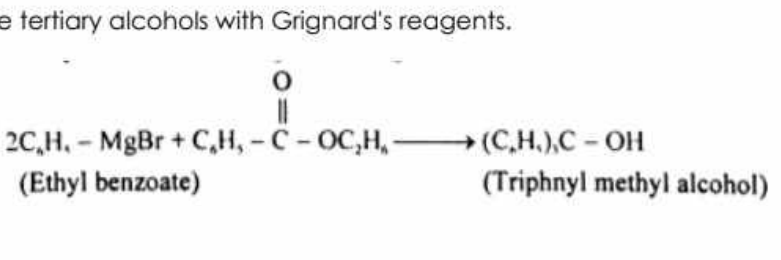
Answer



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 breaks.

$$CH - CH_2OH \xrightarrow{Neuclophile} CH_3 - CH_2 + OH$$

$$CH - CH_2O - H \xrightarrow{Neuclophile} CH_2CHO + H^-$$

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 a solution of ZnClO is concentrated HCl.

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

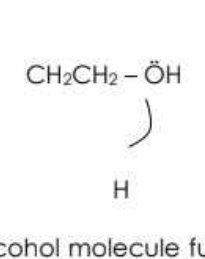
2) Secondary alcohol forms an insolution Sec alkyl chloride in 5-10 minutes.

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

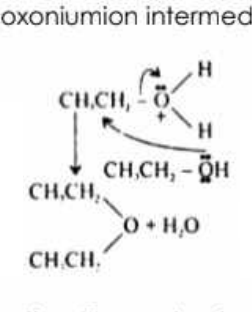
Q9: Write down the mechanisms for alcohol condensation to give an ether?

Answer

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



Step 2: The O of the second alcohol molecule functions as the nucleophile and attacks to displace the good leaving group a natural 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 suitable 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 susceptive esters.

This alkyl halides an also esters of halogen acids.

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

Glycerin reacts with a mixture on concentrated HN03 and H2S04 to give an ester called Nixoglecerine.

CH₂OH CH₂ONO₂
| |
CHOH + 3HNO₃ $\xrightarrow{H_2SO_4}$ CHONO₂ + 3H₂O
| |
CH₂OH CH₂ONO₂
Glycerine Nitroglycerine

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

Answer

Alcohols are easily oxidized by alkaline KMn04 or K2Cr07 + H2S04 solution to give different products.

i) Primary alcohols:

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

$$CH_3 - CH_2OH \xrightarrow{K_2Cr_2O_7+H_2SO_4} CH_3CHO + H_2O$$

Acctadehyde

$$CH_3CHO \xrightarrow{K_2Cr_2O_7+H_2SO_4} CH_3COOH$$

Acetic acid

ii) Secondary alcohol:

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

$$CH_3 - CHOH \xrightarrow{K_2Cr_2O_7+H_2SO_4} CH_3 - C = O$$

| |
CH₃ CH₃

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

Answer

Tertiary alcohol:

Tertiary alcohol is not oxidized by alkaline KMn04 when heated with a mixture of K2Cr207 and H2S04. It is first dehydrated to a alkane in the presence of acid. Then alkane is oxidized to a ketone and a carboxylic acid by K_2Cr_2O, and H_2SO_4.

CH₃ CH₃
| |
CH₃ – CH₂ – C – OH $\xrightarrow{K_2Cr_2O_7+H_2SO_4}$ CH₃ –CH – C = H₂O
| |
CH₃ CH₃

Cleavage of 1, 2 Diols.

Oxidation cleavage of Diols.

HO OH
| |
-C – C + HIO₄ ⟶ C = O + O = C + HIO₃ + H₂O
| |

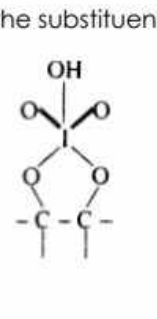
12 or uicinal diols are cleaved by periods and HIO_4 in two carbonyl compounds.

The reaction is selective for I, 2 diols.

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

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

The products are determined by the substituents on the diol.



Q13: Draw and explain the structure of phenols?

