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

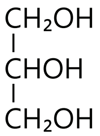
Alcohols and phenols may be classified as mono-, di-, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively in their structures as given below:

C_2H_5OH

Monohydric

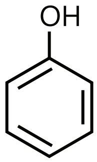
$HOCH_2CH_2OH$

Dihydric

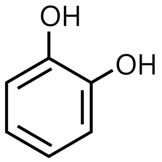


$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

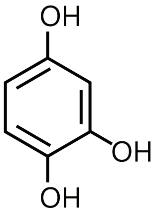
Trihydric



Monohydric



Dihydric



Trihydric

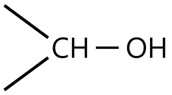
1.1.1 Compounds Containing Csp^3 – OH Bond

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

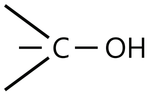
(a) **Primary, secondary and tertiary alcohols:** In these types of alcohols, the –OH group is attached primary secondary and tertiary carbon atom, respectively as depicted below.

$-CH_2-OH$

Primary (1°)



Secondary (2°)

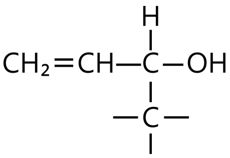


Tertiary (3°)

(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

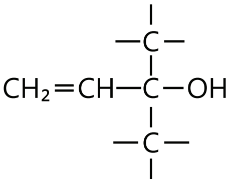
$CH_2=CH-CH_2-OH$

Primary (1°)



$$CH_2=CH-\overset{\displaystyle H}{\underset{\displaystyle -C-}{C}}-OH$$

Secondary (2°)

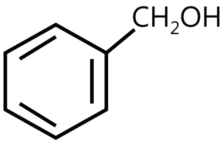


$$CH_2=CH-\overset{\displaystyle -C-}{\underset{\displaystyle -C-}{C}}-OH$$

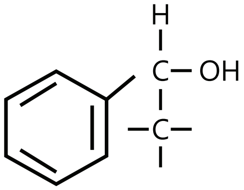
Tertiary (3°)

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

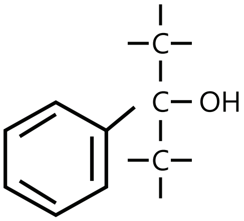
For example Allylic and benzylic alcohols may be primary, secondary or tertiary



Primary



Secondary

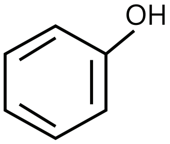


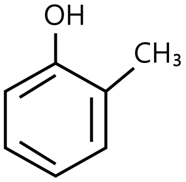
Tertiary

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

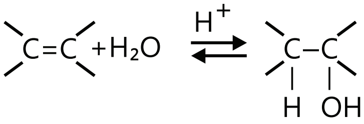
Vinylic alcohol : $CH_2=CH\text{-}OH$





2. PREPARATION OF ALCOHOLS

2.1 From Alkenes

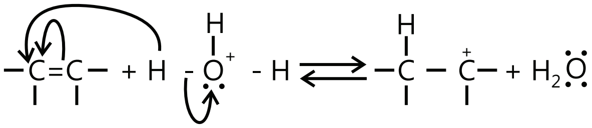


2.1.1 By Acid Catalyzed Hydration

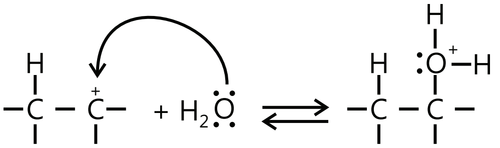
Alkenes react with water in the presence of acid as catalyst to form alcohol. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markonikov's rule.

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

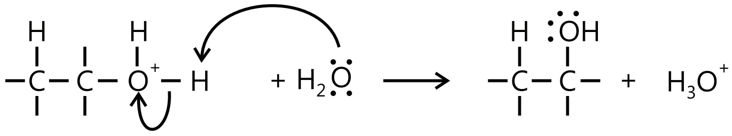
Step 1 $H_2O + H^+ \rightarrow H_3O^+$



Step 2



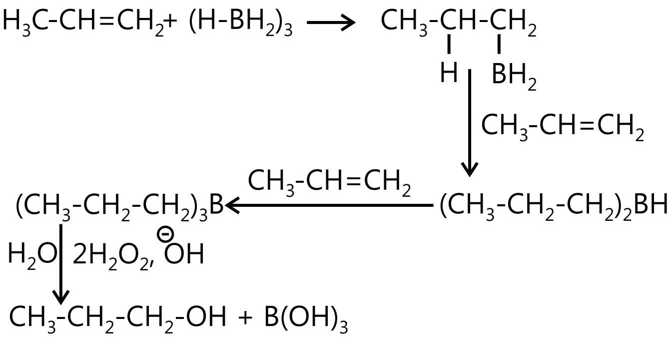
Step 3



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.

