22. ALCOHOLS, PHENOLS AND ETHERS

ALCOHOLS

1. INTRODUCTION

(a) These are the organic compounds in which –OH group is directly attached with carbon.

(b) These are hydroxyl derivatives of alkanes, mono alkyl derivatives of water.

(c) Their general formula is $C_nH_{n+1}OH$ or $C_nH_{2n+2}O$.

1.1 Classification of Alcohols

Mono, Di, Tri or Polyhydric Compounds

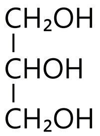
Alcohols and phenols may be classified as mono-, di-, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures as given below:

C_2H_5OH

Monohydric

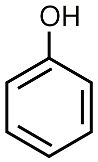
$HOCH_2CH_2OH$

Dihydric

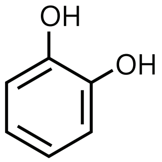


$CH_2OH-CHOH-CH_2OH$

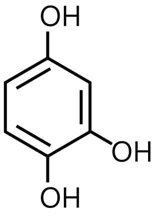
Trihydric



Monohydric



Dihydric



Trihydric

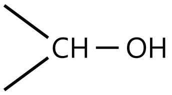
1.1.1 Compounds Containing Csp^3 – OH Bond

In this class of alcohols, the –OH group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified

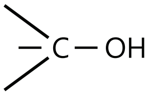
(a) **Primary, secondary and tertiary alcohols:** In these types of alcohols, the –OH group is attached primary secondary and tertiary carbon atom, respectively as depicted below.

$-CH_2-OH$

Primary (1°)



Secondary (2°)

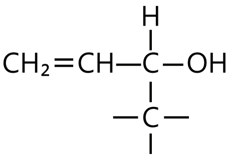


Tertiary (3°)

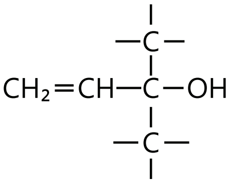
(b) **Allylic alcohols:** In these alcohols, the –OH group is attached to an sp^3 hybridised carbon next to the carbon-carbon double bond, i.e. to an allylic carbon. For example

$CH_2=CH-CH_2-OH$

Primary (1°)



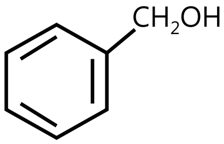
Secondary (2°)

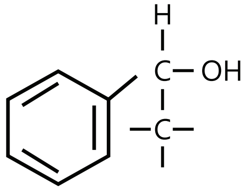


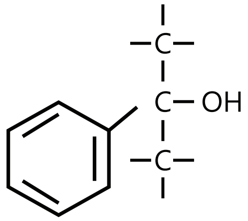
Tertiary (3°)

(c) **Benzylic alcohols:** In these alcohols, the –OH group is attached to an sp^3 –hybridized carbon atom next to an aromatic ring.

For example Allylic and benzylic alcohols may be primary, secondary or tertiary


Primary

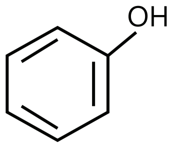
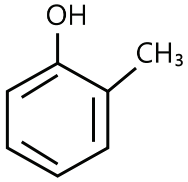

Secondary


Tertiary

1.1.2 Compounds Containing Csp^2–OH Bond

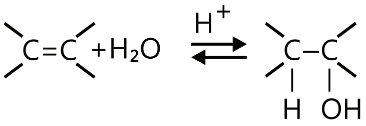
These alcohols contain –OH group bonded to a carbon- carbon double i.e., to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols

Vinylic alcohol : CH_2=CH-OH

2. PREPARATION OF ALCOHOLS

2.1 From Alkenes

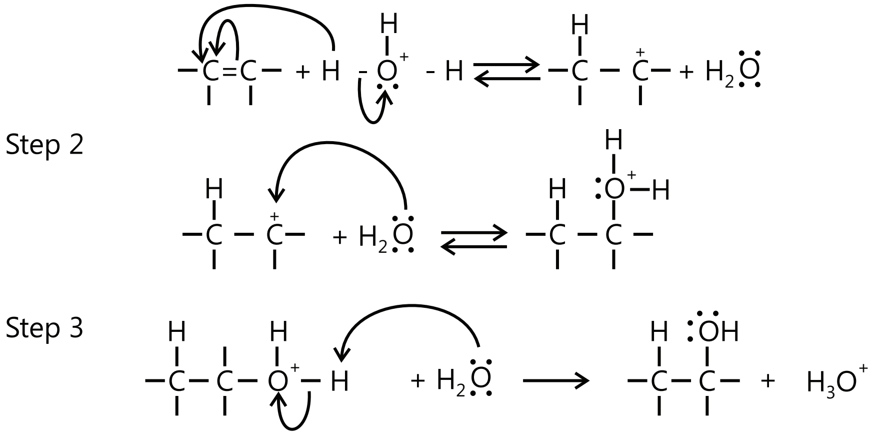


2.1.1 By Acid Catalyzed Hydration

Alkenes react with water in the presence of acid as catalyst to form alcohol. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markonikov's rule.

Mechanism: The mechanism of the reaction involves the following three steps:

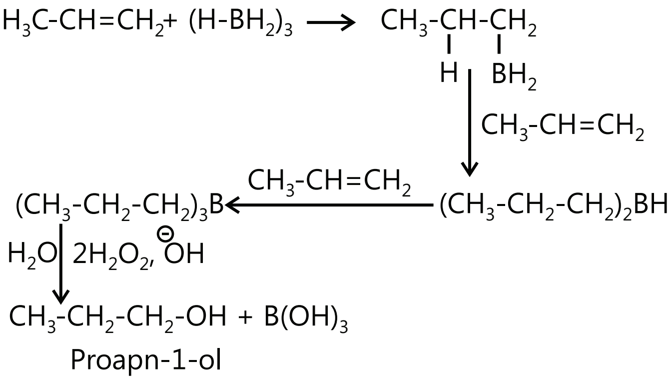
Step 1 $H_2O + H^+ \longrightarrow H_3O^+$



2.1.2 By Hydroboration-Oxidation

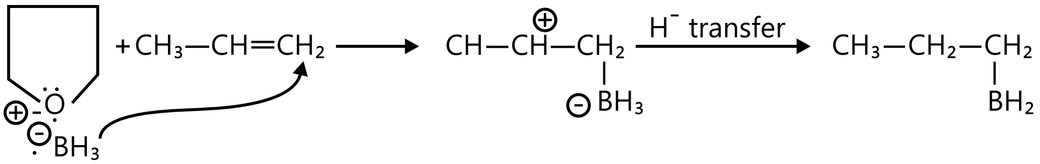
Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product. This is oxidized to alcohols in the presence of aq. sodium hydroxide (NaOH) and peroxide.

Note: This is the addition of water at double bond according to Anti-Markonikov Rule.

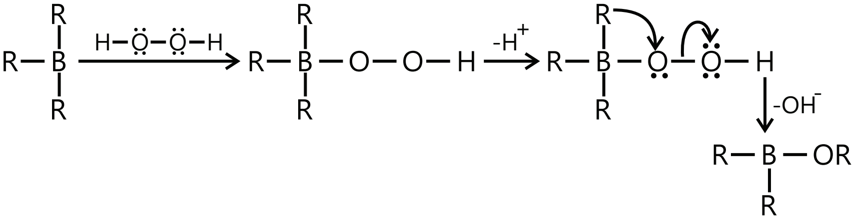


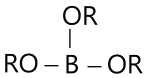
Mechanism of hydroboration – deboration

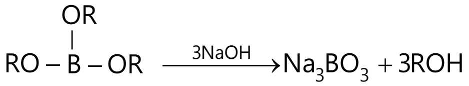
$$CH_3-CH=CH_2 \xrightarrow{B_2H_6\text{-}THF/H_2O_2/OH^-} CH_3-CH_2-CH_2-OH$$



These steps are repeated thrice to form $(CH_3-CH_2-CH_2)_3B$ and then



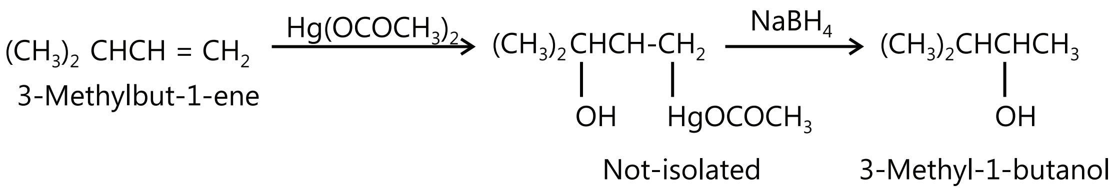

With H_2O_2, finally $RO-\overset{\displaystyle OR}{\overset{|}{B}}-OR$ is formed by above mentioned method.

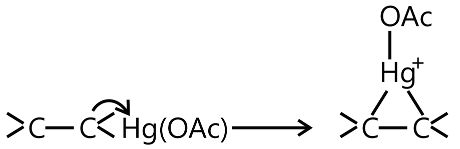

$$RO-\overset{\displaystyle OR}{\overset{|}{B}}-OR \xrightarrow{3NaOH} Na_3BO_3 + 3ROH$$

2.1.3 Oxymercuration Demercuriation

Involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a mercurinium ion, an organometallic cation containing a three-membered ring.

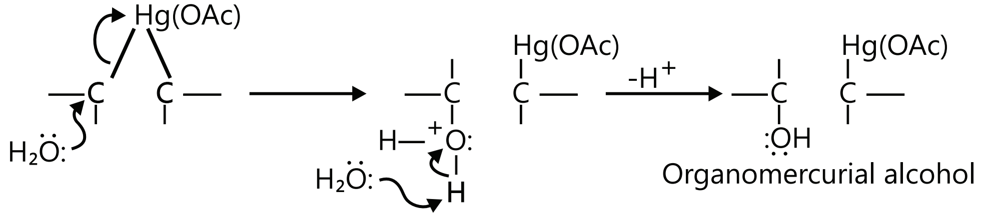
With mercuric acetate, the product is 3-methyl-2-butanol (Markonikov's addition with no rearrangement, oxymercuration-demercuration reaction)

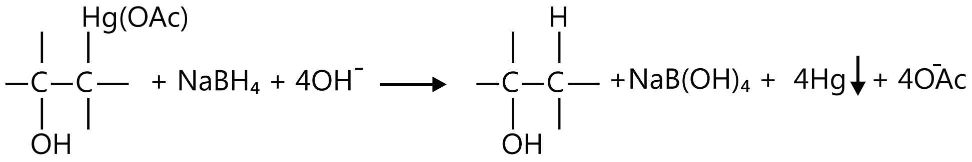




mercurinium ion

Mercuration commonly takes place in a solution containing water and an organic solvent to dissolve the alkene. Attack on the mercurinium ion by water gives (after deprotonation) an organomercurial alcohol.





$$\underset{\text{OH}}{-\mathrm{C}}-\overset{\text{Hg(OAc)}}{\mathrm{C}}- + NaBH_4 + 4OH^- \longrightarrow \underset{\text{OH}}{-\mathrm{C}}-\overset{\text{H}}{\mathrm{C}}- + NaB(OH)_4 + 4Hg\downarrow + 4\overset{-}{O}Ac$$

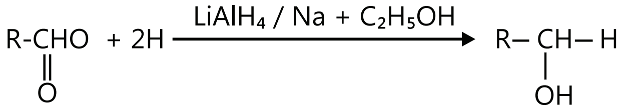
Organomercurial alcohol

alcohol

The second step is demercuration, to form the alcohol. Sodium borohydride (NaBH$_4$, a reducing agent replaces the mercuric acetate with hydrogen.)

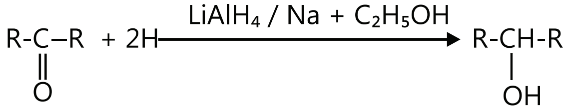
2.2 From Carbonyl Compounds

2.2.1 By Reduction of Carbonyl Compounds



$$\underset{\underset{\text{O}}{\|}}{\text{R-CHO}} + 2H \xrightarrow{LiAlH_4\ /\ Na\ +\ C_2H_5OH} \text{R}-\underset{\underset{\text{OH}}{|}}{\text{CH}}-\text{H}$$

1° alcohol

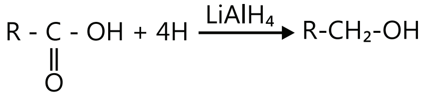


$$\text{R-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{–R} + 2H \xrightarrow{LiAlH_4\ /\ Na\ +\ C_2H_5OH} \text{R-}\underset{\underset{\text{OH}}{|}}{\text{CH}}\text{-R}$$

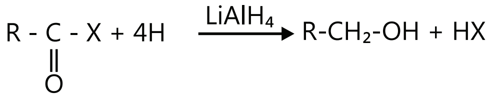
2° alcohol

2.3 From Acid Derivatives

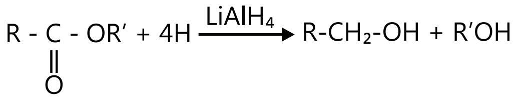
2.3.1 By Reduction of Acid and its Derivatives



$$\text{R - }\underset{\underset{\text{O}}{\|}}{\text{C}}\text{ - OH} + 4H \xrightarrow{LiAlH_4} \text{R-CH}_2\text{-OH}$$



$$\text{R - }\underset{\underset{\text{O}}{\|}}{\text{C}}\text{ - X} + 4H \xrightarrow{LiAlH_4} \text{R-CH}_2\text{-OH} + HX$$

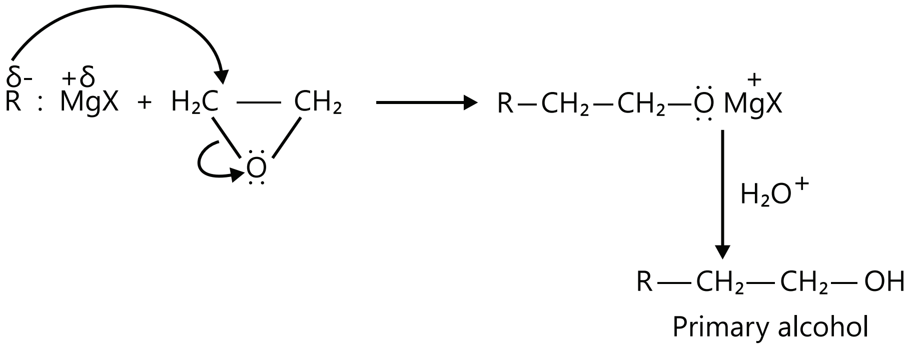


$$\text{R - }\underset{\underset{\text{O}}{\|}}{\text{C}}\text{ - OR}' + 4H \xrightarrow{LiAlH_4} \text{R-CH}_2\text{-OH} + R'OH$$

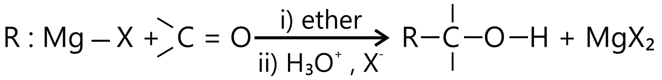
$RCOOCOR + 8H \xrightarrow{LiAlH_4} 2\ RCH_2OH + H_2O$

2.4 From Grignard Reagents

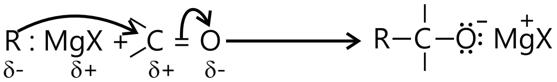
2.4.1 Reaction with Oxirane

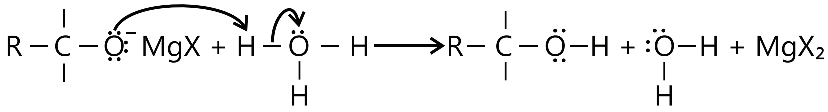


2.4.2 Reaction with Carbonyl Compounds

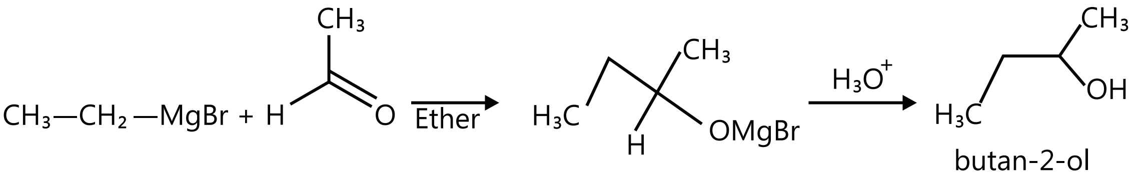


$$R:Mg-X + \rangle C=O \xrightarrow[\text{ii) } H_3O^+,\ X^-]{\text{i) ether}} R-\overset{|}{\underset{|}{C}}-O-H + MgX_2$$

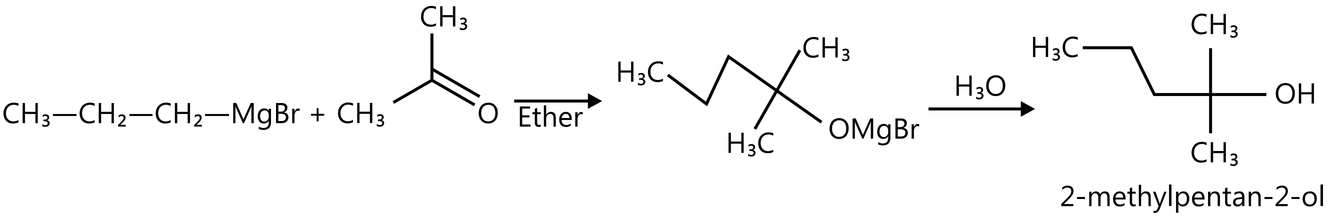




2.4.3 Reaction with Acetaldehyde



2.4.4 Reaction with Ketone



2.5 By Fermentation

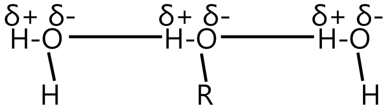
Fermentation is a low decomposition of complex organic compounds into simpler compound in the presence of suitable micro-organisms which are the source of biochemical catalyst known as yeast.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \longrightarrow \underset{\text{n–Butylalcohol}}{CH_3CH_2CH_2CH_2OH} + CH_3COCH_3$$

3. PHYSICAL PROPERTIES OF ALCOHOLS

(a) The lower alcohols are liquids while higher having more than 12 carbon atoms are solids. They are colourless, neutral substance with characteristic sweet, alcoholic odour and burning taste.

(b) The lower alcohols are readily soluble in water and the solubility decreases with the increase in molecular weight.

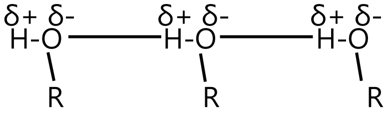


The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarized –OH groups present both in alcohols and water.

However, in higher alcohols, the hydrocarbon character (alkyl chain) increases, showing a steric hindrance. Hence, the solubility in water decreases.

When the ratio of C:OH is more than 4, alcohols have little solubility in water.

(c) Boiling points of alcohols are much higher than those of the corresponding alkanes. It is due to the intermolecular hydrogen bonding present between the hydroxyl groups of the two molecules of an alcohol with the result several molecules are associated to form a large molecule.



Among the isomeric alcohols, b.p. and m.p. show the following trend.

Primary > Secondary > Tertiary

This is because of the fact that in secondary and tertiary alcohols, the alkyl part (hydrogen character) outweighs the –OH group due to branching.

(d) Lower alcohols form solid addition compounds with anhydrous metallic salts like $CaCl_2$ and $MgCl_2$, viz., $CaCl_2$, $4C_2H_5OH$ and $MgCl_2.6C_2H_5OH$

By analogy to water of crystallization, these alcohols molecules are referred to as alcohols of crystallization. For this reason, alcohols cannot be dried over anhydrous calcium chloride.