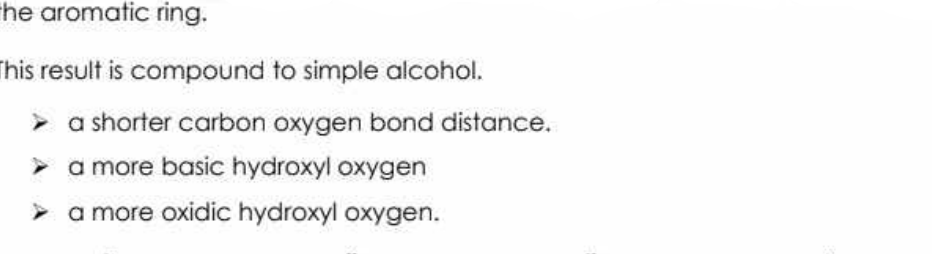
Answer

The alcohol functional group consist on an O atom bonded to a sp2 hybridized aromatic C atom and a H atom via O bonds.

Both the C-O and O-H bonds are polar due to the high electronegativity of the O atom. Conjugation exist between an unshared 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.

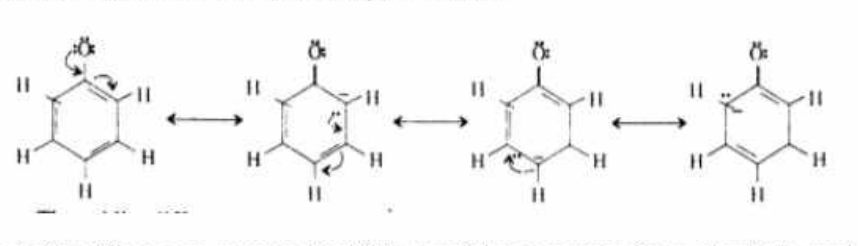


Q14: Write down the acidity of phenols?

Answer

Phenols are more acidic (PKa >>I0) 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.



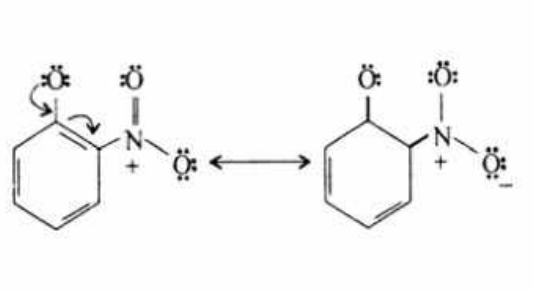
The acidity difference means that it is possible separate from alcohols and / or carboxylic acids.

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

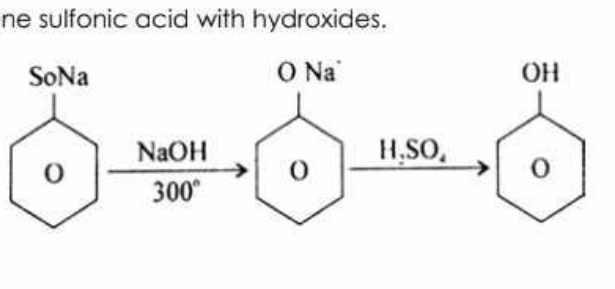
Substituents particularly those located others place to the OH group can dramatically influence the acidity of the phenol due to resonance and / or inductive effect. Electron withdrawing group enhance the acidity electron donating. Substituents decrease the acidity. The resonance sterilization of O-nitrophenol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



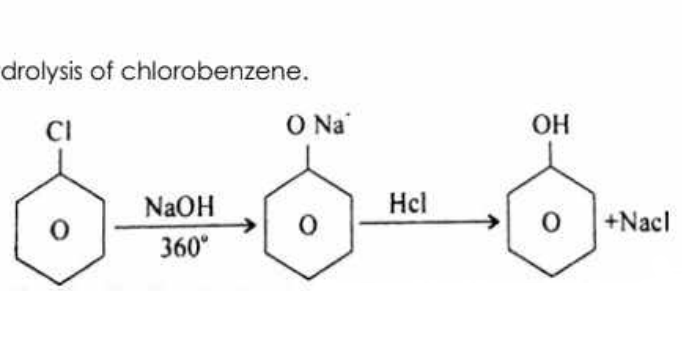
Q16: Write down the reaction for the preparation of phenol?