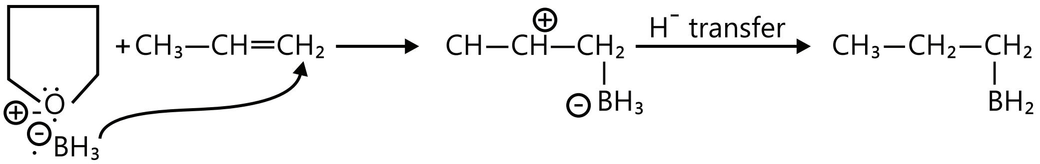
Note: This is the addition of water at double bond according to Anti-Markonikov Rule.



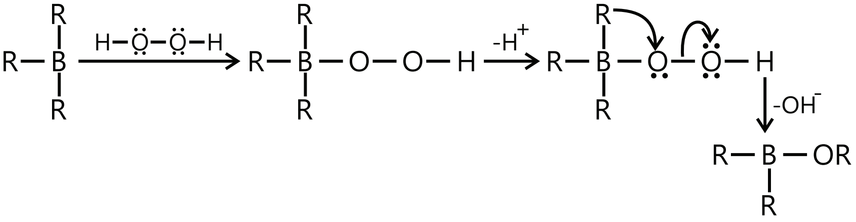
Proapn-1-ol

Mechanism of hydroboration – deboration

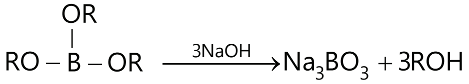
$$CH_3—CH=CH_2 \xrightarrow{B_2H_6\text{-THF}/H_2O_2/OH^-} CH_3—CH_2—CH_2—OH$$



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



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

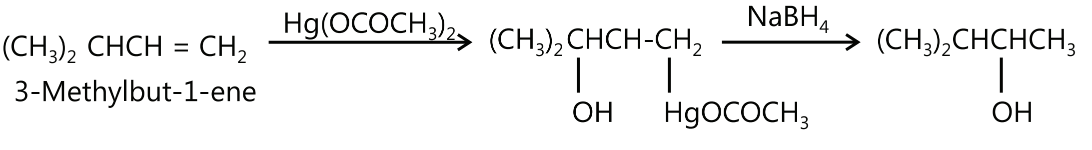


$$RO-\overset{\overset{OR}{|}}{B}-OR \xrightarrow{3NaOH} Na_3BO_3 + 3ROH$$

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.

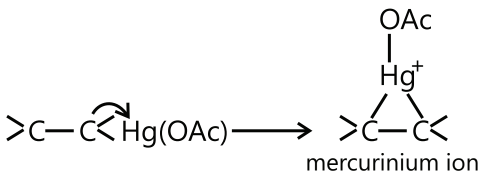
With mercuric acetate, the product is 3-methyl-2-butanol (Markonikov's addition with no rearrangement, oxymercuration-demercuration reaction)



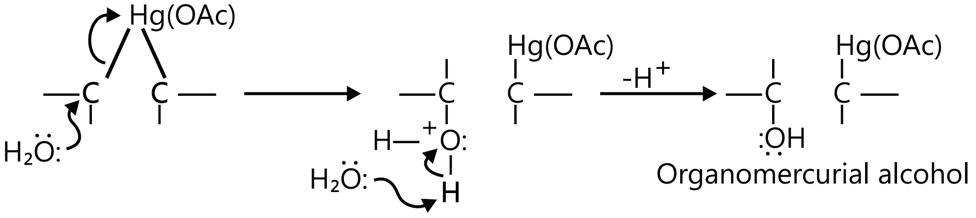
3-Methylbut-1-ene

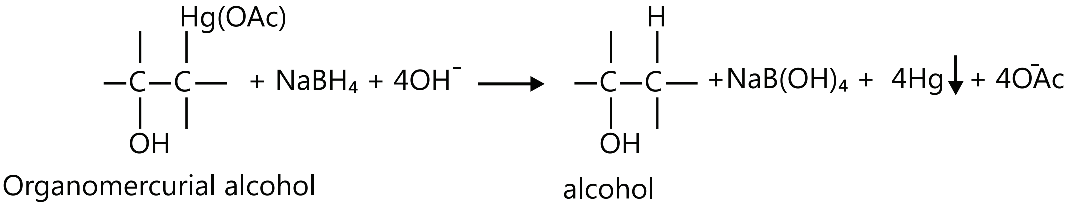
Not-isolated

3-Methyl-1-butanol



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.

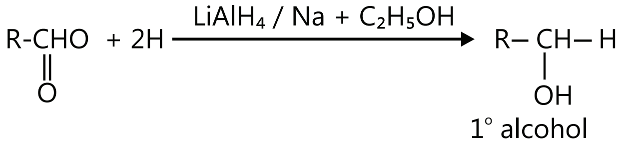




The second step is demercuration, to form the alcohol. Sodium borohydride ($NaBH_4$, a reducing agent replaces the mercuric acetate with hydrogen.)