MASTERJEE CONCEPTS

Preparation of alcohols:

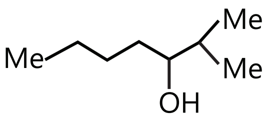
- Key takeaway - Hydration and oxymercuration-demercuration gives Markonikov's product but hydroboration-oxidation gives Anti-markonikov's product.
- Misconception - Hydroboration follows Markonikov's rule but in this case, the electron deficient species is Boron and not Hydrogen.
- Note - On replacing water with carboxylic acid in hydroboration-oxidation, the product obtained is alkane instead of alcohol.
- Note - Tertiary alcohols cannot be obtained by reduction of carbonyl compounds.
- Fact - If we use NaOH as a reductant in reduction of carbonyl compounds to alcohols, the process is known as Darzen's process.
- Tips and tricks - In conversion of oxirane to alcohols using Grignard's reagent, the alkyl part adds to the carbon with less steric hindrance as it proceeds via S_N2 mechanism.

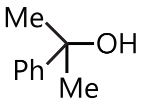
Physical properties of alcohols:

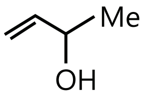
Alcohols generally have high boiling point because of hydrogen bonding.

Vaibhav Krishnan (JEE 2009, AIR 22)

Illustration 1: Write the IUPAC names, as their names by Carbinol system, and classify them as 1°, 2°, 3°, allylic, vinylic, benzylic, and propargylic of the following compound. **(JEE MAIN)**

(A) 

(B) 

(C) 

(D) Et_3C-OH

Sol:

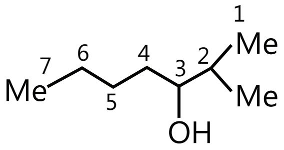
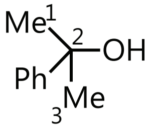
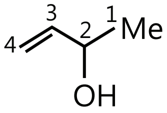
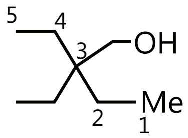
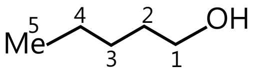
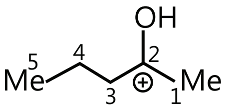
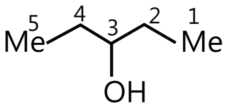
S.No.	Structure	IUPAC name	Carbinol system name	Type of alcohol
a.		2-Methyl heptan-3-ol	n-Butyl isopropyl carbinol	2°
b.		2-Phenyl propan-2-ol	Dimethyl phenyl carbinol	3°
c.		But-3-en-2-ol	Methyl vinyl carbinol	2° allylic
d.		3-Ethyl pentan-3-ol	Triethyl carbinol	3°

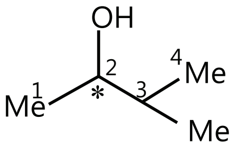
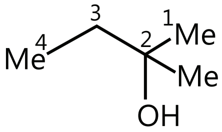
Illustration 2: (a) Write the structure of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC, common and carbinol names. Indicate each as 1°, 2° and 3° and also their stereoisomers, if any-

(b) Write the structures and names of all the cyclic and stereoisomers of C_4H_7OH. **(JEE MAIN)**

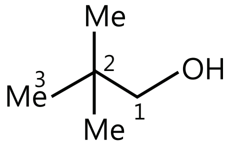
Sol: (a) (i)

	 (I)	 [(II) + (III)] (O.A)	 (IV)
IUPAC	Pentan-1-ol	(±)-Pentan-2-ol	Pentan-3-ol
Common	n-Amyl alcohol	—	—
Carbinol	n-Butyl carbinol	Methyl propyl carbinol	Diethyl carbinol
Type	1°	2°	2°

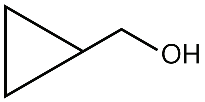
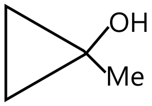
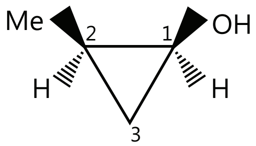
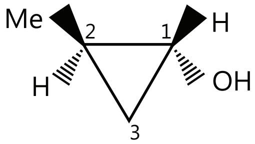
(ii) Write the four atoms in a straight chain and put Me and (–OH) at different positions.

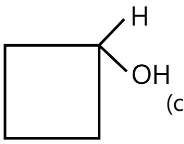
	 [(V) + VI] (O.A)	 (VII)
IUPAC	(±)-3-Methyl butan-2-ol	2-Methyl butan-2-ol
Common	—	t-Pentyl alcohol
Carbinol	Isopropyl methyl carbinol	Dimethylethyl carbinol
Type	2°	3°

(iii) Write the three C atoms in a straight chain and put two Me and (–OH) at different positions.

	 (VIII)
IUPAC	2,2-Dimethyl propan-1-ol
Common	Neopentyl alcohol
Carbinol	t-Butyl carbinol
Type	1°

Hence, total isomers including stereoisomers of $C_5H_{12}O$ are 8.

Name	 (I)	 (II)	 (III + IV) O.A (±) or racemate	 (III + IV) O.A (±) or racemate
	Cyclopropyl methanol	1-Methyl cyclopropanol	(±) or r-cis-2-Methyl cyclopropan-1-ol	(±) or r-trans-2-Methyl cyclopropan-1-ol

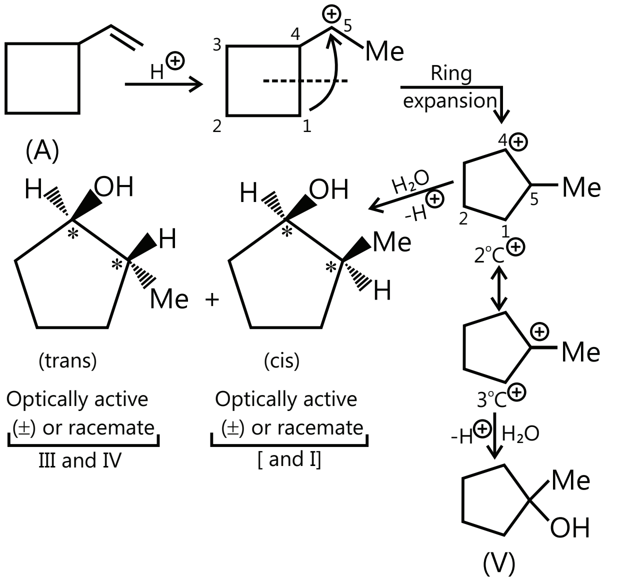


(VII)

(cyclobutanol) Hence, the total isomers including stereoisomers of C_4H_7OH are 7.

Illustration 3: Cyclobutyl ethene (A) $\xrightarrow{\text{Dil. } H_2SO_4}$ (B) (Number of isomeric products including stereo-isomers) **(JEE ADVANCED)**

Sol:



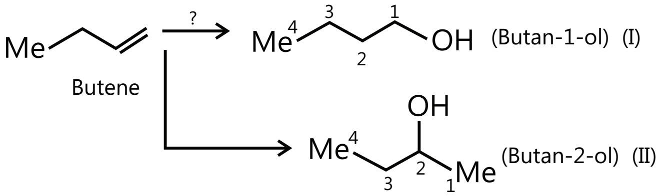
The total number of isomeric products including stereoisomers is 5.

Illustration 4: Synthesize the following:

(a) Butene to butanol and butan-2-ol

(b) 1-Chloro butane to pentanol and pentan-2-ol **(JEE MAIN)**

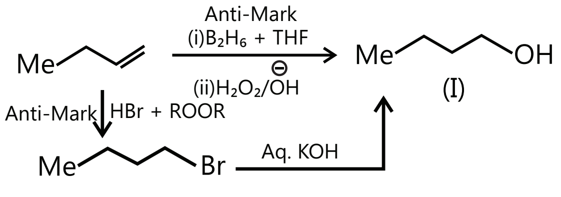
Sol: (a)

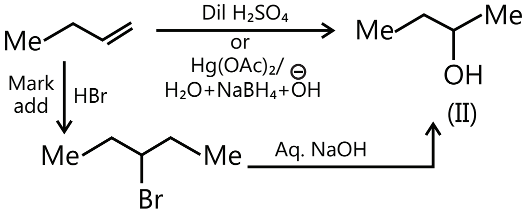


Hydroborato oxidation proceeds with Anti-Markovnikov addition, so it would give (I), while acid-catalysed hydration and mercuration – demercuration reaction proceed with Markovnikov addition, so it would give (II).

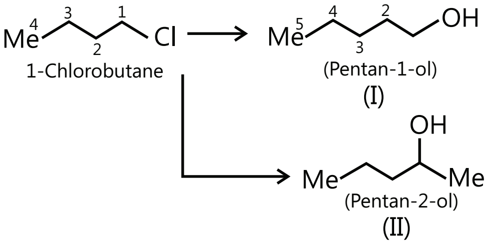
Synthesis:

a.

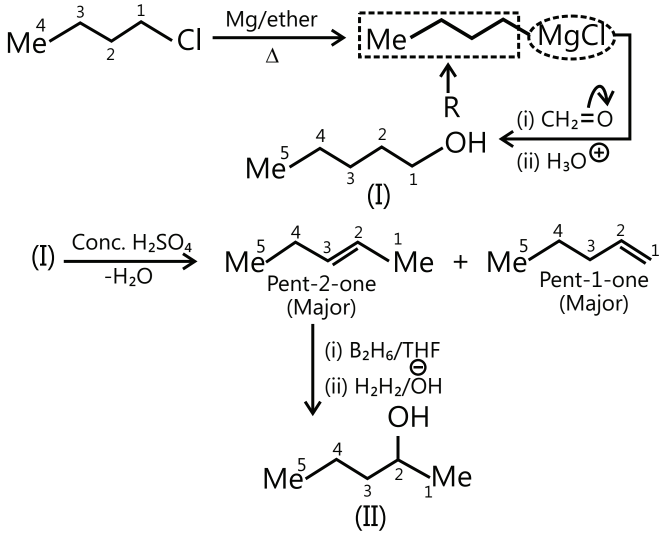




b.



The 4C-atom chain has to be increased to 5C-chain by a G.R. With $CH_2=O(HCHO)$



4. CHEMICAL PROPERTIES OF ALCOHOLS

4.1 Reaction with Active Metals-Acidic Character

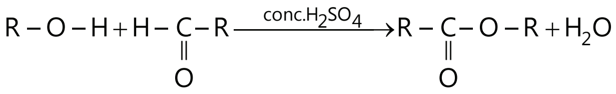
Alcohols are weakly acidic in nature due to which when they react with group one alkali metals they liberate hydrogen gas and form alkoxides.

$$2R-O-H + 2Na \rightarrow 2R-O^- Na^+ + H_2\uparrow$$

The acidic order of alcohols is MeOH > 1° > 2° > 3°. This acidic nature of alcohol is due to the presence of polar O-H bond.

4.2 Esterification/Reaction with Carboxylic Acid

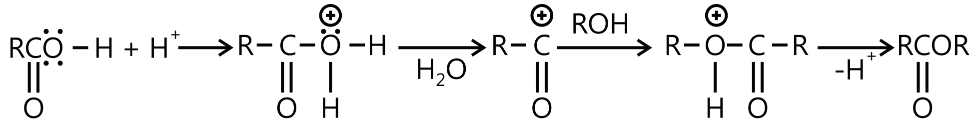
Reaction of alcohol with carboxylic acid in presence of sulphuric acid gives an ester. In this reaction sulphuric acid react as protonating agent as well as dehydrating agent.



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

Mechanism:

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

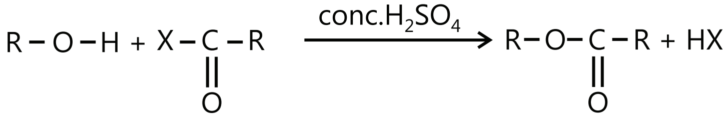


$$R\underset{\overset{\|}{O}}{C}\ddot{O}-H + H^+ \longrightarrow R-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{H}}{\overset{\oplus}{\ddot{O}}}-H \xrightarrow[H_2O]{} R-\underset{\overset{\|}{O}}{\overset{\oplus}{C}} \xrightarrow{ROH} R-\underset{\overset{|}{H}}{\overset{\oplus}{O}}-\underset{\overset{\|}{O}}{C}-R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

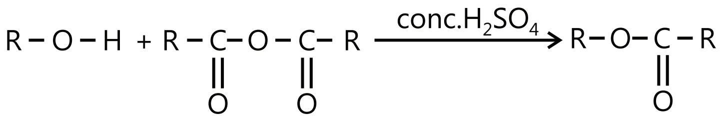
Note : The above reduction is laboratory method of ester preparation.

4.3 Reaction with Acid Derivatives

When alcohols are treated with acid derivatives , hydrogen of hydroxyl group is substituted by acyl group.

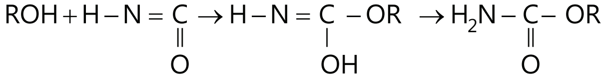


$$R-O-H + X-\underset{\underset{O}{\|}}{C}-R \xrightarrow{conc.H_2SO_4} R-O-\underset{\underset{O}{\|}}{C}-R + HX$$



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

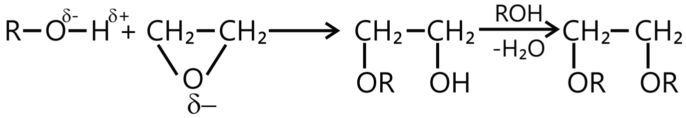
4.4 Reaction with Isocyanic Acid



$$ROH + H-N=\underset{\underset{O}{\|}}{C} \rightarrow H-N=\underset{\underset{OH}{|}}{C}-OR \rightarrow H_2N-\underset{\underset{O}{\|}}{C}-OR$$

Amino ester

4.5 Reaction with Ethylene Oxide



1,2-dialkoxy ethane

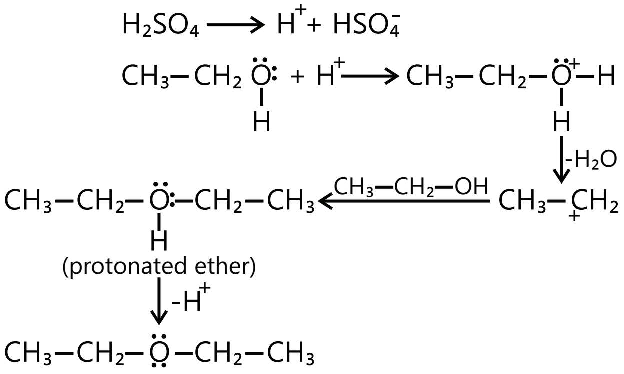
4.6 Reaction with Diazomethane

$$R-O-H + CH_2N_2 \longrightarrow \underset{\text{(ether)}}{R-O-CH_3}$$

4.7 Reaction with H_2SO_4

$$CH_3-CH_2-OH + H_2SO_4 \text{ (excess)} \xrightarrow{140^\circ C} CH_3-CH_2-O-CH_2-CH_3$$

Mechanism:



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

$$CH_3-CH_2\underset{\underset{H}{|}}{\ddot{O}}: + H^+ \longrightarrow CH_3-CH_2-\underset{\underset{H}{|}}{\ddot{O}^+}-H$$

$$\downarrow -H_2O$$

$$CH_3-CH_2-\underset{\underset{H}{|}}{\ddot{O}}\text{:}-CH_2-CH_3 \xleftarrow{CH_3-CH_2-OH} CH_3-\overset{+}{C}H_2$$

(protonated ether)

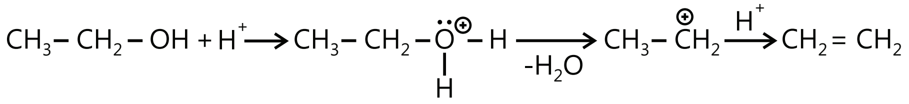
$$\downarrow -H^+$$

$$CH_3-CH_2-\ddot{O}-CH_2-CH_3$$

(ii) $$CH_3-CH_2-OH + \underset{\text{(excess)}}{H_2SO_4} \xrightarrow{160^\circ C} CH_2=CH_2$$

Mechanism:

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



$$CH_3-CH_2-OH + H^+ \longrightarrow CH_3-CH_2-\overset{\oplus}{\underset{H}{O}}-H \xrightarrow[-H_2O]{} CH_3-\overset{\oplus}{C}H_2 \xrightarrow{H^+} CH_2=CH_2$$

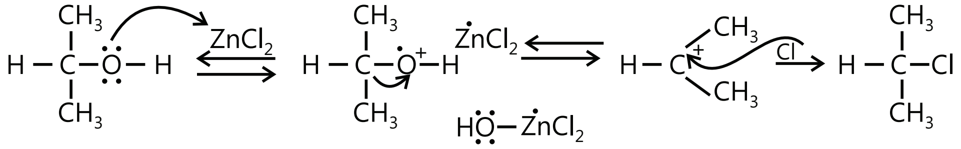
4.8 Action of Halogen Acids

Alcohol react with HX to give RX. Reactivity order of ROH is 1°>2°>3°. Hence primary alcohols react in presence of catalyst (If X is Cl Luca's reagent and if X is Br small amount of H_2SO_4), but secondary and tertiary alcohols can react in absence of catalyst. However, when alcohol react with HI/Red P they reduced in hydrocarbon.

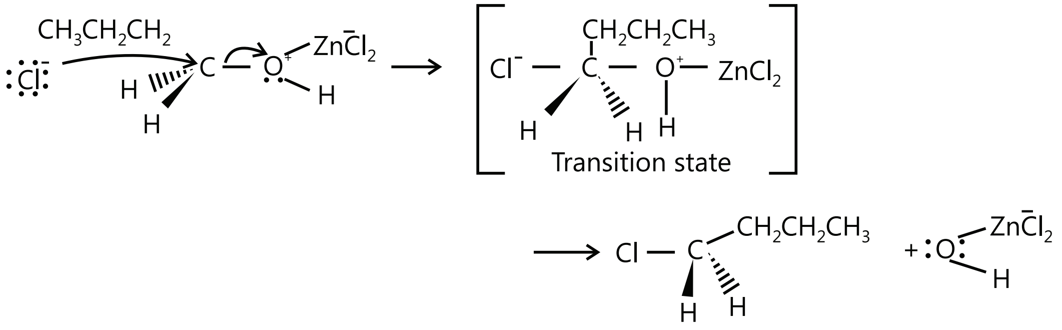
$$C_2H_5OH + HCl \xrightarrow{\text{anhy. } ZnCl_2} C_2H_5Cl + H_2O$$

The reactivity of halogens is in the order: HI > HBr > HCl

S_N1 reaction with the Lucas reagent (fast)



S_N2 reaction with Lucas reagent is slow:

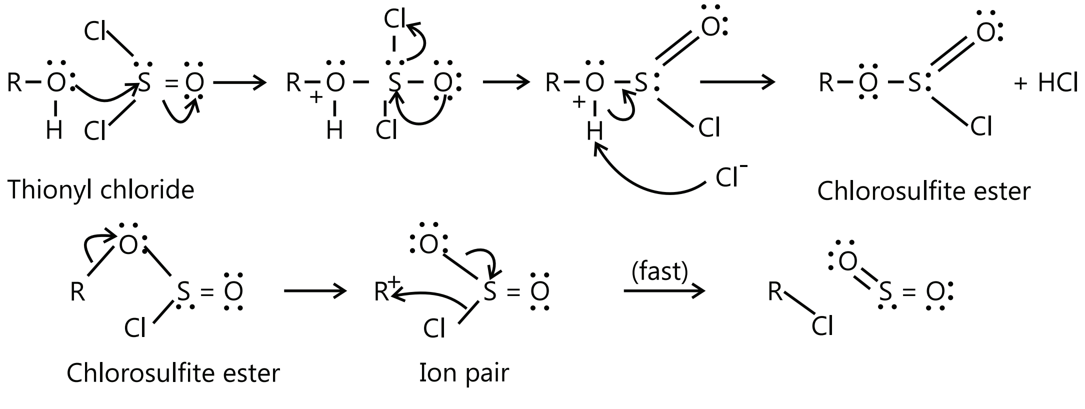


4.9 Action of Thionyl Chloride

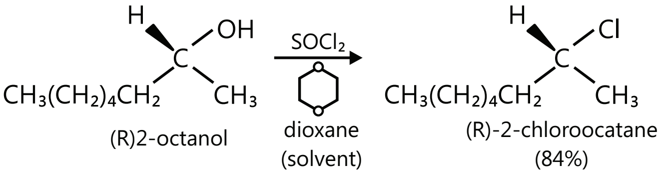
Alcohols react with thionyl chloride to form alkyl halide and reaction is called diarzon process.