Answer

→ Rex of Benzene sulfonic acid with hydroxides.

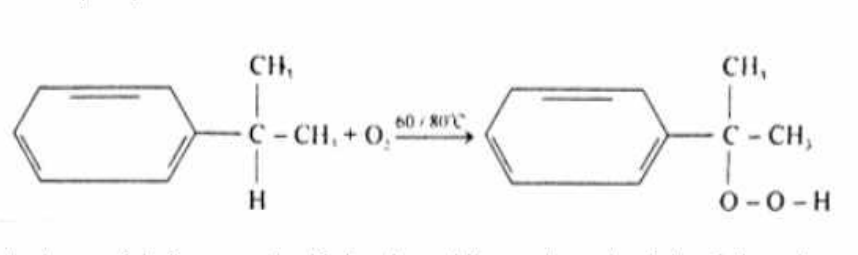


→ Rex of hydrolysis of chlorobenzene.

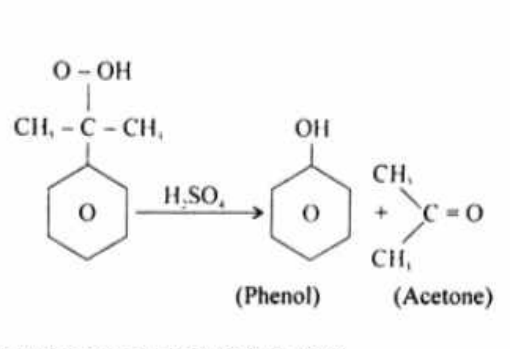


Acidic oxidation of cumene.

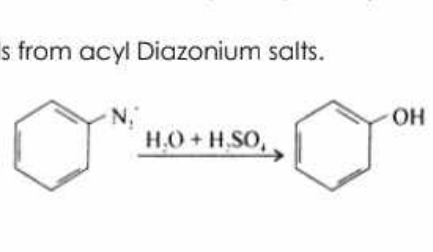
It is recently developed commercial method for the preparation of phenol, cumeneis oxidized by atmosphere oxygen is presence of mate catalyst in to cumene hydroproxide.



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


(Phenol) (Acetone)

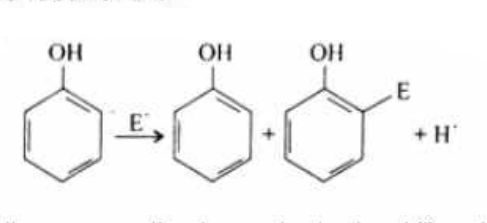
Preparation of phenols from acyl Diazonium salts.



Q17: Write down the reactions of phenols?

Answer

Electrophilic aromatic substitution:



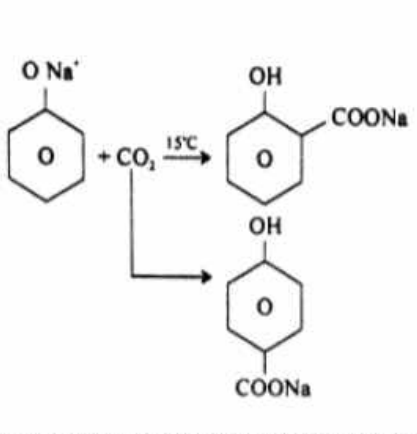
Phenols are potentially very reactive towards electrophilic substitution.

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.

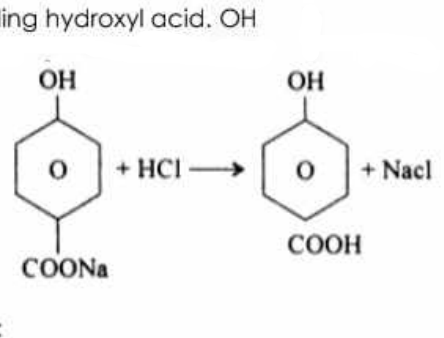
Q18: Write down the reaction of phenol with sodium metal?