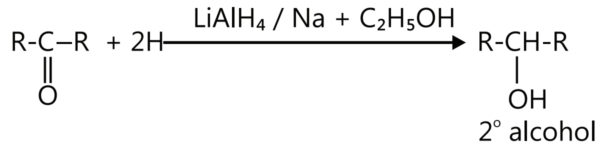
2.2 From Carbonyl Compounds

2.2.1 By Reduction of Carbonyl Compounds



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

1° alcohol

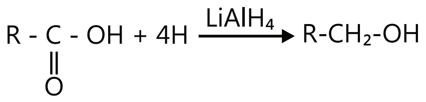


$$\text{R-}\underset{\underset{O}{\|}}{C}\text{–R} + 2H \xrightarrow{LiAlH_4 / Na + C_2H_5OH} \text{R-}\underset{\underset{OH}{|}}{\text{CH}}\text{-R}$$

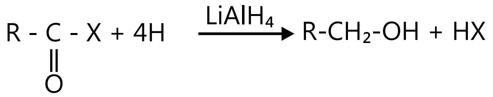
2° alcohol

2.3 From Acid Derivatives

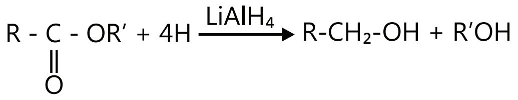
2.3.1 By Reduction of Acid and its Derivatives



$$R - \underset{\underset{O}{\|}}{C} - OH + 4H \xrightarrow{LiAlH_4} R\text{-}CH_2\text{-}OH$$



$$R - \underset{\underset{O}{\|}}{C} - X + 4H \xrightarrow{LiAlH_4} R\text{-}CH_2\text{-}OH + HX$$

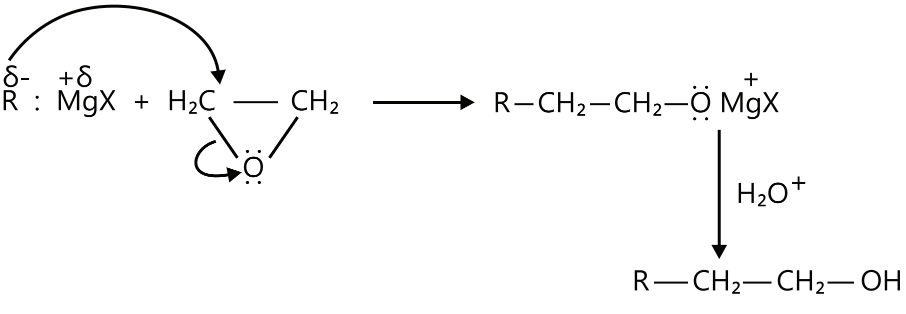


$$R - \underset{\underset{O}{\|}}{C} - OR' + 4H \xrightarrow{LiAlH_4} R\text{-}CH_2\text{-}OH + R'OH$$

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

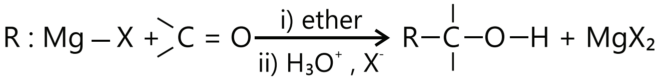
2.4 From Grignard Reagents

2.4.1 Reaction with Oxirane

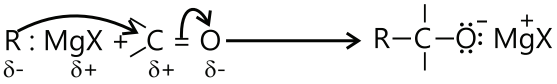


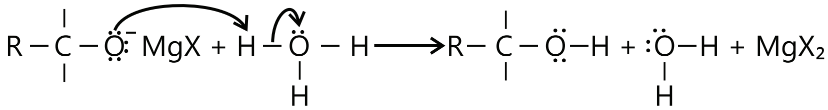
Primary alcohol

2.4.2 Reaction with Carbonyl Compounds

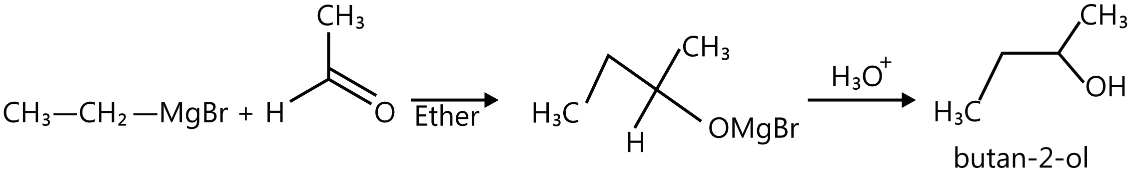


$$R:Mg-X + \rangle C=O \xrightarrow[\text{ii) } H_3O^+,\ X^-]{\text{i) ether}} R-\overset{|}{\underset{|}{C}}-O-H + MgX_2$$