$C_2H_5OH + SOCl_2 \rightarrow C_2H_5Cl + HCl + SO_2$

Meachanism



This mechanism resembles the S_N1, except that the nucleophile is delivered to the carbocation by the leaving group, giving retension of configuration as shown in this following example. (Under different conditions, retension of configuration may not be observed).



4.10 Action of Phosphorus Halides (PX_5 and PX_3)

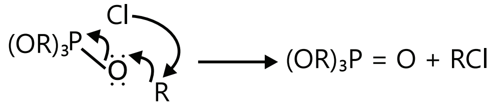
Phosphorous halide react with alcohols to form corresponding haloalkanes.

For Example: $C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + HCl + POCl_3$

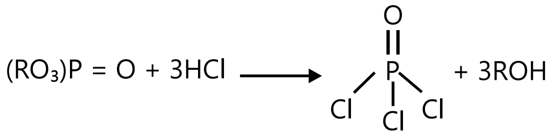
Mechanism:

$3\ R\text{-}OH + PCl_5 \longrightarrow P(OR)_3Cl_2 + 3HCl$

$P(OR)_2Cl_2 + ROH \longrightarrow P(OR)_3Cl + HCl$



$(OR)_3P\text{-}Cl$ … $\longrightarrow (OR)_3P = O + RCl$



$$(RO_3)P = O + 3HCl \longrightarrow POCl_3 + 3ROH$$

4.11 Action of Ammonia

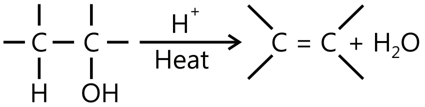
When vapours of ammonia with alcohol passed over heated alumina mixture of primary, secondary and tertiary amines is formed.

$$ROH + NH_3 \xrightarrow{Al_2O_3} \underset{1^0\text{amine}}{RNH_2} \xrightarrow[Al_2O_3]{ROH} \underset{2^0\text{amine}}{R_2NH} \xrightarrow[Al_2O_3]{ROH} \underset{3^0\text{amine}}{R_3N}$$

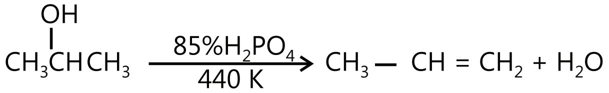
The ease of dehydration of alcohols is in the order Tertiary > Secondary > Primary

4.12 Dehydration

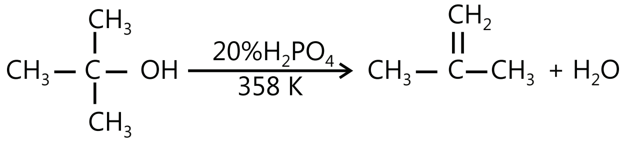
Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with acid e.g., concentrated H_2SO_4 or H_3PO_4 or catalysts such as anhydrous zinc chloride or alumina



$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow[\text{Heat}]{H^+} >C=C< + H_2O$$

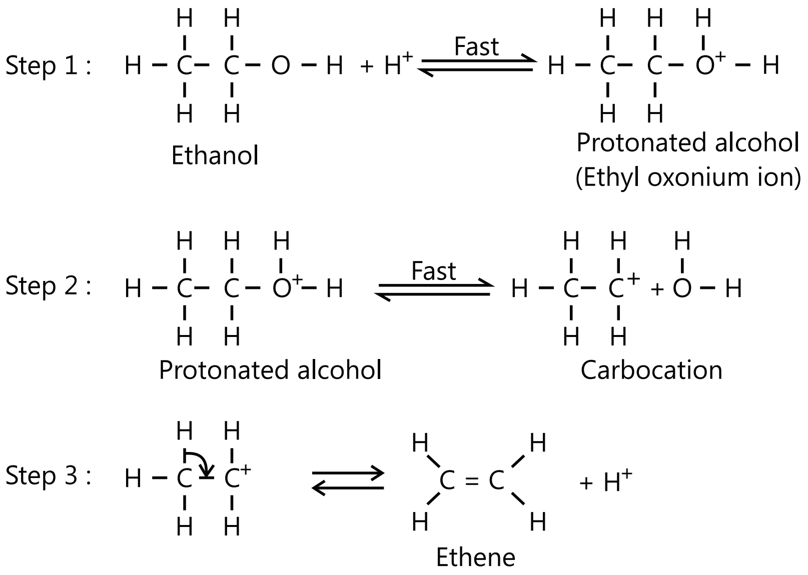


$$CH_3\overset{OH}{C}HCH_3 \xrightarrow[440\ K]{85\%H_2PO_4} CH_3-CH=CH_2 + H_2O$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[358\ K]{20\%H_2PO_4} CH_3-\overset{CH_2}{\overset{||}{C}}-CH_3 + H_2O$$

Mechanism of dehydration



The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethane is removed as it is formed. The relative ease of dehydration, i.e., 3° > 2° > 1°, of alcohols follows the order of stability of carbonium ions.

(a) With heated alumina (Al_2O_3): When vapours of an alcohol are passed over heated alumina, different products are obtained at different temperatures as given below:

(i) At 513 – 523 K (240° – 250° C), intermolecular dehydration takes places to form ethers e.g.,

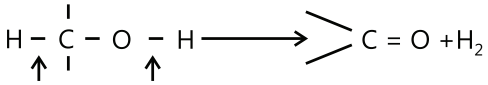
$$\underset{\text{Ethyl alcohol}}{2CH_3CH_2OH} \xrightarrow[\text{513-523 K}]{Al_2O_3} \underset{\text{Diethyl ether}}{CH_3CH_2-O-CH_2CH_3} + H_2O$$

(ii) At 633 K (360°C), intermolecular dehydration takes place to form alkenes, e.g.,

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{633K}]{Al_2O_3} \underset{\text{Ethene}}{CH_2 = CH_2} + H_2O$$

4.13 Oxidation of Alcohols

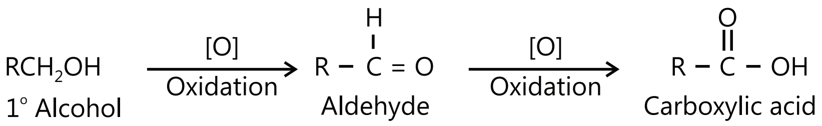
(a) Oxidation: Oxidation of alcohols involves the formation of carbon-oxygen double bond with cleavage of O–H and C–H bond.



$$H-\overset{|}{\underset{|}{C}}-O-H \longrightarrow \; >C=O + H_2$$

These are also called dehydrogenation reactions since it involves loss of hydrogen from the alcohol molecule. The oxidation of alcohols can be carried out with a variety of reagents such as neutral, acidic or alkaline $KMnO_4$, acidified $K_2Cr_2O_7$ or dil. HNO_3. The ease of oxidations and nature of the products, however, depends upon the type of alcohol used.

(i) Primary Alcohols are easily oxidized first to aldehydes and then to acids, both containing the same number of carbon atoms as the original alcohol.

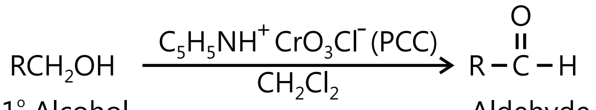


$$\underset{1^\circ\text{ Alcohol}}{RCH_2OH} \xrightarrow[\text{Oxidation}]{[O]} \underset{\text{Aldehyde}}{R-\overset{H}{\overset{|}{C}}=O} \xrightarrow[\text{Oxidation}]{[O]} \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH}$$

E.g., $CH_3CH_2OH+[O] \xrightarrow[-H_2O]{K_2Cr_2O_7\ +\ DilH_2SO_4} CH_3CHO \xrightarrow{[O]} CH_3COOH$

Ethyl alcohol Acetaldehyde Acetic acid

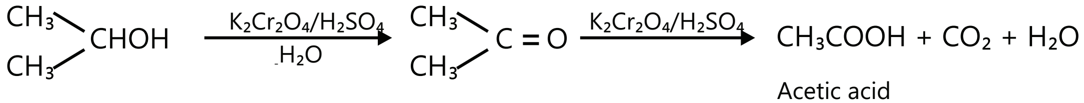
The oxidation can, however, be stopped at the aldehyde stage if Cr(VI) reagent such as Collin's reagent ($CrO_3.2C_5H_5N$, chromium trioxide-pyridine complex), Corey's reagent or pyridinimum chlorochromate (PCC, $CrO_3.C_5H_5N.HCl$ or C_5H_5NH + CrO_3Cl^-) pyridinimum dichromate [PDC, $(C_5H_5NH)_2^{2+}$ $Cr_2O_7^{2-}$] in anhydrous medium (i.e., CH_2Cl_2) are used as the oxidizing agents.



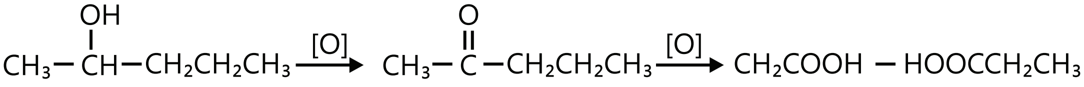
$$RCH_2OH \xrightarrow[CH_2Cl_2]{C_5H_5NH^+ CrO_3Cl^- (PCC)} R-\overset{\overset{O}{\|}}{C}-H$$

1° Alcohol Aldehyde

(ii) **Secondary Alcohols** are easily oxidized to ketones with the same number of carbon atoms. However, ketones resist further oxidation but in some conditions, they are oxidized to carboxylic acids containing lesser number of carbon atoms than the original alcohol.



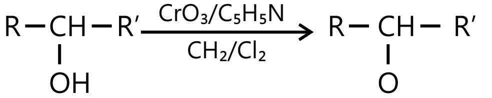
Isopropyl alcohol Acetone Acetic acid



$$CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CH_2CH_3 \xrightarrow{[O]} CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3 \xrightarrow{[O]} CH_2COOH - HOOCCH_2CH_3$$

Pentane-2-ol Pentane-2-one Acetic acid Propionic acid

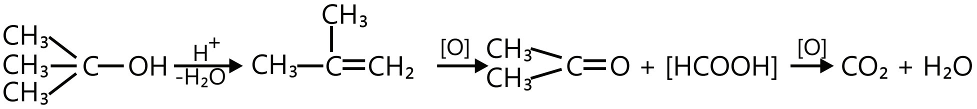
This oxidation be stopped at the ketone stage by using chromic anhydride (CrO_3)



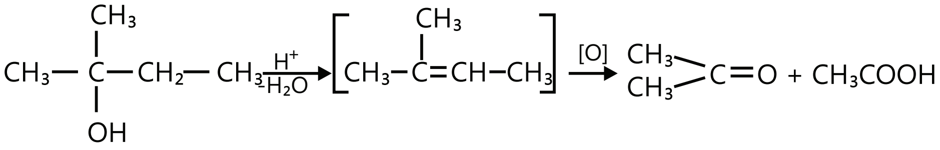
$$R-\underset{\underset{OH}{|}}{C}H-R' \xrightarrow[CH_2/Cl_2]{CrO_3/C_5H_5N} R-\underset{\underset{O}{|}}{C}H-R'$$

Ketone

(iii) **Tertiary Alcohols** are resistance to oxidation in neutral or alkaline $KMnO_4$ solution but are readily oxidized in acidic solution ($K_2Cr_2O_7/H_2SO_4$ or $KMnO_4/H_2SO_4$) to a mixture of a ketone, and an acid each containing lesser number of carbon atoms than the original alcohol. The oxidation presumably occurs via alkenes formed through dehydration of alcohols under acidic conditions. For example



tert-Butyl alcohol 2-Methylprop-1-ene Acetone Formic acid

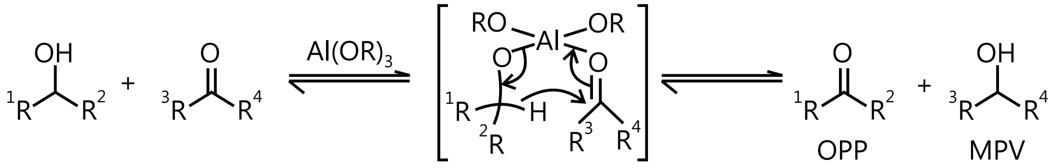


2-Methylbutan-2-ol 2-Methylbut-2-ene Acetone Acetic acid

4.14 Oppenauer Oxidation

The aluminium-catalyzed hydride shift from the α-carbon of an alcohol component to the carbonyl carbon of a second component, which proceeds over a six-membered transition state, is named Meerwein-Ponndorf-Verley-Reduction (MPV) or Oppenauer Oxidation (OPP) depending on the isolated product. If aldehydes or ketones are the desired products, the reaction is viewed as the Oppenauer Oxidation.

Non-enolizable ketones with a relatively low reduction potential, such as benzophenone, can serve as the carbonyl component used as the hydride acceptor in this oxidation.



Action of heated copper: Different classes of alcohols give different products when their vapors are passed over heated copper at 573 K (300° C)

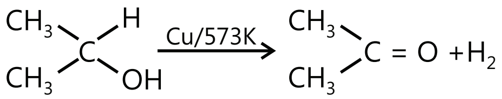
(a) **Primary alcohols** undergo dehydrogenation to give aldehydes.

$$CH_3CH_2OH \xrightarrow{Cu/573K} CH_3\,CHO + H_2$$

Ethanol
Ethyl alcohol

Ethanal
Acetaldehyde

(b) **Secondary alcohols** also undergo dehydrogenation to give ketones.

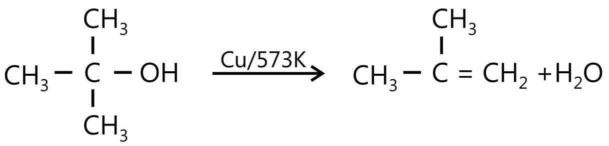


$$(CH_3)(CH_3)C(H)(OH) \xrightarrow{Cu/573K} (CH_3)(CH_3)C = O + H_2$$

Propan-2-ol
(Isopropyl alcohol)

Propanone
(Acetone)

(c) **Tertiary alcohols,** however, undergo dehydration to form alkenes.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow{Cu/573K} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2+H_2O$$

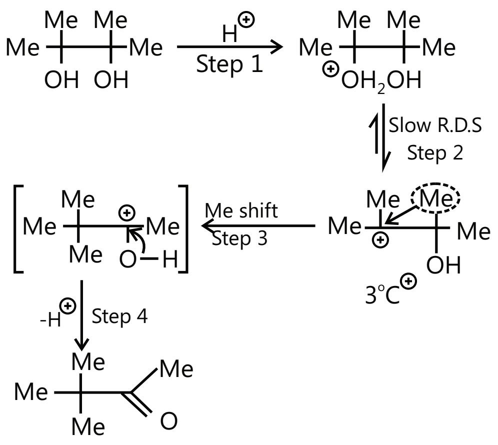
2-Methylpropan-2-ol
(tert-Butyl alcohol)

2-Methylpropene

4.15 Pinacol-Pinacolone Rearrangement Reaction

When pinacols (mostly ditertiary alcohols) are treated with mineral acids, acid chlorides, $ZnCl_2$ or other electrophilic reagent, they rearrange to form ketones called pinacolones with the elimination of H_2O.

Mechanism:



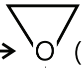
4.16 Dihydric Alcohols

Ethylene glycol or ethane-1, 2-diol

(a) Preparation:

(i) $3CH_2 = CH_2 + \text{(alkaline) } KMnO_4 + 4H_2O$

$\longrightarrow 3HOH_2C\text{-}CH_2OH + 2MnO_2 + 2KOH$

(ii) $CH_2 = CH_2 \xrightarrow[575\ K]{O_2/Ag}$  (Epoxy ethane) or

(Ethylene epoxide) $\xrightarrow[\text{Hydrolysis}]{H_2O/473K}$ $HOH_2C\text{-}CH_2OH$

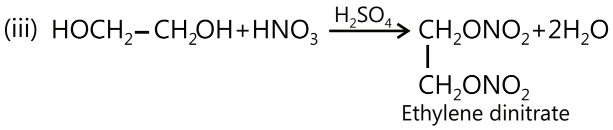
Ethylene glycol undergoes extensive intermolecular H-bonding . As a result, dihydric alcohols are highly associated and have high b.p., high viscosity, and are highly soluble in H_2O.

(b) Reactions:

(i) $HOCH_2-CH_2OH \xrightarrow[\text{or } SOCl_2]{PCl_5 \text{ or } HCl,\ 433K} CH_2Cl-CH_2Cl$

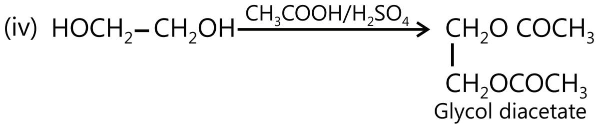
(ii) $HOCH_2-CH_2OH \xrightarrow[-H_2O]{2HI} [I\text{-}CH_2\text{-}CH_2\text{-}I]$

$\longrightarrow CH_2{=}CH_2 + I_2$

(iii) 

$$HOCH_2-CH_2OH + HNO_3 \xrightarrow{H_2SO_4} \begin{array}{l} CH_2ONO_2 + 2H_2O \\ | \\ CH_2ONO_2 \end{array}$$

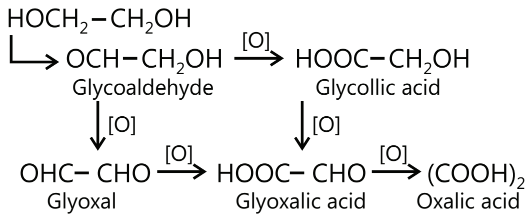
Ethylene dinitrate

(iv) 

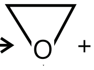
$$HOCH_2-CH_2OH \xrightarrow{CH_3COOH/H_2SO_4} \begin{array}{l} CH_2O\ COCH_3 \\ | \\ CH_2OCOCH_3 \end{array}$$

Glycol diacetate

(c) Oxidation: Ethylene glycol on oxidation with conc. HNO_3 mainly gives glycolic acid and oxalic acid. The other oxidation products such as glyoxal and glyoxalic acid are also formed in small quantities because they are more readily oxidized than glycol itself.



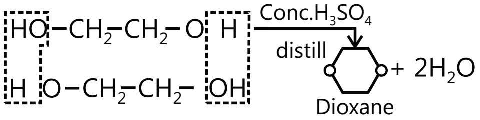
(d) Dehydration:

(i) $HOCH_2 - CH_2OH \xrightarrow{773K}$  $+ H_2O$

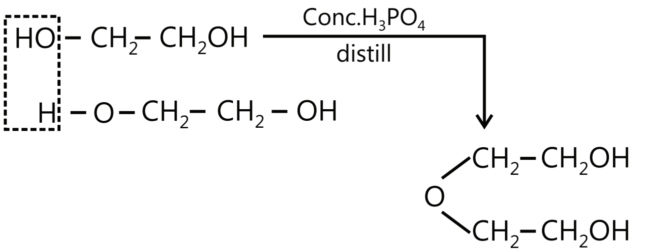
(ii) $HOCH_2 - CH_2OH \xrightarrow[-H_2O]{\text{Anhd.}ZnCl_2} [CH_2 = CHOH]$

Vinyl alcohol

$\xrightleftharpoons{\text{Tautomerise}} CH_3- CHO$

(iii) With conc. H_2SO_4: 

(iv)



Diethylene glycol

Trihydric Alcohols; Glyerol or Glycerine 1, 2, 3-Propanetriaol

(a) Preparation:

(i) $$CH_3CH=CH_2 \xrightarrow[-HCl]{Cl_2 773K} Cl-CH_2-CH=CH_2$$

$$\xrightarrow[423\text{ K, 1-2 atm}]{\text{aq. KOH or aq. }Na_2CO_3} \underset{\text{Allyl alcohol}}{HO-CH_2-CH=CH_2}$$

$$\xrightarrow[Cl^{\oplus}\ \overset{\ominus}{O}H]{HOCl} HO-CH_2-CHCl-CH_2OH$$

$$\xrightarrow[-NaCl]{\text{aq. NaOH}} HOCH_2-CHOH-CH_2OH$$

(b) Properties: Due in the presence of three (–OH) groups, it undergoes extensive intermolecular H-bonding and thus it has high boiling point viscosity and is highly soluble in H_2O.