Answer

Kolbe Schmitt reaction (carboxylation of phenol)

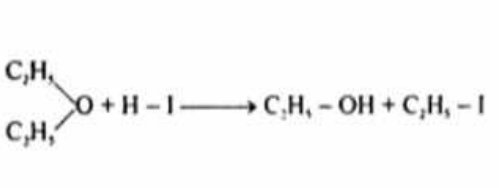


Carbon of CO_2 acts as electrophilic centre in this reaction acidification of the salt gives corresponding hydroxyl acid. OH

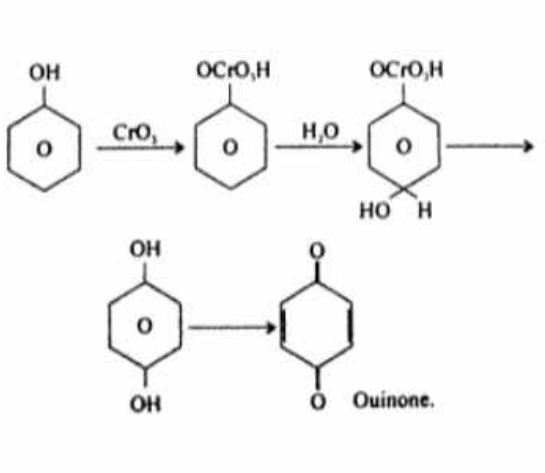


Oxidation of Phenols:

Phenols are very reactive towards diethyl ethers reacts with HI to form C₂Hs—OH and C₂HsI.



Oxidizing agents. The oxidation takes place through several steps eventually storying 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 solubility 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 melting points is 41 °c. Phenol are made acidic (Pka>>10) than alcohols (Pka>>16-20). It is

sparingly soluble in H_2O forming pink solution at room temperature but completely soluble above 68.5ºC. Phenols ion have resonance structure but alcohols do not have such type structure.

Q20: Write down the preparation of ethers?

Answer

By heating access of alcohol with concentrated H_2SO_4 at 140ºC dehydration to ethers occurs to ethers occurs.

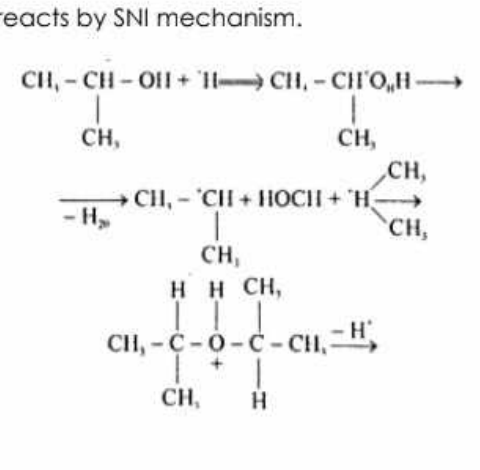
$$2CH_3CH_2OH \xrightarrow{140^0C} CH_3 - CH_2 - O - C_2H_5 + 2H_2O$$

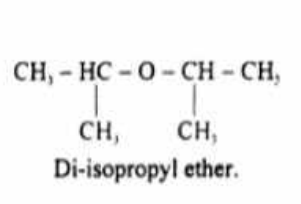
H2SO4

Primary alcohol reacts through SN2 mechanism

$$CH_3CH_2OH + CH_3 - CH_2 - OSo_3H \longrightarrow \underset{H}{CH_3 - CH_2 - O} - C_2H_5$$

Secondary alcohol reacts by SNI mechanism.





$$CH_3-\underset{CH_3}{HC}-O-\underset{CH_3}{CH}-CH_3$$

Di-isopropyl ether.

Two different primary alcohol give three ethers when treated with H2S04

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

Ter-butyl and ethyl alcohol give on ether.

Q21: Write down the physical properties of ethers?

Answer

Ethers are colourless, low boiling, highly flammable compounds.

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

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

Q22: How ethers show resistance to oxidation?

Answer

Ethers are resistance to attack by the usual chemical oxidizing agents. Moreover, reagent like NH3 Na, alkali and acids have no action on ethers.

Q23: How ethers react with H-Br?

Answer

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

R R
\ \
Ö - H – Br ⟶ Ö + ⟶ H + Br
/ /
R R

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-I to form oxonium ion which react with I to form R-OH and RI.

R R
\ \
Ö - H – I ⟶ Ö + ⟶ H + I
/ /
R R

R
\
Ö + - H +I ⟶ ROH + RT
/
R