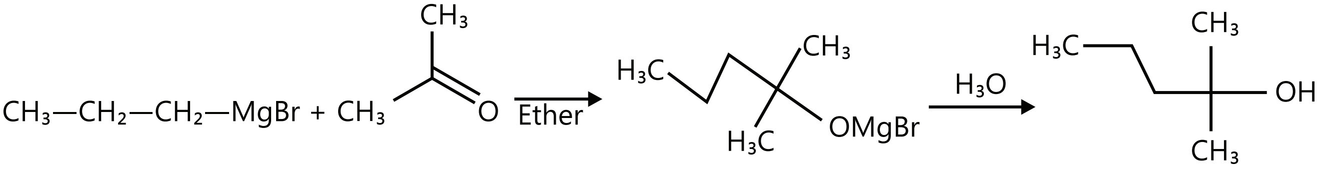


2.4.3 Reaction with Acetaldehyde



butan-2-ol

2.4.4 Reaction with Ketone



2-methylpentan-2-ol

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.

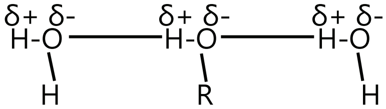
$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} \longrightarrow \underset{\text{n–Butylalcohol}}{CH_3CH_2CH_2CH_2OH} + CH_3COCH_3$$

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.

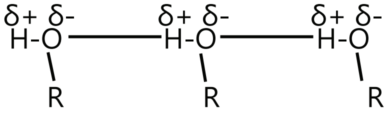
The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarized –OH groups present both in alcohols and water.



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.

PLANCESS CONCEPTS

Preparation of alcohols:

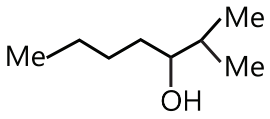
- Key takeaway - Hydration and oxymercuration-demercuration gives Markonikov's product but hydroboration-oxidation gives Anti-markonikov's product.
- Misconception - Hydroboration follows Markonikov's rule but in this case, the electron deficient species is Boron and not Hydrogen.
- Note - On replacing 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.

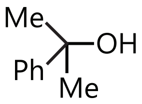
Physical properties of alcohols:

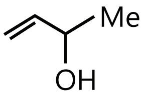
Alcohols generally have high boiling point because of hydrogen bonding.

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:

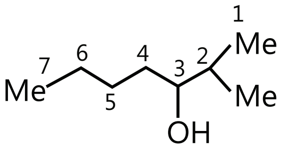
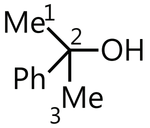
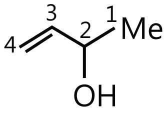
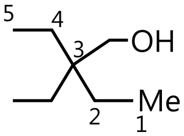
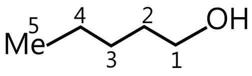
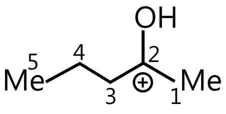
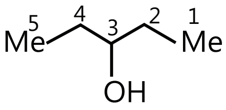
S.No.	Structure	IUPAC name	Carbinol system name	Type of alcohol
a.		2-Methyl heptan-3-ol	n-Butyl isopropyl carbinol	2°
b.		2-Phenyl propan-2-ol	Dimethyl phenyl carbinol	3°
c.		But-3-en-2-ol	Methyl vinyl carbinol	2° allylic
d.		3-Ethyl pentan-3-ol	Triethyl carbinol	3°

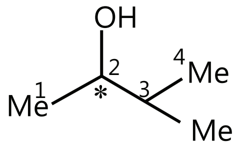
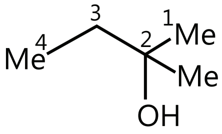
Illustration 2: (a) Write the structure of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC, common and carbinol names. Indicate each as 1°, 2° and 3° and also their stereoisomers, if any-

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

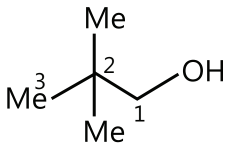
Sol: (a) (i)

	 (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°

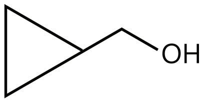
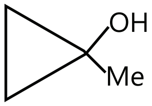
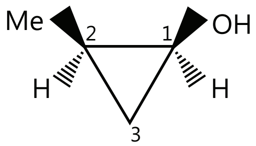
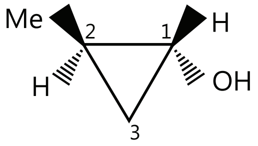
(ii) Write the four atoms in a straight chain and put Me and (–OH) at different positions.