(c) Reaction: When glycerol is treated with a small amount of HI or PI_3 allyl iodide is formed.

$$HOCH_2-CHOH-CH_2OH \xrightarrow{3HI\ (-3H_2O)} \underset{\substack{\text{1,2,3-Triiodopropane (glycerol tri-iodide)}\\ \text{(Unstable)}}}{[ICH_2-CHI-CH_2I]} \xrightarrow{I_2} \underset{\text{Allyliodide}}{CH_2=CH-CH_2I}$$

When large moment of HI is used, the main product is isopropyl iodide.

$$\begin{tikzcd} \underset{\text{Allyliodide}}{CH_2=CH-CH_2I} \arrow[r, "+HI"] & {[ICH_3-CHI-CH_2I]} \arrow[d, "-I_2"] \\ CH_3-CHI-CH_3 & CH_3-CH=CH_2 \arrow[l, "+HI"'] \end{tikzcd}$$

(d) Nitration:

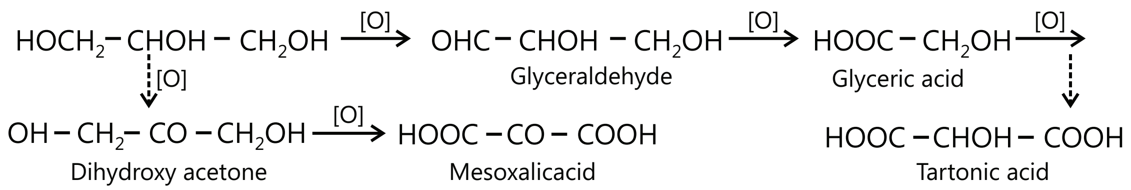
$$HOCH_2-CHOH-CH_2OH \xrightarrow[(283\text{-}298\text{ K})]{\substack{Conc.HNO_3\\ +Conc.\ H_2SO_4}} \underset{\text{(Glyceryl trinitrate)}}{O_2NOCH_2-CHONO_2}-\underset{\text{(Nitroglycerine)}}{CH_2ONO_2}$$

A mixture of glycerol trinitrate and glyceryl dinitrate absorbed on Kieselguhr is called dynamite discovered by Alfred Noble.

(e) Dehydration with $KHSO_4$ or conc. H_2SO_4:

$$\begin{tikzcd} HOCH_2-CHOH-CH_2OH \arrow[dr, "{KHSO_4,\ 473\text{-}508K}", "-2H_2O"'] & \\ CH_2=CH-CHO \arrow[r, shift left, harpoon, "\text{Unstable}"] & {[CH_2=C=CHOH]} \arrow[l, shift left, harpoon, "\text{Tautomerisation}"] \end{tikzcd}$$

(f) Oxidation:



(i) With dil. HNO_3, a mixture of glyceric and tartaric acid is obtained.

(ii) With conc. HNO_3 mainly glyceric acid is obtained.

(iii) With bismuth nitrate, only mesoxalic acid is obtained.

(iv) Mild oxidizing agent, such as Br_2 water, sodium hypobromite (Br_2/NaOH) and fenton's regagent (H_2O_2 + $FeSO_4$) give a mixture of glyceraldehyde and dihydroxy acetone. This mixture is called glycerose.

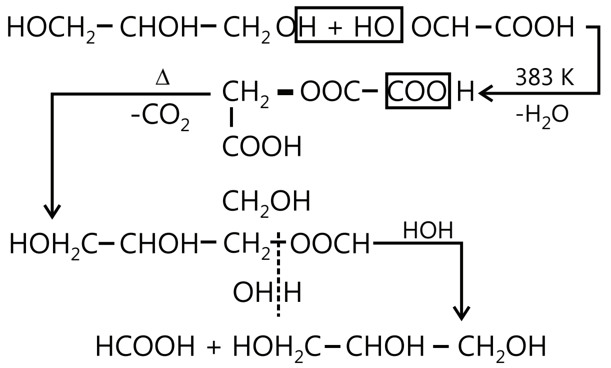
(g) Reaction with HIO_4: $HOCH_2-CHOH-CH_2OH + 2HIO_4$

$$\xrightarrow{\Delta} 2HCHO + HCOOH + 2HIO_3 + H_2O$$

(h) With acidic $KMnO_4$: $HOCH_2-CHOH-CH_2OH + 6[O]$

$$\longrightarrow HOOC-COOH \text{ (oxalic acid)} + CO_2 + 3H_2O$$

(i) Reaction with oxalic acid: When oxalic acid is heated with glycerol at 383 K, it forms glycerol mono-oxalate which loses a molecule of CO_2 to give glycerol mono- formate which in turn on hydrolysis gives formic acid.



(ii) At 230° C (503 K), oxalic acid reacts with glycerol to form glycerol dioxalate which loses two molecules of CO_2 to give allyl alcohol.

5. DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

(a) Lucas test: This test is based on the difference in the three types of alcohols (having δ or less carbon towards Lucas reagent (a mixture of conc. Hydrochloric acid and anhydrous zinc chloride)

$$ROH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$$

Since alkyl halides are insoluble, their formation is indicated by the appearance of a turbidity in the reaction mixture. The order of reactivity is tertiary >secondary >primary, the tertiary alcohols produce turbidity immediately, the secondary alcohols give turbidity within 5 – 10 minutes, and the primary alcohols do not give turbidity at all, at room temperature.

(b) **Catalytic dehydrogenation** (action of reduced copper at 300°). Discussed earlier,

(i) Primary alcohols form aldehydes

(ii) Secondary alcohols form ketones.

(iii) Tertiary alcohols form olefins.

(c) **Victor Meyer test:** This test is based on the different behaviour of primary, secondary and tertiary nitroalkanes towards nitrous acid. The test involves the following steps.

(i) Alcohols is treated with concentrated hydroiodic acid or red phosphorus and iodine to form the corresponding alkyliodide.

(ii) Alkyl iodide is reacted with silver nitrite to form the corresponding nitroalkane.

(iii) The nitroalkane is treated with nitrous acid ($NaNO_2$ + HCl) followed by treatment with alkali (NaOH or KOH). Upon such treatment different alcohols give different colours.

- Primary alcohols produce a blood red colour
- Secondary alcohols produce a blue colour
- Tertiary alcohols produce no colour.

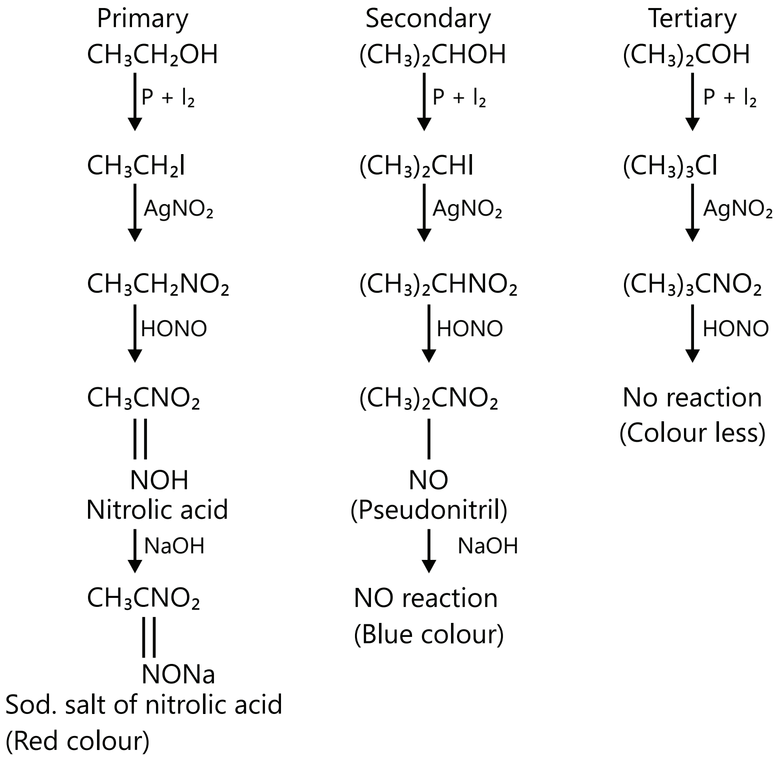
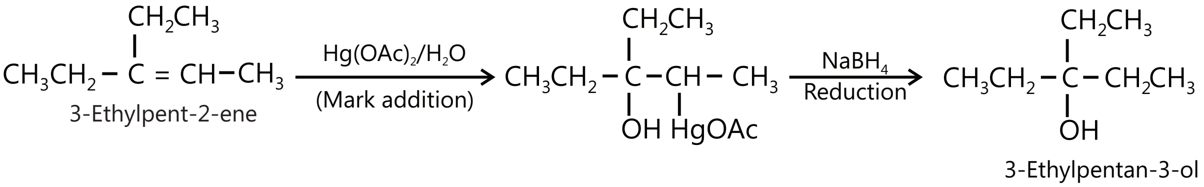


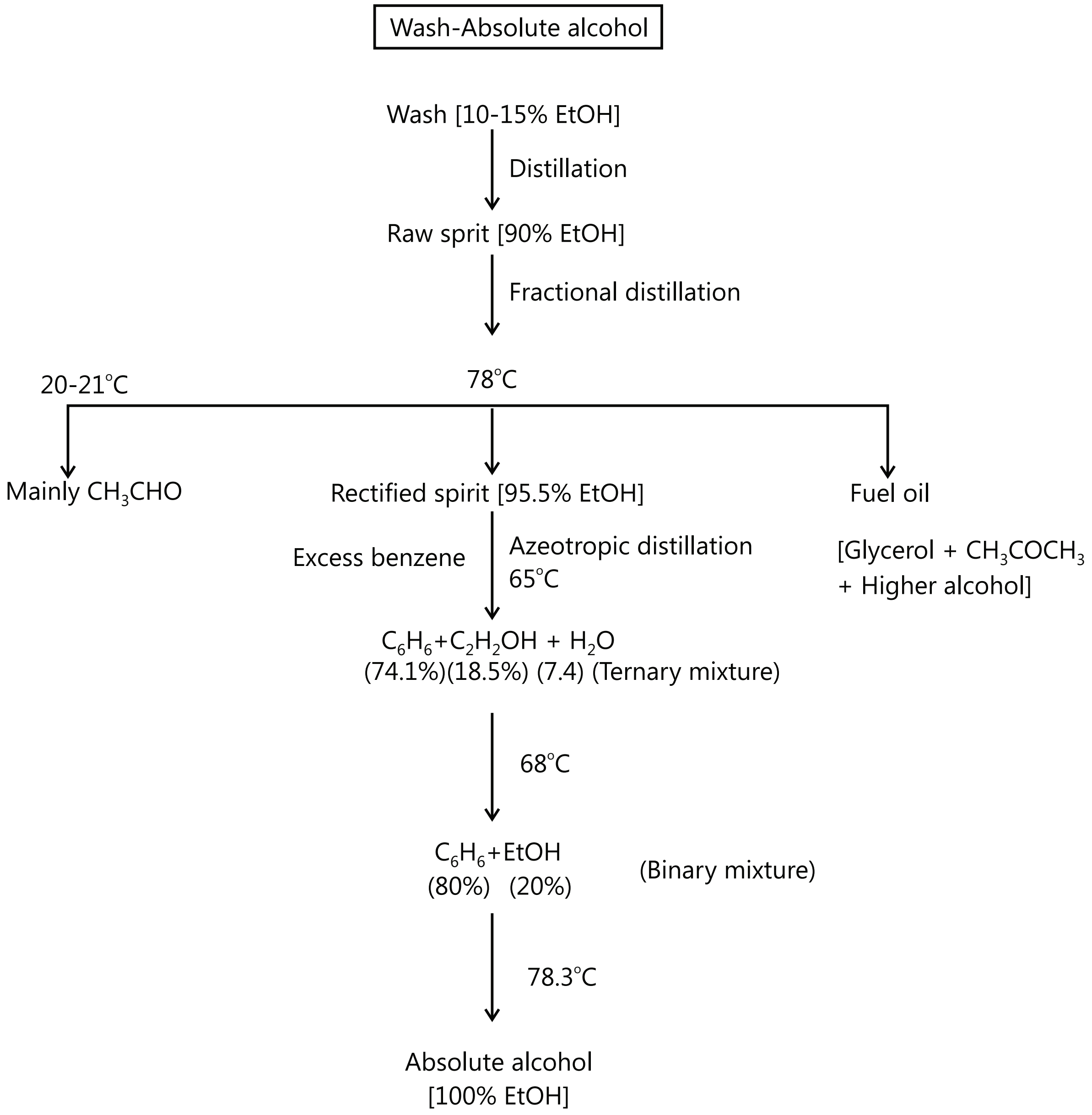
Illustration 5: Give the structure of the major organic product when 3-ethylpent-2-ene is treated with $Hg(OAc)_2$, H_2O, $NaBH_4$. **(JEE MAIN)**

Sol:



$$CH_3CH_2-\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow[\text{(Mark addition)}]{Hg(OAc)_2/H_2O} CH_3CH_2-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}}}-\underset{\displaystyle HgOAc}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{Reduction}]{NaBH_4} CH_3CH_2-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_2CH_3}{\overset{|}{C}}}}-CH_2CH_3$$

Absolute alcohol:



Flowchart 22.1 Preparation of absolute alcohol

MASTERJEE CONCEPTS

Chemical properties of alcohols:

(a) Rate of reaction of alcohols with carbonyl compounds depends on two factors:

  (i) Leaving group ability of the substituent: Better the leaving group, faster the reaction.

  (ii) Bulkiness of the alkyl part of alcohol: Bulkier the alkyl part, slower is the reaction because of steric hinderance.

(b) Only alkyl methyl ether can be prepared by reaction of alcohol with Diazomethane.

(c) In reaction of alcohols with excess of sulphuric acid at lower temperatures, we obtain ethers. But, as the temperature increases, alkenes become the favourable product. Also, in case of secondary and tertiary alcohols, alkene is the predominant product due to ease of elimination.

(d) In reaction of alcohols with $SOCl_2$ it proceeds via S_Ni mechanism. Thus, the configuration in case of chiral carbon is retained. But, if pyridine is used as a solvent, the reaction proceeds via S_N2 mechanism with inversion of configuration.

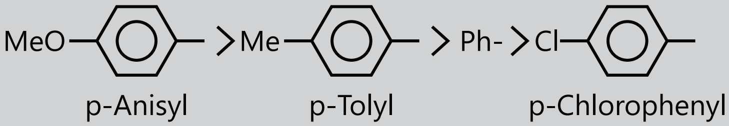
(e) In reaction of alcohols with PCl_5 and PCl_3 proceeds via S_N2 mechanism.

(f) Weak oxidizing agents like PCC, PDC etc oxidize 1^0 alcohols to aldehydes while strong reagent oxidizes 1^0 alcohols to carboxylic acids. All these oxidizing agents oxidize 2^0 alcohols to ketones but 3^0 alcohols are not affected.

(g) In pinacol-pinacolone rearrangement, With unsymmetrical glycols, the product obtained is determined mainly by the OH that is lost as H_2O to give more stable carbocation and, thereafter, by the better migrating group.

  (i) The order of migratory aptitudes is Ar > > H > R.

  (ii) The migratory order in aryl: Ar containing more e^--donating (or more e^- rich) migrates. For example,



  (iii) The phenyl group is more e^- rich than (Me) group, therefore, (Ph) group migrates in preference of (Me) group

  (iv) The migrating group should be trans (anti) to the leaving (–H) group.

  (v) The (–OH) group will be lost from the C atom which would leave the most stable carbocation.

  (vi) The rate determining step (R.D.S. and slow) is the formation of stable carbocation, i.e., conversion in step 2 to step 3.

T P Varun (JEE 2012, AIR 64)

Illustration 6: Arrange the following compounds in the decreasing order of their b.p s' and solubility in H_2O.

(JEE MAIN)

(a) (I) Methanol (II) Ethanol (III) Propan-1-ol

(IV) Butan-1-ol (V) Butan-2-ol (VI) Pentan-1-ol

(b) (I) Pentanol (II) n-Butane (III) Pentanal

(IV) Ethoxy ethane

(c) (I) Pentane (II) Pentane – 1, 2, 3-triol

(III) Butanol

Sol: (c) **B.P. order:** VI > IV > V > III > II > I

Solubility order: I > II > III > V > IV > VI

Explanation: All of the mare alcohol so all have H-bonding. As the molecular mass and surface area increases, the B.P. increases and solubility decreases.

Out of (IV) and (V), there is branching in (V) and has less surface are than (IV), So the boiling point of (IV) > (V), but solubility of (V) > (IV)

(b) **B.P.order :** I > III > IV > II

Solubility order: I > III > IV > II

In (I), there is H-bonding, in (II) (aldehyde), dipole-dipole interaction, in (III) (ether), slightly polar due to EN of O and in (IV) (alkane), Van der Waals interaction (non-polar)

(c) **B.P. Order:** II > III > I

Solubility Order: II > III > I

In (II), there (–OH) groups, more H-Bonding; in (II), one (–OH) group, less H-bonding; in (I) (alkane), Van der Waals interaction

Illustration 7: Explain the following: **(JEE MAIN)**

(a) Which has higher B.P.?

(i) Phenol (ii) Benzenethiol

(b) Which has higher melting point?

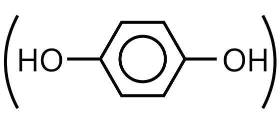
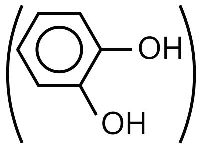
(i) Hydroquinone (ii) Catechol

(c) Explain the less solubility and lower b.p. of :

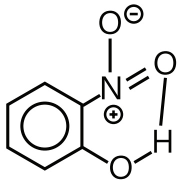
(i) o-Nitrophenol (ii) o-Hydroxy benzaldehyde

(iii) o-hydroxybenzoic acid (salicylic acid) compared with their p-and m-isomers.

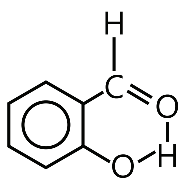
Sol: (a) Although the molecular mass of benzenethiol (Ph – SH) is higher, phenol has high boiling point. It is because there is no H-bonding in PhSH.

(b) Hydroquinone  (I) has high M.P. than catechol  (II) because of the Symmetrical packing of p- is its crystal lattice which requires more energy for its melting.