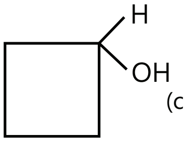
	 [(V) + VI] (O.A)	 (VII)
IUPAC	(±)-3-Methyl butan-2-ol	2-Methyl butan-2-ol
Common	—	t-Pentyl alcohol
Carbinol	Isopropyl methyl carbinol	Dimethylethyl carbinol
Type	2°	3°

(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

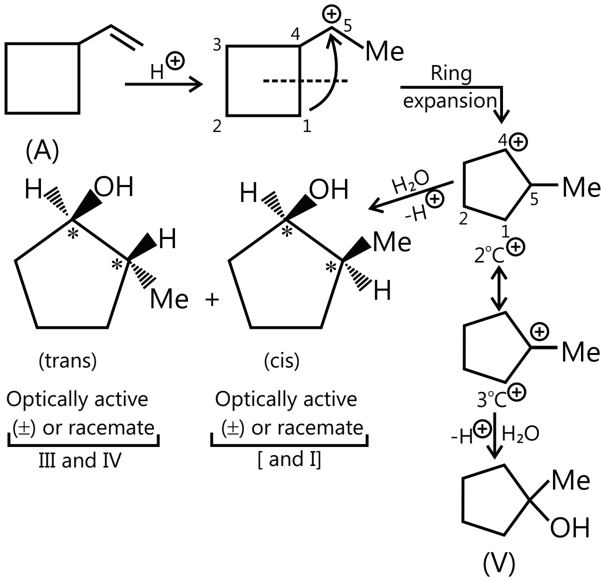


(VII)

(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) $\left(\begin{array}{l}\text{Number of}\\ \text{isomeric products}\\ \text{including stereo-}\\ \text{isomers}\end{array}\right)$ **(JEE ADVANCED)**

Sol:



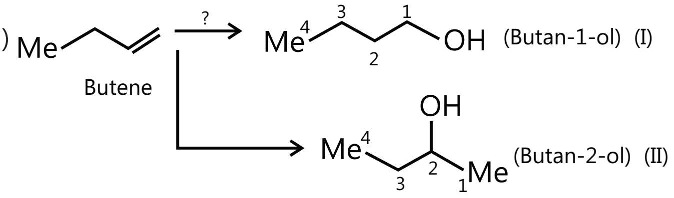
The total number of isomeric products including stereoisomers is 5.

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)**

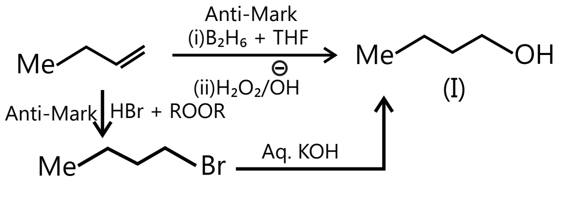
Sol: (a)

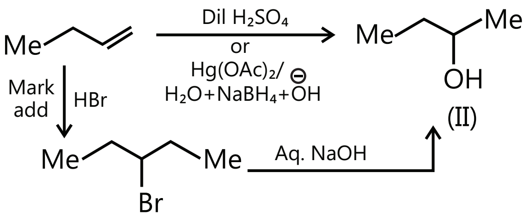


Hydroborato oxidation proceeds with Anti-Markovnikov addition, so it would give (I), while acid-catalysed hydration and mercuration – demercuration reaction proceed with Markovnikov addition, so it would give (II).

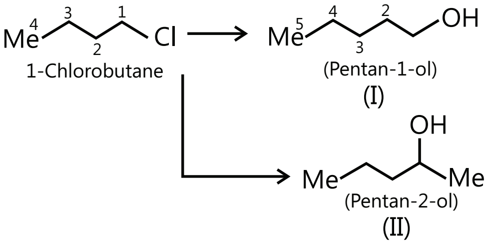
Synthesis:

a.

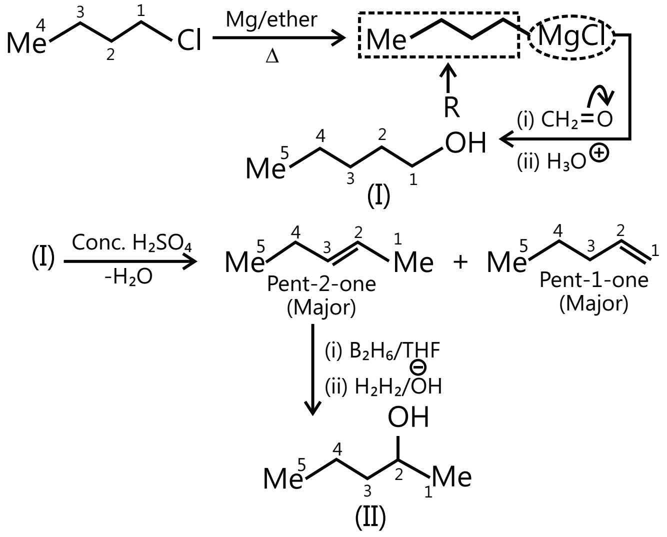




b.