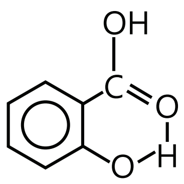
(c) In ortho-isomers of (I), (II) and (III), intramolecular H-bonding (chelation) occurs which inhibits the intermolecular attraction between these molecules and thus, lowers the b.p. and also reduces H-bonding of these molecules with H_2O thereby, decreases water solubility. Intermolecular chelation does not occur in p –and m-isomers.



o-Nitophenol



o-Hydroxybenzaldehyde
(Salicylaldehyde)



o-Hydroxybenzoic acid
(Salicylic acid)

Illustration 8: Synthesize the following: **(JEE MAIN)**

(a) Benzene to (4-chorophenyl)propan-1-ol)

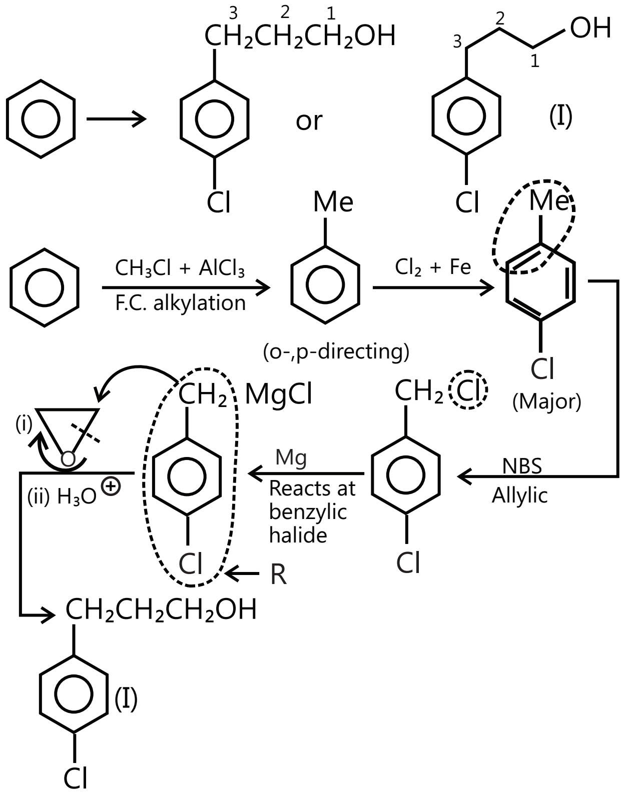
(b) Ethyne to butanol

(c) Propane to allyl alcohol

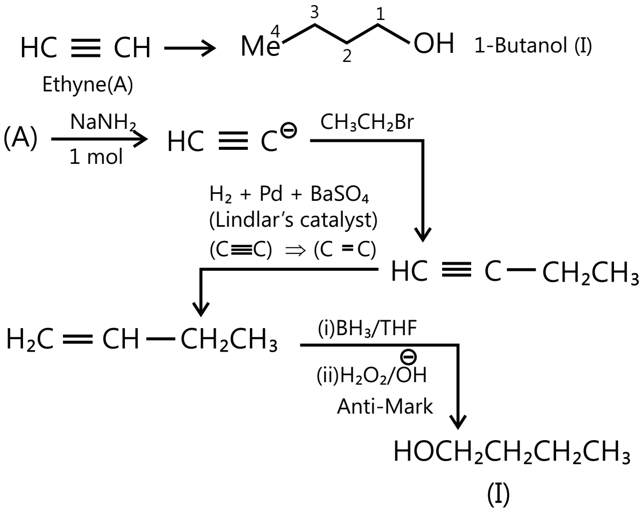
(d) Propane to propanol and propan-2-ol

Synthesis:

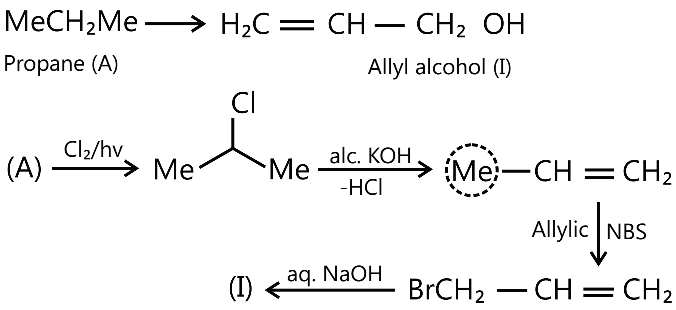
(a)



(b)



(c)



(d)

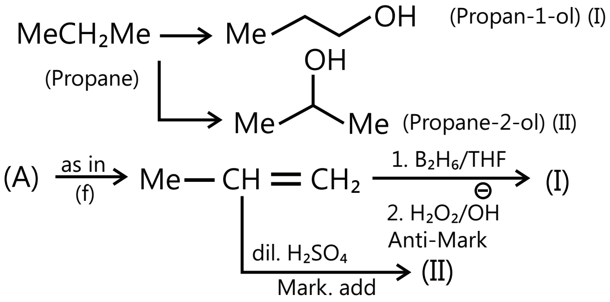
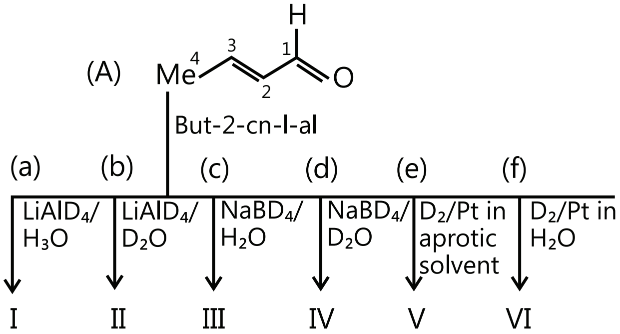
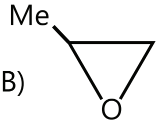


Illustration 9: Complete the following: **(JEE MAIN)**



(B)

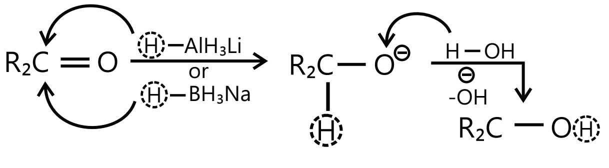


with reagents (a) to (f)

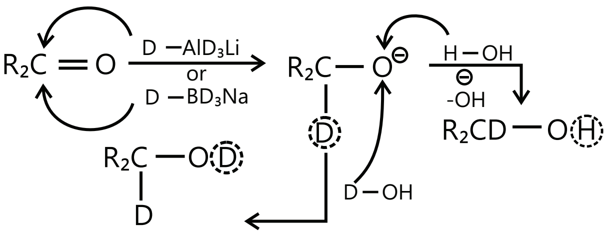
Mechanism:

[D form $LiAlD_4$ and $NaBD_4$ is added to C of (C = O) group and solvent gives H or D to O atom to form OH or OD, e.g.,]

(i)

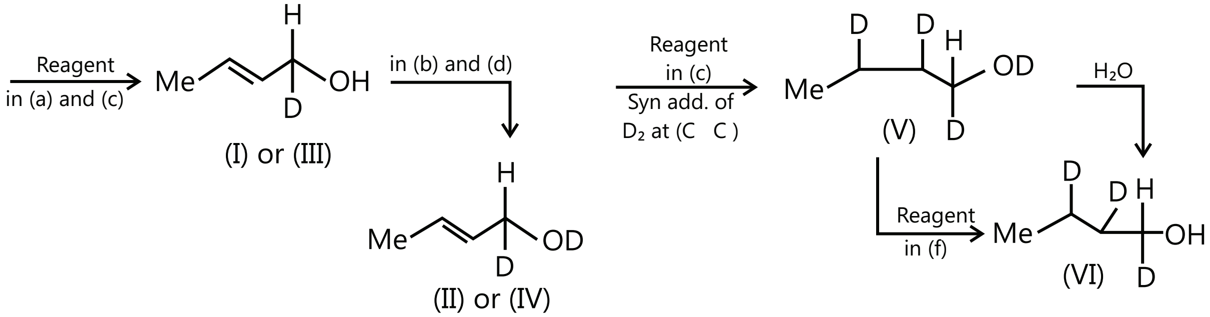


(ii)

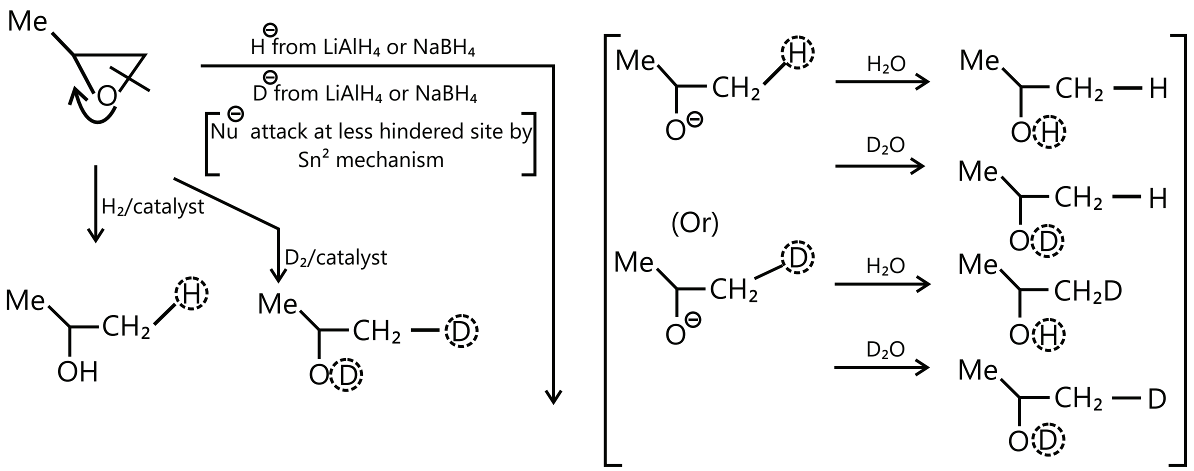


(iii) LAH and $NaBH_4$ do not reduce (C = C) bond whereas catalytic hydrogenation reduces (C = C) bond to (C – C) bond

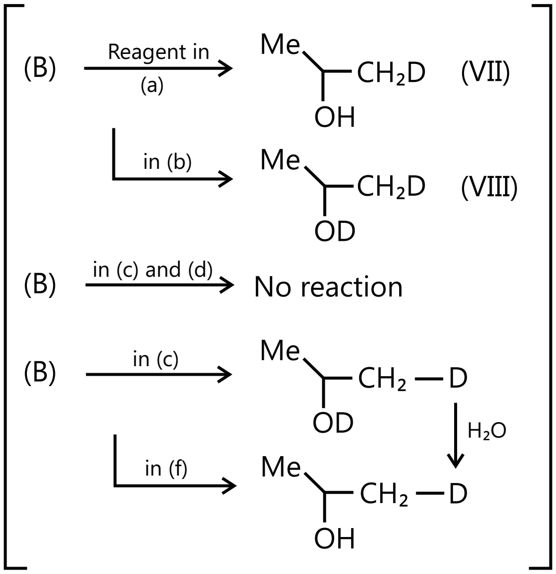
(iv) LAH and catalytic hydrogenation reduce epoxide but NaBH$_4$ does not



The D of ROD rapidly exchanges for the H of H_2O Mechanism in (B).

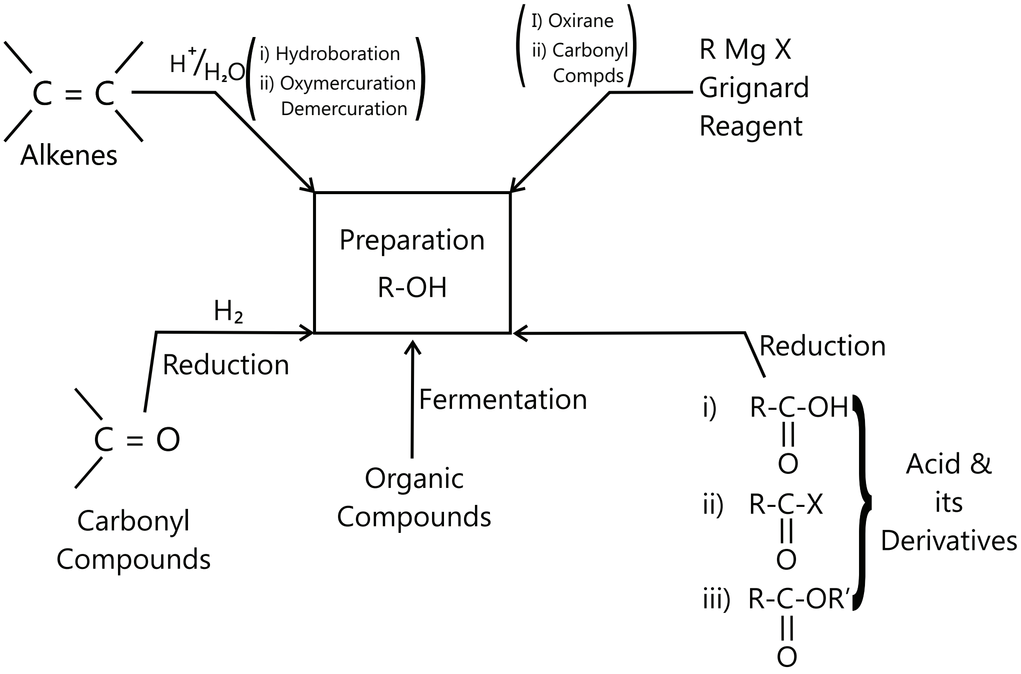


Reaction:

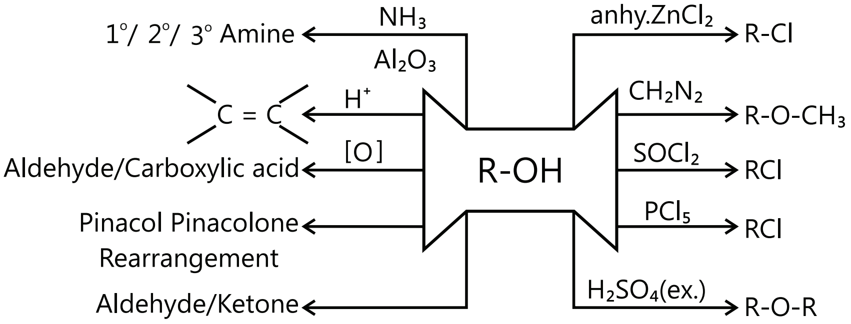


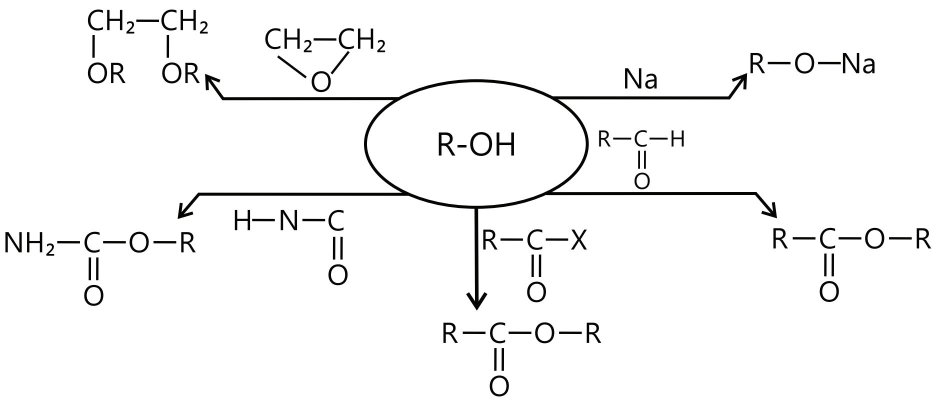
The D of ROD rapidly exchanges for H of H_2O

POINTS TO REMEMBER



Reactions of Alcohols





Alcohol

GMP

(1) Alkene $\xrightarrow{\text{HO}}$

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

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

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

(5) 1° amine $\xrightarrow{HNO_2}$

Exception-Methyl amine gives

CH_3-O-CH_3 or ether

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

(1° alc.) (2° alc.)

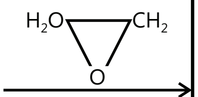
(7) Acid or Acid derivative $\xrightarrow[\text{Bouveault Blanc reduction}]{\text{Na/EtOH}}$

(1° alc.) (2° alc.)

(8) HCHO or Ald. or ketone $\xrightarrow[H_2O]{\text{RMgX}}$

(1° alc.) (2° alc.) (3° alc.)

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



(10) CH_3MgBr $\xrightarrow[H_3O^+]{}$

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

$\boxed{\text{R-OH}}$ $\rightarrow$

GR

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

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

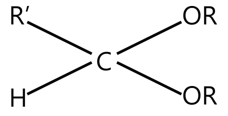
(3) $\xrightarrow{NH_3}$ 1° ,2° ,3° amines

(4) $\xrightarrow[\text{Tho}_2]{H_2S}$ R - SH Thiol

(5) $\xrightarrow[H_2S]{\text{Na}}$ RONa

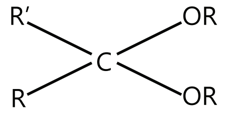
(6) $\xrightarrow{CH_3MgX}$ CH_4

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



Acetal

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



Ketal

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

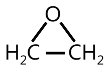
(10) $\xrightarrow{H_2SO_4}$ $ROSO_2OH$(Alkyl hydrogen sulphate)

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

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

(13) $\xrightarrow{CH\equiv CH}$ $H_2C\text{-}CH(OR)_2$ Acetal

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



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

(16) $\xrightarrow{CH_2=C=O}$ $ROCOOH_3$ Ether

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

(18) $\xrightarrow[\text{1°or2° alcohol, Cu or ZnO, 300°C}]{\text{Catalytic dehydrogenation}}$ Aldehyde or ketone

Exception -3° alc → Alkene

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

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

(21) 2°alc. $\xrightarrow{[O]}$ Ketone $\xrightarrow{[O]}$

(22) 3°alc. $\xrightarrow{[O]}$

(23) 3° alc. $\xrightarrow[\text{(orange)}]{OH, CrO_4^-}$ No reaction (No. green colour)

Formation of EtOH by fermention

(1) Cane sugar $\xrightarrow[\text{Sucrose}]{\text{Crystallization}}$ Molasses

$\xrightarrow[\text{Hydrolysis}]{\text{Invertase}}$ Invert sugar $\xrightarrow[\text{Fermentation}]{\text{Zymase}}$ EtOH

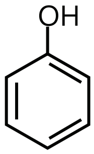
(2) Grain $\rightarrow$ Starch $\xrightarrow[\text{HOH}]{\text{Diastase}}$ Maltose

$\xrightarrow[\text{Hydrolysis}]{\text{Maltase}}$ Glucose $\xrightarrow[\text{Fermentation}]{\text{Zymase}}$ EtOH

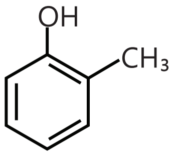
PHENOLS

1. INTRODUCTION

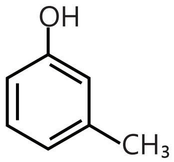
When OH group is attached at benzene ring,the compound is known as phenol



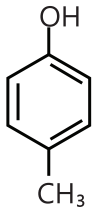
Nomenclature of Phenols



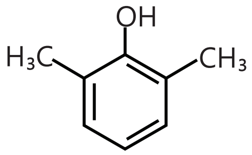
2-Methyl phenol
(o-Cresol)



3-Methyl phenol
(o-Cresol)

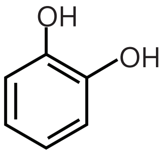


2-Methyl phenol
(o-Cresol)

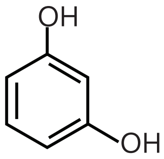


2-6 Dimethyl phenol

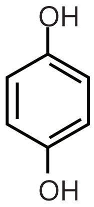
Some dihydric and trihydric phenols are given below:



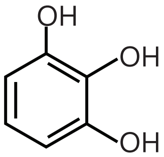
1,2-Benzenediol
(Catechol)



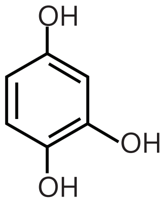
1,3-Benzenediol
(Resorcinol)



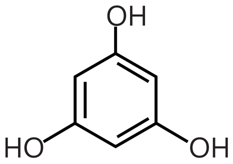
1,4-Benzediol
(Quinol)



1,2,3-Benzenediol
(Pyragallol)



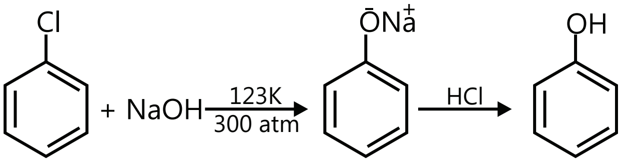
1,3,4-Benzenetriol



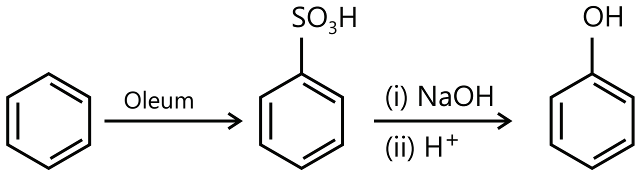
1,3,5-Benzenetriol

2. METHODS OF PREPRATION OF PHENOLS

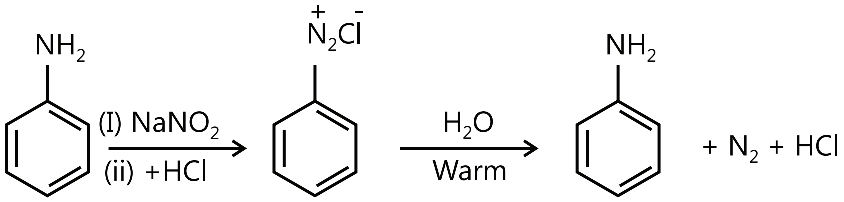
2.1 From Haloarenes



2.2 From Benzenesulphonic Acid



2.3 From Diazonium Salts



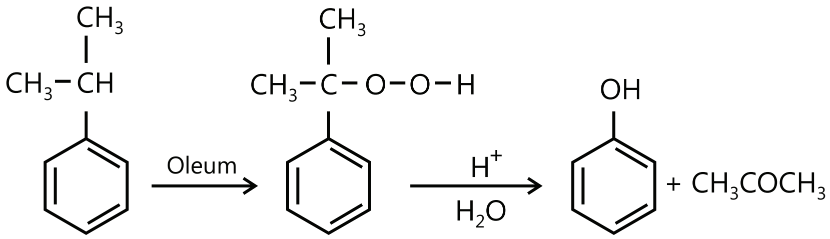
Aniline

Benzene diazonium chloride

When diazonium salts react with water vapour it gives phenol.

2.4 From Cumene

When cumene (isopropylbenzene) is oxidized in the presence of air and acid, it gives phenol and acetone.



Cumene

Cumene hydroperoxide

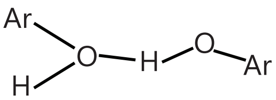
3. PHYSICAL PROPERTIES OF PHENOLS

(a) Pure phenols are generally colorless solids or liquids. The light colour usually associated with phenols is due to its oxidations by air in presence of light.

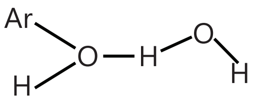
(b) Phenols, generally are insoluble in water; but phenol itself, and polyhydric phenols are fairly soluble in water which is believed to be due to the formation of hydrogen bond with water.

(c) Due to intermolecular hydrogen bonding, phenols usually have relatively high boiling points than the corresponding hydrocarbons aryl halides and alcohols. For example, phenol (mol. Wt. 94) boils at 182°C while toluene (mol. Wt. 92) boils at 110°C.

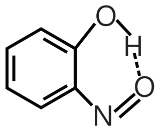
Higher b.p. than alcohols is due to higher polarity of the O-H bond and consequently stronger intermolecular hydrogen bonding in phenols than in alcohols. Appreciable solubilities of the phenol and polyhydric phenols in water is also due to strong hydrogen bonding between phenols and water molecules.



Intermolecular hydrogen bonding phenols

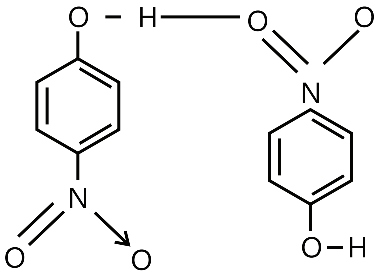


Hydrogen bonding between phenols and water molecules

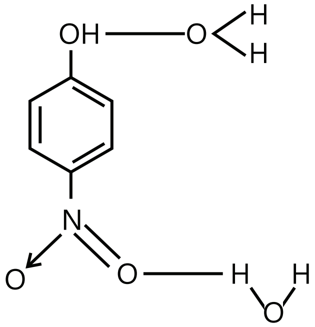


o-Nitro phenol (Intermolecular H-bonding possible due to close mass of NO_2 and -OH groups)

Phenols containing groups like-NO_2 or –COOH in the ortho position to the –OH group can also form intermolecular hydrogen bonds (e.g. o-nitro phenol) which is responsible for their lower boiling points and less solubility in water than the corresponding meta or para isomer. Due to possibility of intermolecular hydrogen bonding (also known as chelatom) in the ortho isomer, intermolecular hydrogen bonding is not possible and hence the ortho isomer can neither get associated nor can from hydrogen bonding with water with the results it has a low b p. and less solubility in water than the meta and para isomers which can associate (union of two or more molecules of the same speoins) as well as can form hydrogen bonding with water.



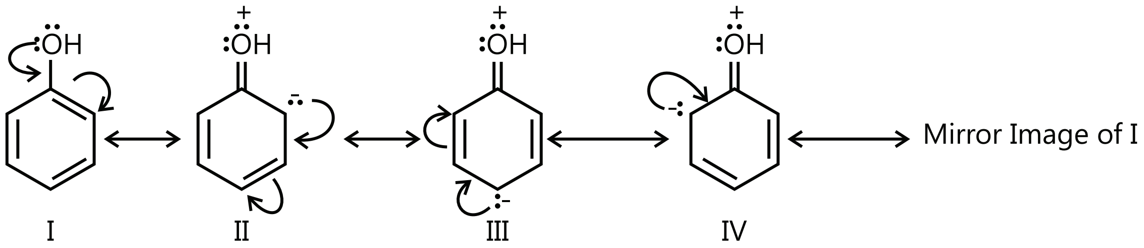
p-Nitro phenol (1 molecules) (intermolecular H-bonding) is not possible due large distance between-NO_2 and -OH occups hence intermolecular H-bonding is possible.



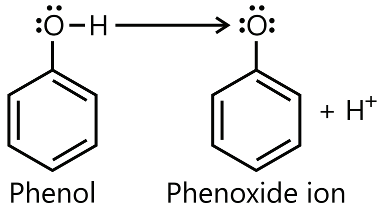
Hydrogen bonding between p-nitro and water

(d) They possess characteristic colour. They are highly toxic in nature and possess antiseptic properties. They may produce wounds on skin.

(i) Phenol exists as resonance hybrid of the following structures.

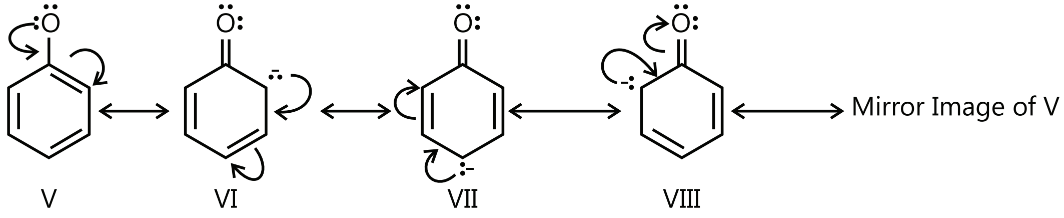


Due to resonance oxygen atom of the –OH group acquires & positive charge (see structures III to V) and hence attract electron pair of the O–H bond leading to the release of hydrogen atom as proton.



Since resonance is not possible in alcohols (due to absence of conjugation of the lone pair of electron of oxygen with a double bound), the hydrogen atom is more firmly linked to the oxygen atom and hence alcohols are neutral in nature.

(ii) Once the phenoxide ion is formed, is stabilizes itself by resonance, actually phenol acid ion is more stable than the parent phenol.



Comparison of acidity of phenols and carbonic acid

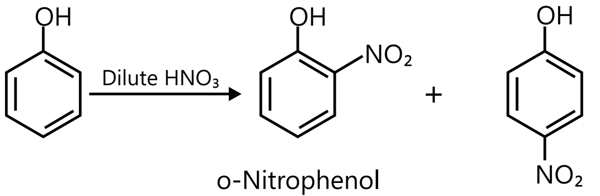
Relative acidity of the various common compounds.

RCOOH >	H_2CO_3 >	C_6H_5OH >	HOH >	ROH
Carboxylic acid	Carbonic acid	Phenol	Water	Alcohols.

4. CHEMICAL PROPERTIES OF PHENOLS

4.1 Nitration

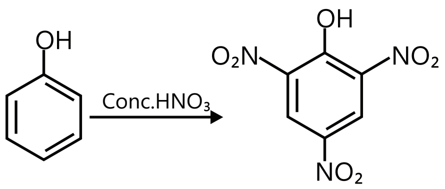
(a) When phenol react with dilute nitric acid at low temperature (290 K), give a mixture of ortho and para nitro phenols.



o-Nitrophenol

p-Nitrophenol

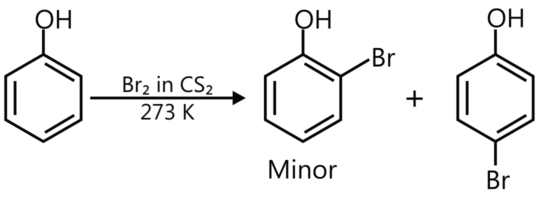
(b) When phenols react with concentrated nitric acid, it gives 2, 4, 6-trinitrophenol.



2,4,6-Trinitrophenol
(Picric acid)

4.2 Halogenation

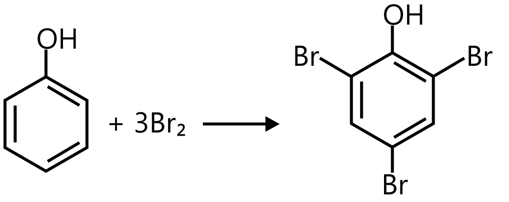
(a) When the reactions carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, monobromophenols are formed.



Minor

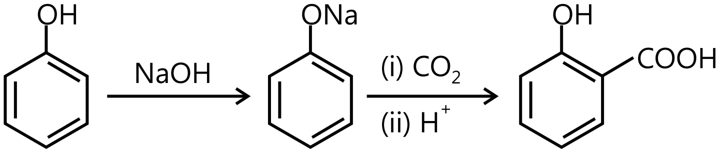
Major

(b) When phenol is treated with bromine water 2, 4, 6-tribromophenol is formed as white precipitate.



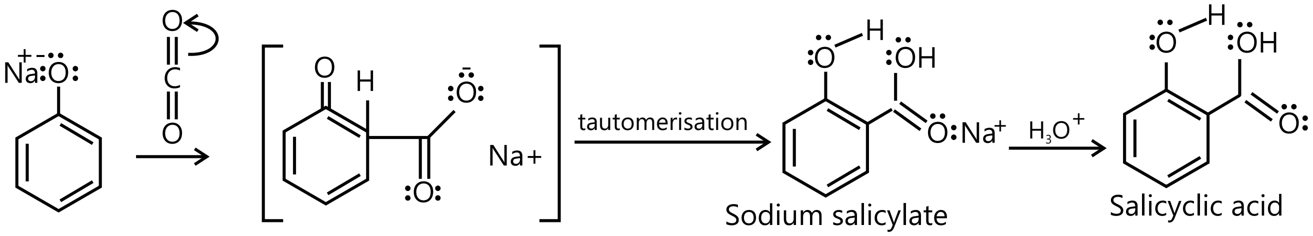
2,4,6-Trinitrophenol

4.3 Kolbe's Reaction



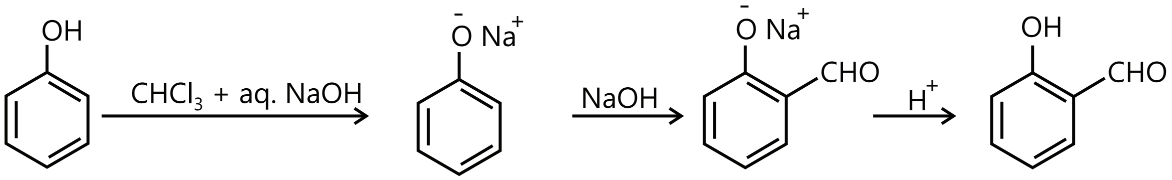
2-Hydroxybenzoic acid
(Salicylic acid)

Mechanism of Reaction



4.4 Reimer-Tiemann Reaction

On treating phenol with chloroform in the presence of sodium hydroxide, a–CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer – Tiemann reaction. The intermediate substituted benzal chloride is hydrolyzed in the presence of alkali to produce salicyladehyde.

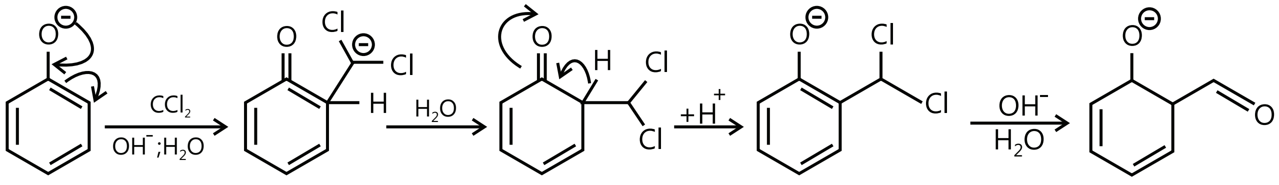


Intermediate

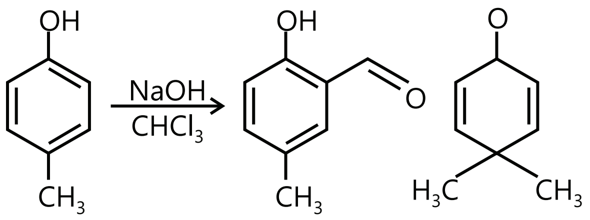
Salicylaldehyde

The mechanism of the Reimer – Tiemann reaction is believed to involve the formation of dichloromethylene.

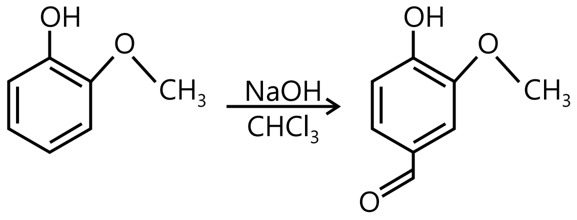
$NaOH + CHCl_3 \rightarrow :CCl_2 + NaCl + H_2O$



Phenols with blocked p-positions give cyclohexadienones containing the dichloromethyl group.



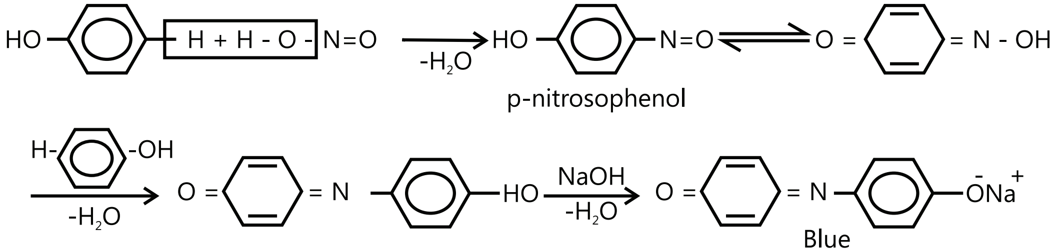
In the Reimer-Tiemann reaction, the o-isomer predominates, but if one of the o-position is occupied the aldehyde group tend to go to the p-positions; e.g. guaiacol forms vanillin



4.5 Libermann's Reaction

When phenol is treated with sodium dissolved in conc. Sulphuric acid a red colouration appears which changes to blue on adding aqueous NaOH. This reaction is called Libermann's reaction.

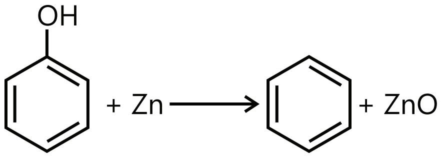
$$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{\text{Nitrous acid}}{2HNO_2}$$



Indophenol (Red)

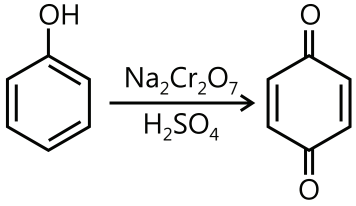
4.6 Reaction of Phenol with Zinc Dust

When phenol is heated with zinc dust, it gives benzene.



4.7 Oxidation

Oxidation of phenol with chromic acid produces a conjugate diketone known as benzoquinone. In the presence of an oxidizing agent, phenols are slowly oxidized to dark coloured moisture containing benzoquinone.

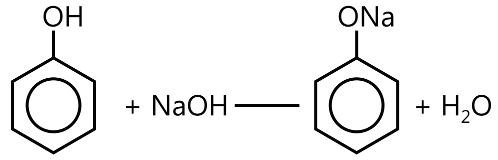


Benzoquinone

5. DISTINCTION BETWEEN ALCOHOL AND PHENOLS

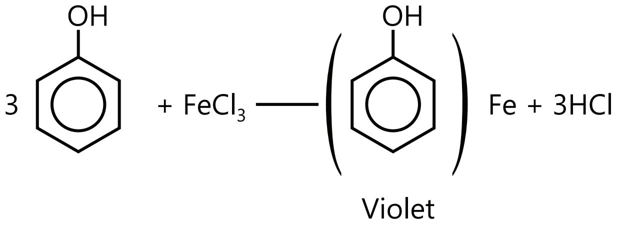
(a) Phenols turns blue litmus red but alcohols do not.

(b) Phenols neutralize base, while alcohols do not.



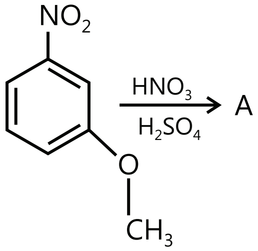
R-OH + NaOH —— No reaction

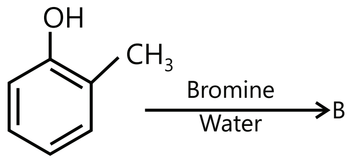
(c) Phenols give violet colour with $FeCl_3$. while alcohols do not.



R-OH + $FeCl_3$ —— No reaction

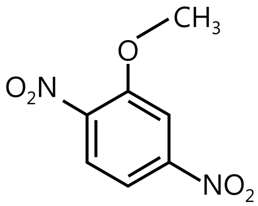
Illustration 1: Identify the major products in the following reactions:

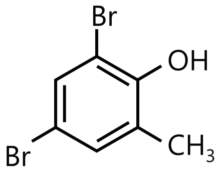
(I)


(II)


Sol: (I) The nitrating mixture gives the attachment of the nitro group on the ortho position. The presence of methoxy group is an electron-donating groupwhich makes the ortho position more electron-rich enabling the attachment of the electron-withdrawing NO_2 group.

(II) Bromine is an electrophile and the presence of electron donating groups i.e. –OH and CH_3 make the ortho and the para positions available for the attachment.