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

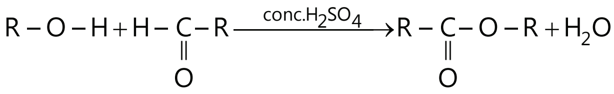
Alcohols are weakly acidic in nature due to which when they react with group one alkali metals they liberate hydrogen gas and form alkoxides.

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

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

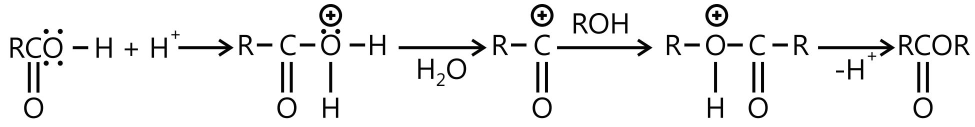
Reaction of alcohol with carboxylic acid in presence of sulphuric acid gives an ester. In this reaction sulphuric acid react as protonating agent as well as dehydrating agent.



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

Mechanism:

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

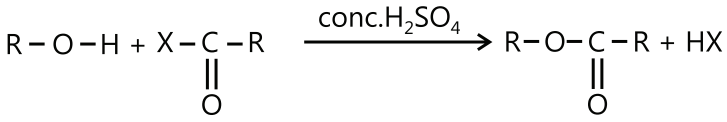


$$R\underset{\underset{O}{\|}}{C}\ddot{O}-H + H^+ \longrightarrow R-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\oplus}{\ddot{O}}}-H \xrightarrow[H_2O]{} R-\underset{\underset{O}{\|}}{\overset{\oplus}{C}} \xrightarrow{ROH} R-\underset{\underset{H}{|}}{\overset{\oplus}{O}}-\underset{\underset{O}{\|}}{C}-R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

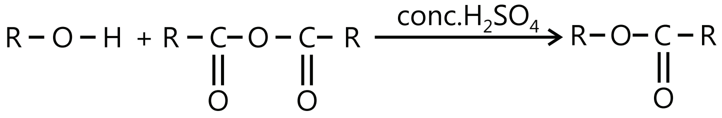
Note : The above reduction is laboratory method of ester preparation.

4.3 Reaction with Acid Derivatives

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

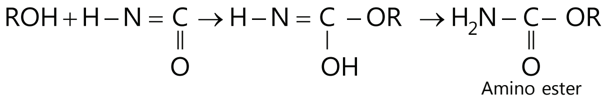


$$R-O-H + X-\underset{\underset{O}{\|}}{C}-R \xrightarrow{conc.H_2SO_4} R-O-\underset{\underset{O}{\|}}{C}-R + HX$$



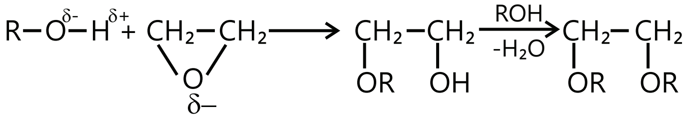
$$R-O-H + R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow{conc.H_2SO_4} R-O-\underset{\underset{O}{\|}}{C}-R$$

4.4 Reaction with Isocyanic Acid



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

4.5 Reaction with Ethylene Oxide



1,2-dialkoxy ethane

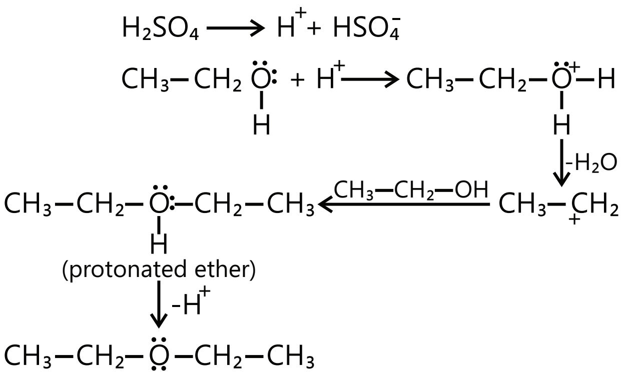
4.6 Reaction with Diazomethane

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

4.7 Reaction with H_2SO_4

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

Mechanism:



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

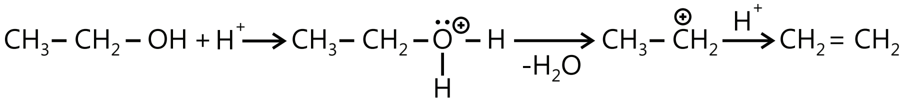
$$CH_3-CH_2\underset{\underset{H}{|}}{\ddot{O}}: + H^+ \longrightarrow CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{\ddot{O}}}-H \xrightarrow{-H_2O} CH_3-\overset{+}{C}H_2$$

$$CH_3-\overset{+}{C}H_2 \xrightarrow{CH_3-CH_2-OH} CH_3-CH_2-\underset{\underset{H}{|}}{\ddot{O}}-CH_2-CH_3 \xrightarrow{-H^+} CH_3-CH_2-\ddot{O}-CH_2-CH_3$$