A =


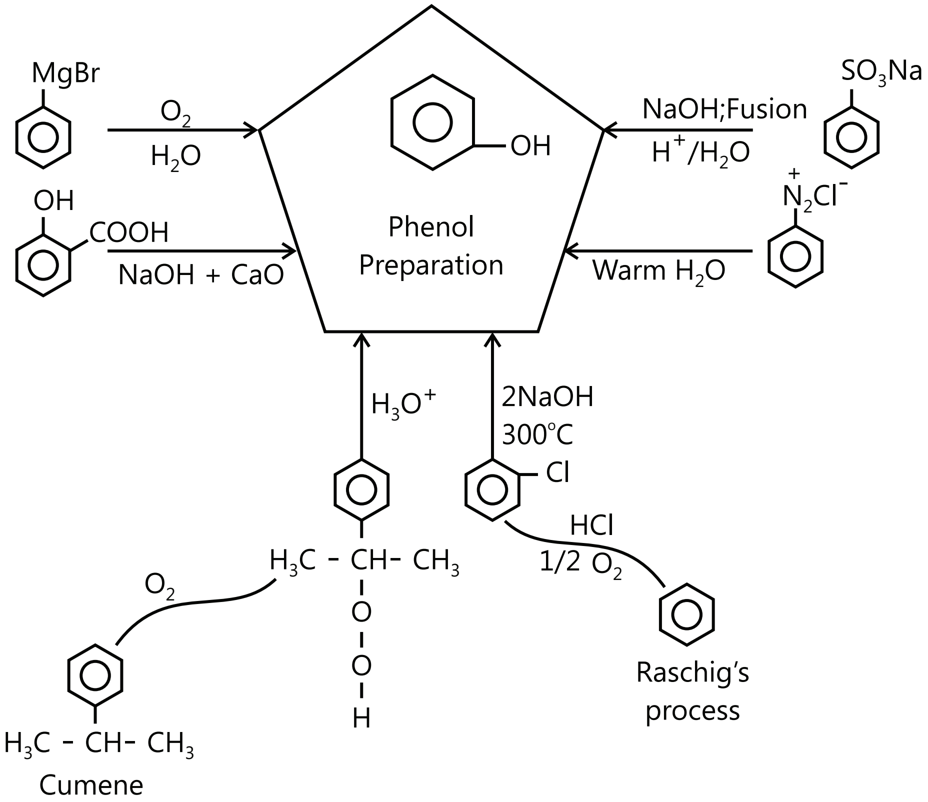
B =


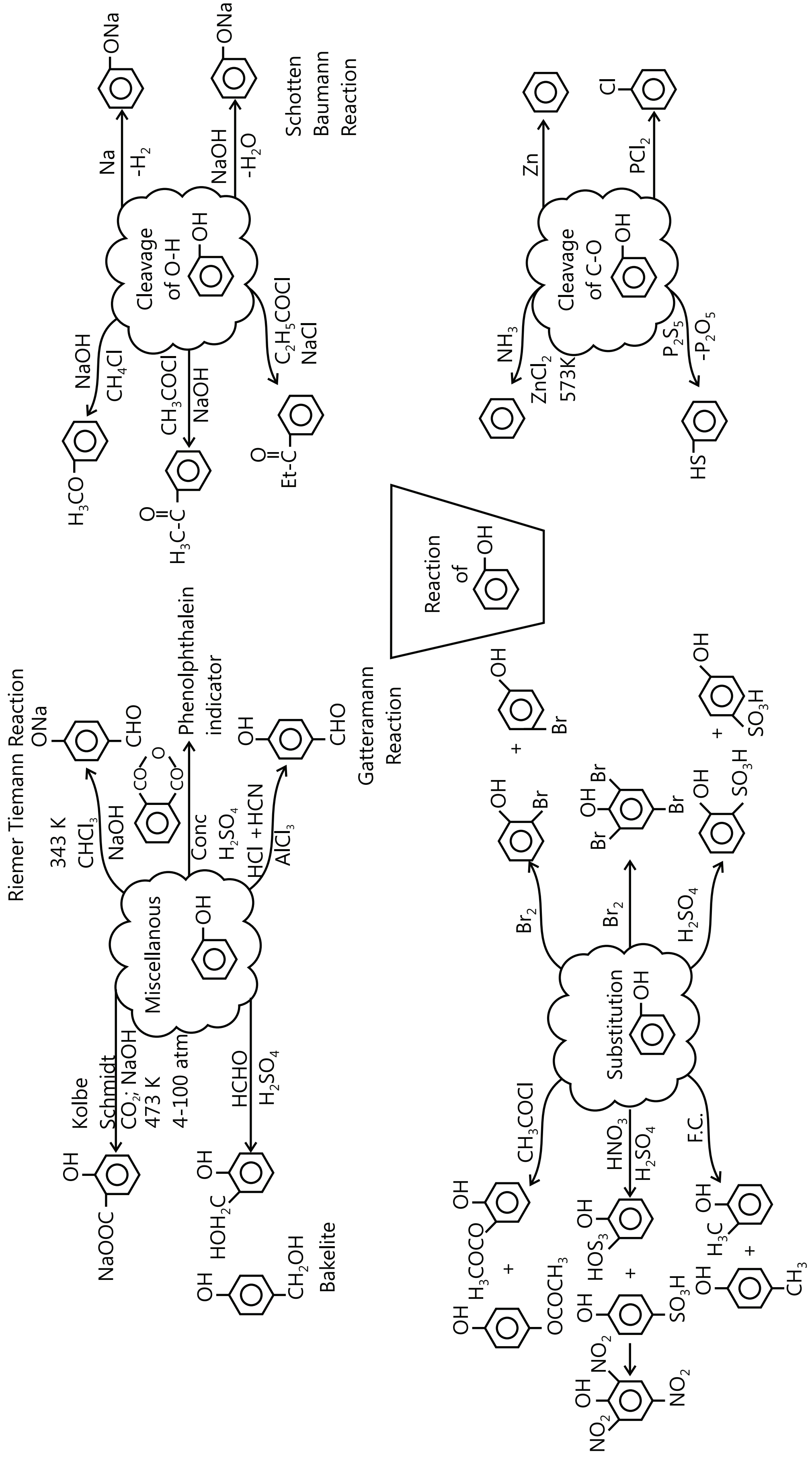
MASTERJEE CONCEPTS

- Phenols although colourless turn reddish due to atmospheric oxidation.
- Phenols and alcohol have high boiling point due to intermoelcular hydrogen bonding
- Out of three isomeric nitrophenols, only ortho isomer is steam volatile and has lesser solubility and lower boiling point than meta and para. Ortho cannot form H-bond with water and in ortho there exist intramolecualr H- Bonding.
- Phenols are stronger acids than alcohols but weaker than carboxylic acid and carbonic acid.
- Phenols are stronger acids than alcohols because the phenoxide ion formed after the release of proton is stabilised by resonance where as alkoxide ion does not.
- TEST OF PHENOL– Phenols give violet colour with neutral $FeCl_3$. Depending upon the nature of Phenol, colour varies from violet to blue green or even red.
- Preparation of phenol from cumene proceeds via peroxide radical mechanism.

Saurabh Chaterjee JEE Advanced 2013, AIR

POINTS TO REMEMBER



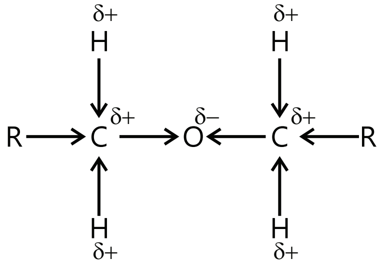

Reaction of
OH
Cleavage of O-H
Na
$-H_2$
ONa
NaOH
$-H_2O$
Schotten Baumann Reaction
NaOH
CH_4Cl
H_3CO
CH_3COCl
NaOH
H_3C-C
O
C_2H_5COCl
NaCl
Et-C
Cleavage of C-O
Zn
PCl_2
Cl
NH_3
$ZnCl_2$
573K
P_2S_5
$-P_2O_5$
HS
Miscellanous
Riemer Tiemann Reaction
343 K
$CHCl_3$
NaOH
CHO
Phenolphthalein indicator
CO
Conc
H_2SO_4
HCl +HCN
$AlCl_3$
Gatteramann Reaction
Kolbe Schmidt
CO_2; NaOH
473 K
4-100 atm
NaOOC
HCHO
H_2SO_4
HOH_2C
CH_2OH
Bakelite
Substitution
Br_2
Br_2
H_2SO_4
Br
+
SO_3H
CH_3COCl
HNO_3
H_2SO_4
F.C.
H_3COCO
$OCOCH_3$
HOS_3
NO_2
H_3C
CH_3

ETHERS

1. INTRODUCTION

The ethers are those compounds that have a C–O–C in their structure where, importantly, each C can only be part of an alkyl or an aryl group – i.e. R–O–R′. The electronegative oxygen, flanked as it is by two electron pushing alkyl groups, has very little tendency to participate in any reaction. This lack of reactivity is also attributed to the two alkyl groups enveloping the oxygen, shielding it from reagents. The ether molecule appears to have an outer unreactive alkyl shield or sphere with the "reactive" oxygen sitting in the centre.

Without any hydrogens directly attached to the oxygen, the molecules are not capable of forming H-bonds. The consequence of this is that the melting and boiling points are lower than the corresponding alcohols. Compatibility / solubility with water is also affected; though the smallest ether is miscible with water, any increase in the size of the alkyl chain drastically lowers the ether's solubility in water and soon forms immiscible mixtures.



2. METHODS OF PREPARATION OF ETHERS

(a) **Williamson' Synthesis:** Heating of alkyl halide with sodium or potassium alkoxide gives ether. This is a good method for preparation of simple as well as mixed either.

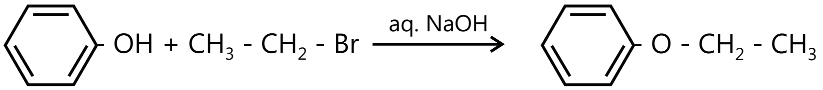
$$R-X+Na-O-R' \xrightarrow{R} R-O-R'+NaX$$

This method is not applicable to tert alkyl halides because the alkoxide ions being both powerful nucleophiles and bases could bring dehydrogenation of the tertiary alkyl halides to form alkenes.

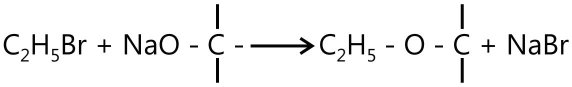
$$R\ -ONa \longrightarrow R\ -O^{-} + Na^{+}$$

$$R-\ddot{\underset{\cdot\cdot}{O}}-\ Na + R'\ -X \longrightarrow R\ -\ \ddot{\underset{\cdot\cdot}{O}}\ -\ R + Nax$$

$$R-X + \begin{array}{l} R'-O-Na \\ Ar-O-Na \end{array} \longrightarrow \begin{array}{l} R-O-R \\ \underset{\text{Aryl Ether}}{R-O-Ar} \end{array}$$



The reactivity of primary (1º) alkyl halide is in the order CH_3- > $CH_3 - CH_2$- > $CH_3 - CH_2 - CH_2$- and the tendency of the alkyl halide to undergo elimination is 3º > 2º > 1º. Hence for better yield the alkyl halide should be primary of the alkoxide should be secondary or tertiary.



$$C_2H_5Br + NaO - \overset{|}{\underset{|}{C}} - \longrightarrow C_2H_5 - O - \overset{|}{\underset{|}{C}} + NaBr$$

(b) By Heating excess of alcohols with conc. H_2SO_4 e.g.,

$$\underset{\text{Ethanol (2 molecules)}}{C_2H_5 - OH + HO - C_2H_5} \xrightarrow[140^{\circ}C]{\text{conc. } H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5 - O - C_2H_5} + H_2O$$

Recall that 2° and 3° alcohols under the above conditions give alkenes as the main product. Moreover, this method is limited only for the preparation of simple ethers.

(c) By heating alkyl halide with dry silver oxide (only for simple ethers)

$$C_2H_5I + Ag_2O + IC_2H_5 \longrightarrow C_2H_5OC_2H_5 + 2AgI$$

Remember that reaction of alkyl halides with moist silver oxides ($Ag_2O + H_2O = AgOH$) gives alcohols.

(d) By the use of diazomethane to form methyl ethers.

$$n\text{-}C_7H_{15}OH + CH_2N_2 \xrightarrow{BF_3} \underset{\text{Methyl n-heptyl ether}}{n\text{-}C_7H_{15}OCH_3} + N_2$$

$$n\text{-}C_7H_{15}OH + CH_2N_2 \xrightarrow{BF_3} \underset{\text{Anisole}}{C_6H_5OCH_3}$$

3. PHYSICAL PROPERTIES OF ETHERS

(d) Due to absence of intermolecular H-bonding, B.P of ether is much lower than isomeric alcohols.

(e) Ethers are slightly polar with some net dipole. (e.g. 1.18 D for diethyl ether.)This is due to a bend structure with bond angle of 110^0 which causes because of repulsion between bulky alkyl groups.

4. CHEMICAL PROPERTIES OF ETHERS

Ethers are less reactive than compounds containing other functional group. They do not react with active metals like Na, strong base like NaOH, reducing or oxidizing agents.

4.1. Formation of Peroxides

On standing in contact with air, ethers are overrated into unstable peroxides ($R_2O \rightarrow O$) which are highly explosive even in low concentrations. Hence ether is always purified before distillation. Purification (removal of peroxide) can be done by washing ether with a solution of ferrous salt (which reduces peroxide to alcohols) or by distillation with conc. H_2SO_4 (which oxidizes peroxides).

The presence of peroxides in ether is indicated by formation of red colour when ether is shaken with an aqueous solution of ferrous ammonium sulphate and potassium thiocyanate. The peroxide oxidizes Fe^{2+} to Fe^{3} which reacts with thiocyanate ion to given red colour of ferric thiocyanate

$$\text{Peroxide} + Fe^{2+} \longrightarrow Fe^{3+} \xrightarrow{CNS^-} \underset{\text{Red}}{Fe\,(CNS)_3}$$

However, the formation of peroxide is prevented by adding a little Cu_2O to it.

4.2 Basic Nature

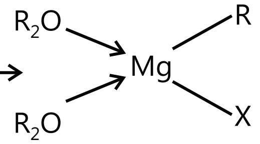
Owing to the presence of unshared electron pairs on oxygen, ethers are basic, Hence they dissolve in strong acids (e.g., HCl, conc. H_2SO_4) at low temperature to form oxonium salts.

$$\underset{\text{Diethyl ether}}{(C_2H_5)_2\,O} + H_2SO_4 \longrightarrow \underset{\text{Diethyloxonium hydrogen sulphate}}{[(C_2H_5)_2\,OH]^- HSO_4^-}$$

On account of this property ether is removed from ethyl bromide by shaking with conc. H_2SO_4. The oxonium salts are stable only at low temperature and in a strongly acidic medium. On dilution, they decompose to give back the original ether and acid.

Ether also form coordination complexes with Lewis acids like BF_3, $AlCl_3$ RMgX, etc.

$R_2\ddot{O}: + BF_3 \longrightarrow R_2O \longrightarrow BF_3$ (b) $R_2O + RMgX \longrightarrow$



It is for this reason that ethers are used as solvent for Grignard reactions.

4.3 Action of Dilute H_2SO_4 (Hydrolysis)

$$C_2H_5\text{-O-}C_2H_5 \xrightarrow[\text{Pressure}]{\text{dil. } H_2SO_4 \text{ heat}} 2C_2H_5\text{-OH}$$

4.4 Action of Concentration H_2SO_4

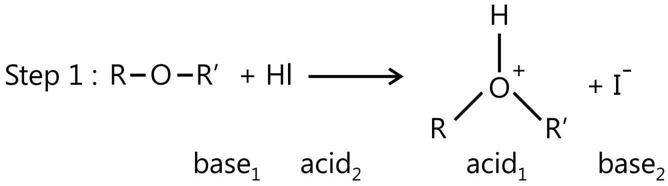
$$C_2H_5\text{-O-}C_2H_5 + H_2SO_4\text{(conc.)} \xrightarrow{\text{Heat}} C_2H_5OH + C_2H_5HSO_4$$

4.5 Action of Conc. HI or HBr.

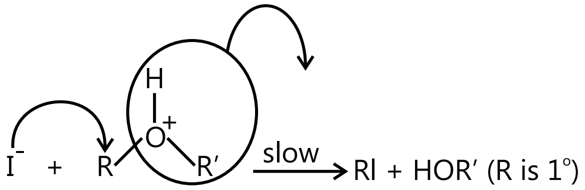
(i) $C_2H_5\text{-O-}C_2H_5 + HI\text{(cold)} \longrightarrow C_2H_5\text{-OH} + C_2H_5\text{+I}$

(ii) $C_6H_5\text{-O-}C_2H_5 + HI \longrightarrow C_6H_5OH + C_2H_5I$

Mechanism of reaction: S_N2 and S_N1 mechanisms for the cleavage of ethers. S_N2 cleavage occurs at a faster rate with HI than with HCl.



Step 2 for S_N2

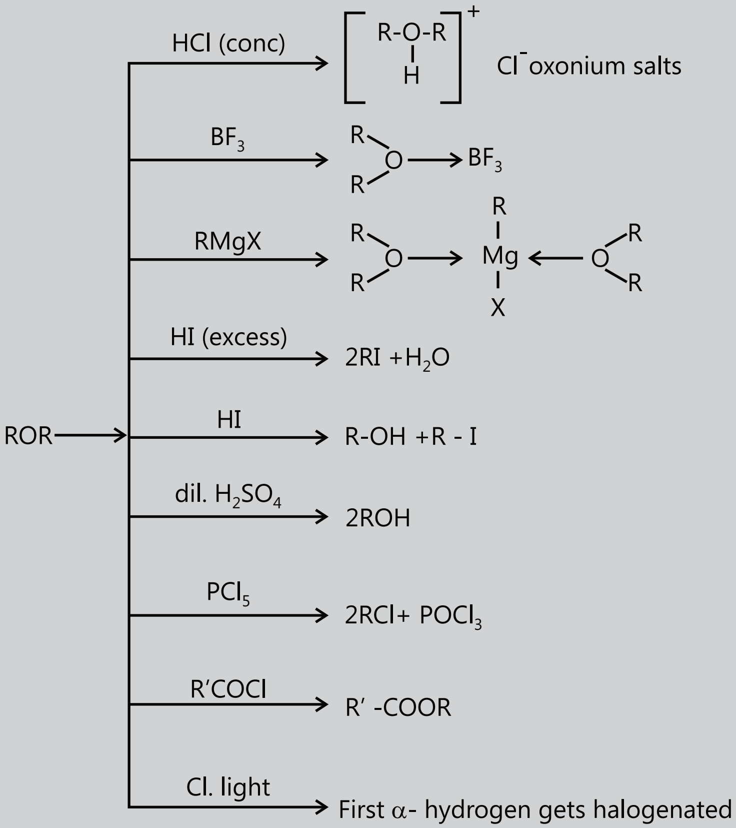


Step 3 for S_N2 $R^+ + I^- \longrightarrow RI$ (R is 3°)

(a) The transfer of H^+ to ROR′ in step 1 is greater with HI, which is a stronger acid, than with HCl Furthermore, in step 2, I, being a better nucleophile than Cl^+, reacts at a faster rate.

MASTERJEE CONCEPTS

- Boiling point of ethers is lower than alcohol due to absence of hydrogen bonding.

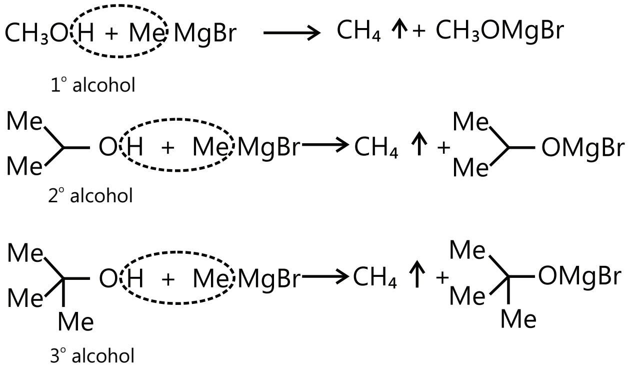


- In reaction with HI, if cold and dilute HI solution is treated with ether, alcohols are formed while in hot and concentrated HI, alkyl halides are formed.
- The reaction mechanism in case of HI depends on the substrate. If the substrates attached to oxygen are 1^0 or 2^0 ,then the mechanism is S_N2 but if the substrate is 3^0 or the carbocation is very stable then the mechanism is S_N1.

Nikhil Khandelwal (JEE 2009, AIR 94)

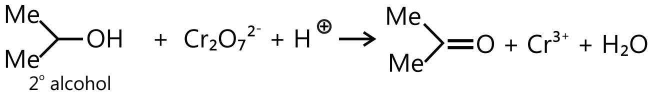
Illustration 1: How are the ethers distinguished from alcohols? **(JEE MAIN)**

Sol: (i) All alcohols give CH_4 (methane gas) when reacted with MeMgBr.