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

Mechanism:

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



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

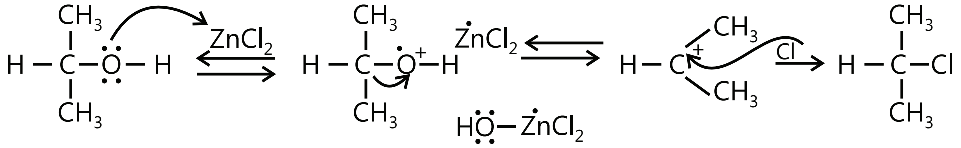
4.8 Action of Halogen Acids

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.

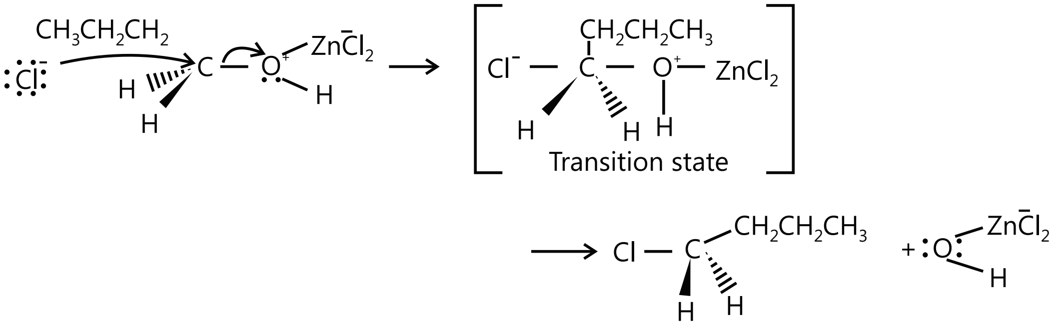
$$C_2H_5OH + HCl \xrightarrow{\text{anhy. } ZnCl_2} C_2H_5Cl + H_2O$$

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:

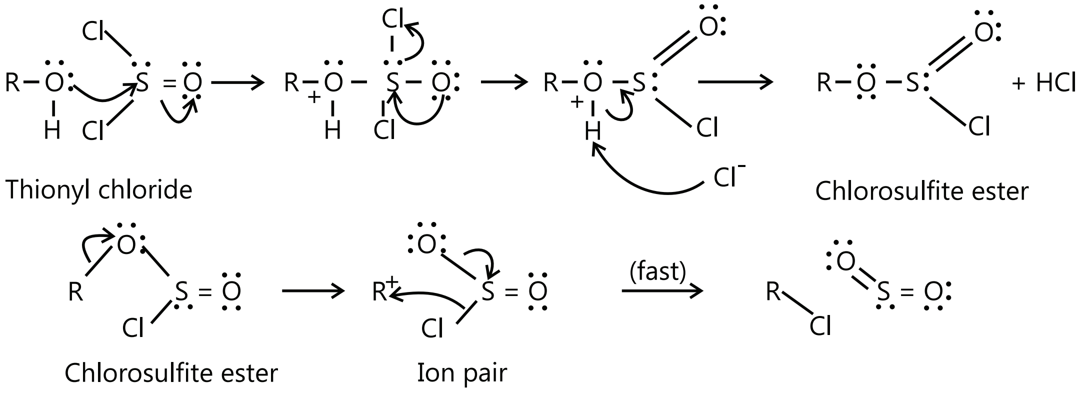


4.9 Action of Thionyl Chloride

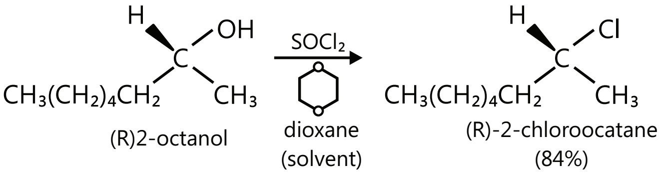
Alcohols react with thionyl chloride to form alkyl halide and reaction is called diarzon process.

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

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)

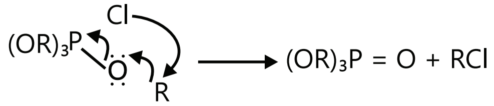
Phosphorous halide react with alcohols to form corresponding haloalkanes.