(ii) $K_2Cr_2O_7$ in acid has bright orange colour. When it oxidizes 1° or 2° alcohol, it is reduced to blue green due to the formation of Cr^{3+}.

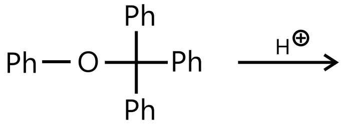
$$\underset{\text{1° alcohol}}{MeCH_2OH} + \underset{\left(\begin{array}{c}\text{Orange}\\ \text{colour}\end{array}\right)}{Cr_2O_7^{2-}} + H^{\oplus} \longrightarrow \underset{\text{Acetic acid (blue-green)}}{Me-COOH + Cr^{3+} + H_2O}$$



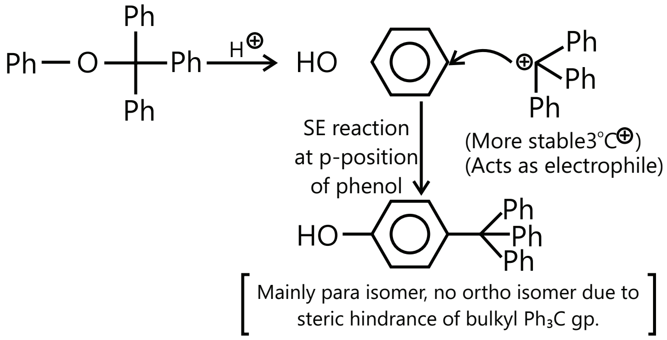
(iii) All alcohols evolve H_2 gas on addition of sodium (Na).

(iv) Dry ethers give negative test with all the reagents (a, b and c).

Illustration 2: Complete the following reaction: **(JEE MAIN)**



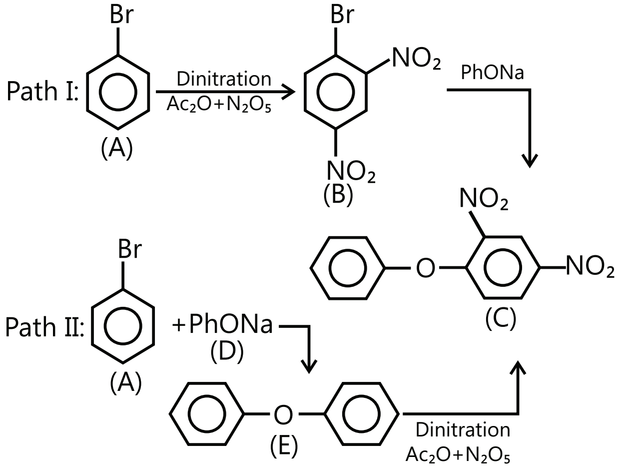
Sol:



[Mainly para isomer, no ortho isomer due to steric hindrance of bulkyl Ph_3C gp.]

Illustration 3: There are two paths for the preparation of phenyl-2, 4-dinitro phenyl either (C). Which path is feasible and why? **(JEE ADVANCED)**

Sol:



a. Path I is feasible. ArSN reaction (Williamson's synthesis) of nucleophile $PhO^{\ominus}$ with (B) is feasible. Also, Br of (B) is activated by the two EWG ($-NO_2$) groups.

b. Path II is not feasible. ArSN reaction of the nucleophile $PhO^{\ominus}$ with (A) is not feasible because no activating group is present in (A).

c. Dinitration of (E) does not give (C) but it gives because the first nitro group is deactivating so that second nitro group enters the other ring at p-position.

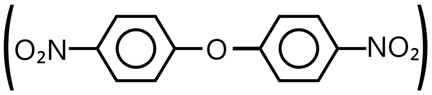
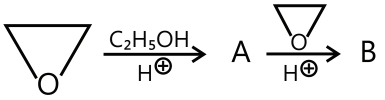
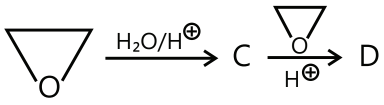
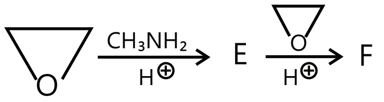


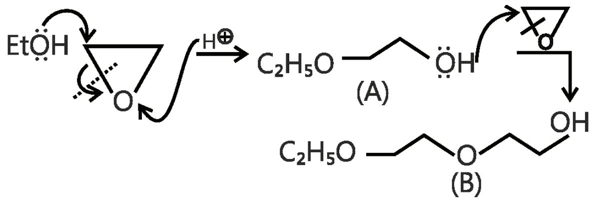
Illustration 4: Complete the following: **(JEE ADVANCED)**

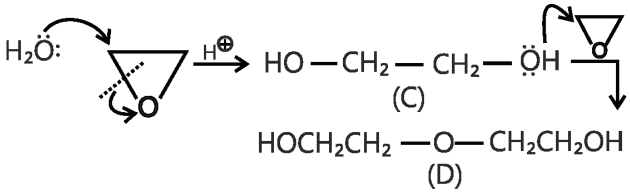
a.


b.


c.


Sol:

a.


b.


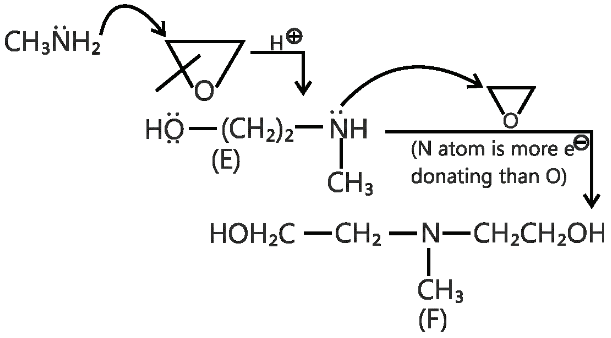
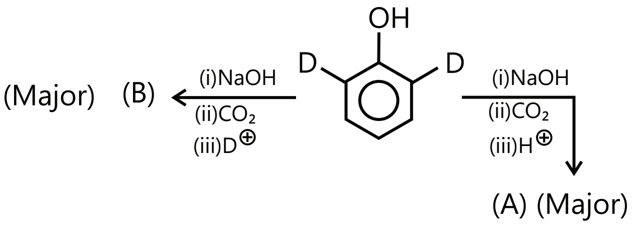
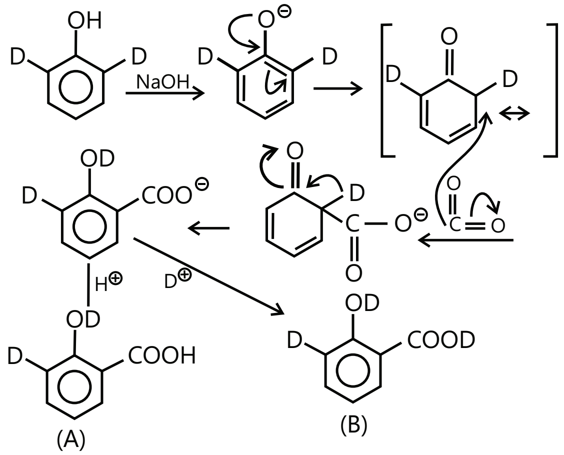
c.


Illustration 5: Complete the following reaction: **(JEE MAIN)**

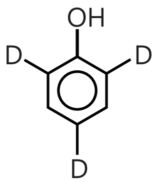


Sol:

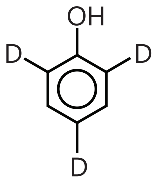


Last image is (A) not (D)

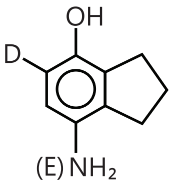
Illustration 6: Complete the following reactions: **(JEE MAIN)**

(i)  $\xrightarrow[EtO^{\ominus}]{CHClBrI}$ (B) (Major)

(A)

(ii)  $\xrightarrow[\overset{\ominus}{O}H]{CBr_2I_2}$ (D) (Major)

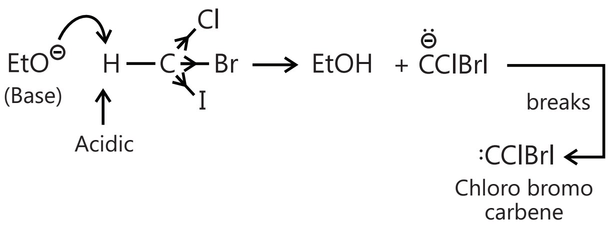
(C)

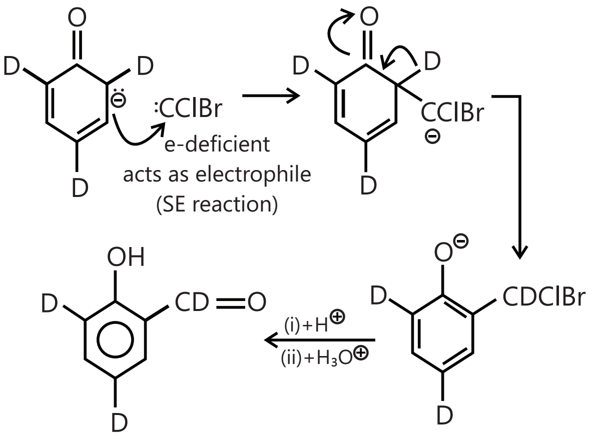
(iii)  $\xrightarrow[t\text{-}BuO^{\ominus}]{CHClBrI}$ (F)

(iv) (E) $\xrightarrow[H_3O^{\oplus}]{CCl_2BrI\ +\ \overset{\ominus}{O}H}$ (G)

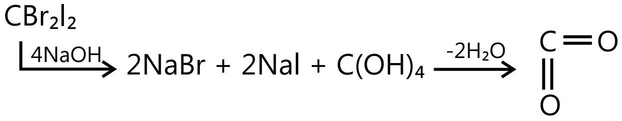
Sol:

(a)



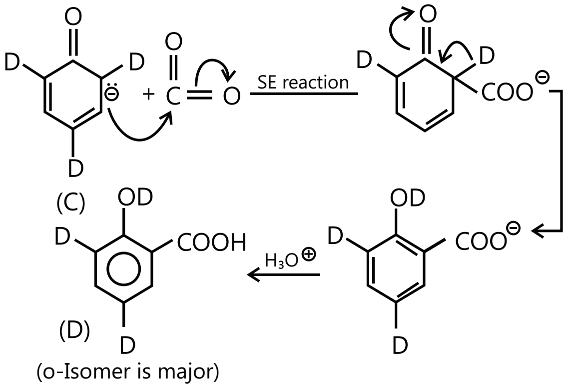


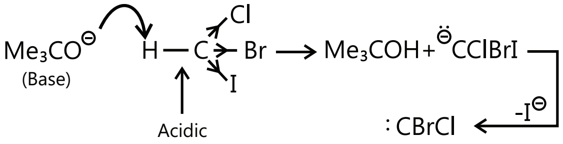
(o-isomer, major)

(b) 

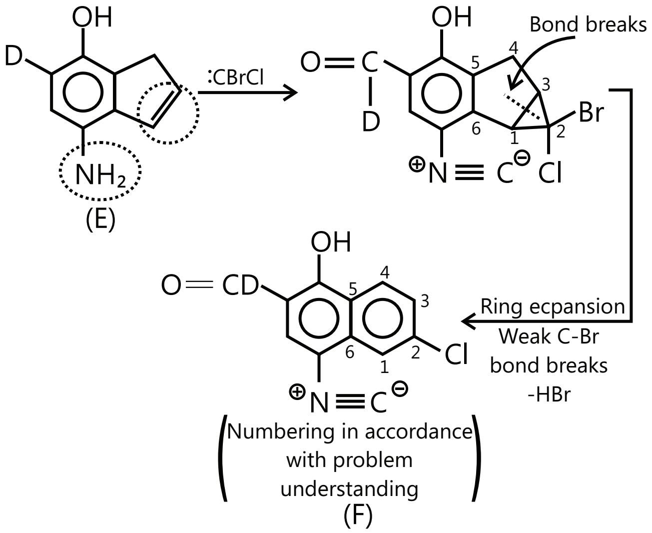
$$CBr_2I_2 \xrightarrow{4NaOH} 2NaBr + 2NaI + C(OH)_4 \xrightarrow{-2H_2O} O=C=O$$

This produces CO_2 ,the reaction is Kolbe reaction.





(c) Carbene also converts (– NH_2) group to $(-\overset{+}{N}\equiv\overset{-}{C}-)$ (Carbylamine reaction) and also adds to (C = C) bond of cyclopentane ring and undergoes Reimer-Tiemann reaction at o-position w.r.t. (–OH) group in benzene ring.



(d) $CCl_2BrI \xrightarrow{4NaOH} 2NaCl + NaBr + NaI$

$+C(OH)_4 \xrightarrow{-2H_2O} CO_2$

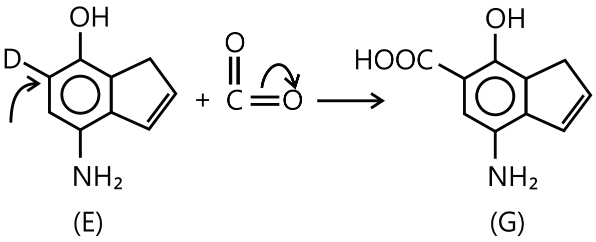
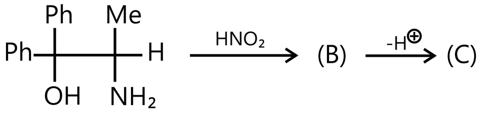
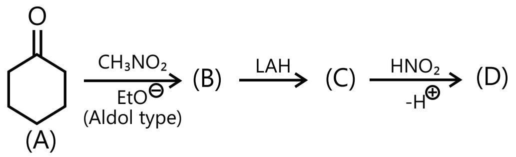


Illustration 7: Complete the following reactions: **(JEE ADVANCED)**

(A)

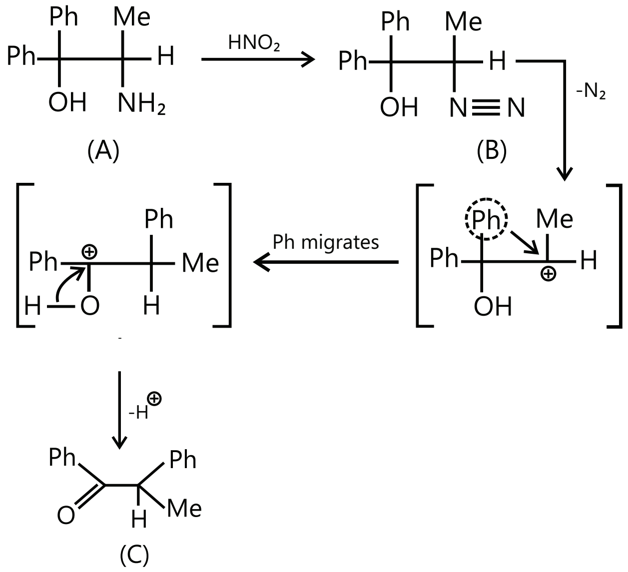


(B)

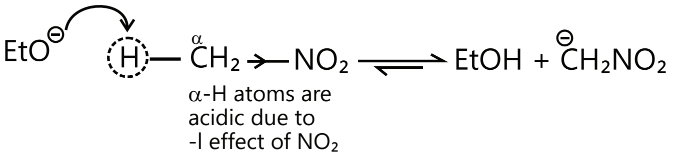


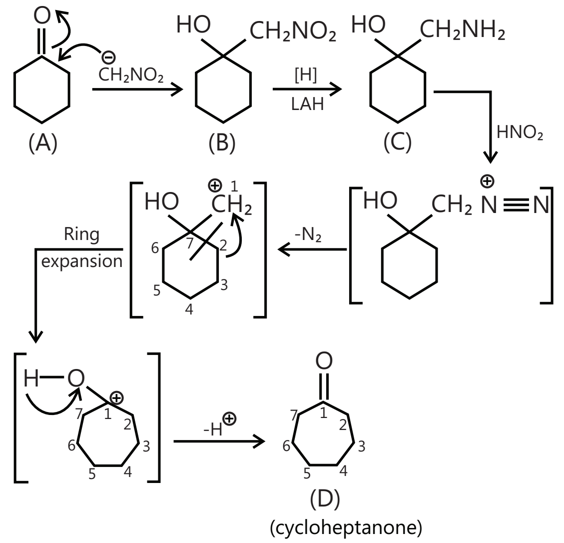
Sol:

(A)

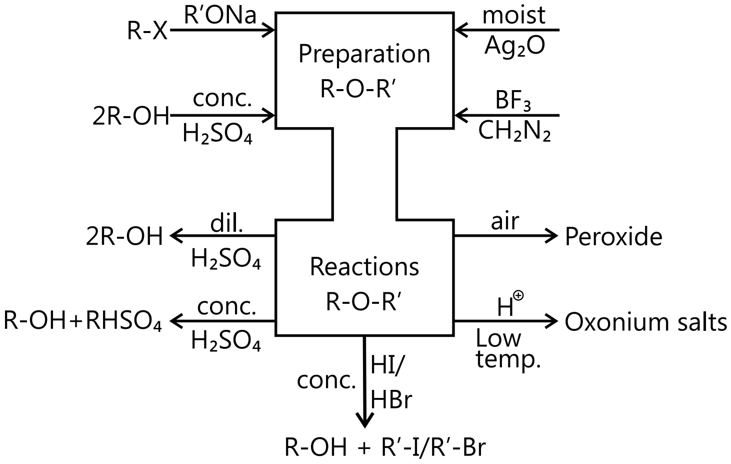


(B)





POINTS TO REMEMBER



Solved Examples

JEE Main/Boards

Example 1: Complete the following reactions:

a. $2Me_3C{-}Br \xrightarrow[\Delta]{Ag_2CO_3} (A)$

b. $2MeOH + MeCH = O + HCl\ (g) \rightarrow (B)$

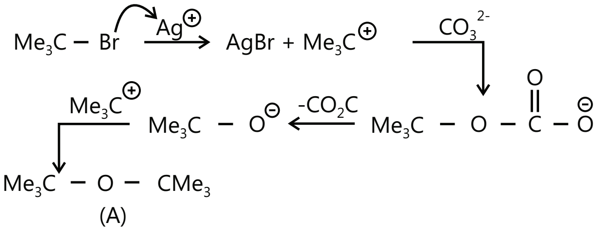
c. $MeOH + H_2C = O + HCl\ (g) \rightarrow (C)$

Sol: A = $Me_3\,C - O - Me_3$ (Di-t-butyl ether)

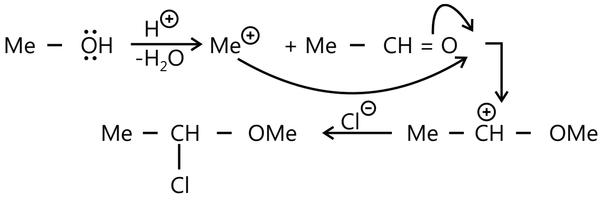
Ag^+ reacts with Br^- leaving $Me_3C^{\ominus}$,which reacts with CO_3^{2-} to give $Me_3C - OCO_2^{\ominus}$. The latter loses CO_2 leaving Me_3COO which reacts with $Me_3C^{\oplus}$ to give the product. Due to steric hindrance, the yield is less.

Mechanism:

a.



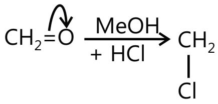
b.



(α Chloroether)

α Chloroethyl methyl ether

c.



—OMe (α Chlorether dimethyl ether)

Example 2: Complete the following reactions:

a. $\underset{\text{Benzene (A)}}{C_6H_6} + MeCOCl \xrightarrow{AlCl_3} B \xrightarrow[H_2SO_4]{HNO_3} C \xrightarrow{NaBH_4} D \xrightarrow[\Delta]{H_2SO_4} E$

b. $(B) \xrightarrow{NaBH_4} F \xrightarrow[\Delta]{H_2SO_4} G \xrightarrow[H_2SO_4]{HNO_3} H$