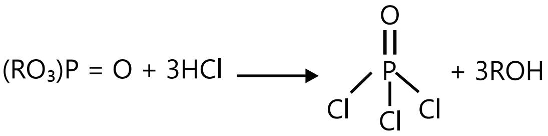
For Example: $C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + HCl + POCl_3$

Mechanism:

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

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





4.11 Action of Ammonia

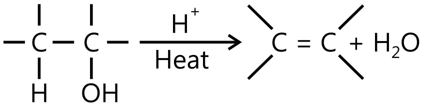
When vapours of ammonia with alcohol passed over heated alumina mixture of primary, secondary and tertiary amines is formed.

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

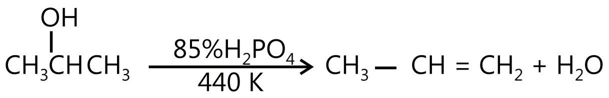
The ease of dehydration of alcohols is in the order Tertiary > Secondary > Primary

4.12 Dehydration

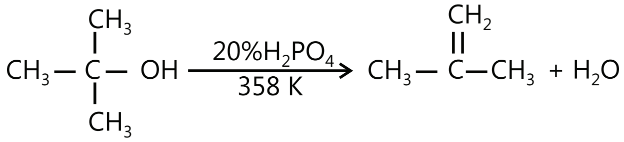
Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with acid e.g., concentrated H_2SO_4 or H_3PO_4 or catalysts such as anhydrous zinc chloride or alumina



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

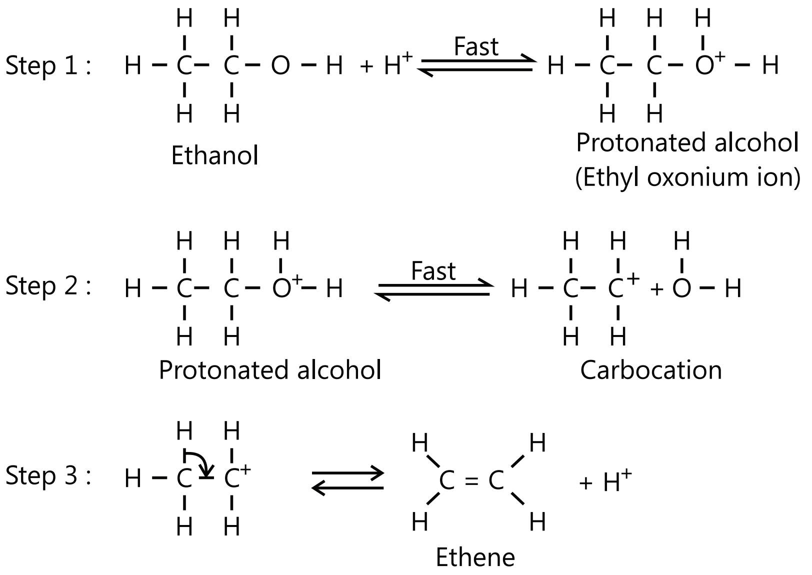


$$CH_3\overset{OH}{\overset{|}{C}H}CH_3 \xrightarrow[440\ K]{85\% H_2PO_4} CH_3-CH = CH_2 + H_2O$$



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

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.,

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

Ethyl alcohol Diethyl ether

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

$$CH_3CH_2OH \xrightarrow[633K]{Al_2O_3} CH_2 = CH_2 + H_2O$$

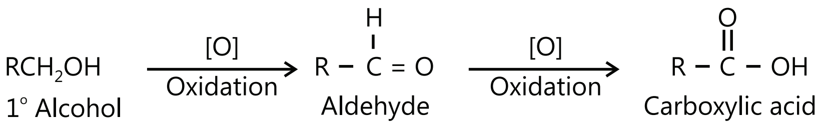
Ethanol Ethene

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.

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.

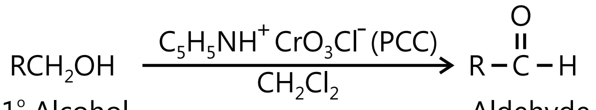


$$RCH_2OH \xrightarrow[\text{Oxidation}]{[O]} R-\overset{H}{\overset{|}{C}}=O \xrightarrow[\text{Oxidation}]{[O]} R-\overset{O}{\overset{||}{C}}-OH$$

1° Alcohol Aldehyde Carboxylic acid

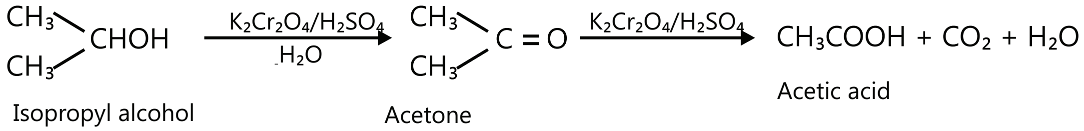
E.g., $\underset{\text{Ethyl alcohol}}{CH_3CH_2OH+[O]} \xrightarrow[\text{-}H_2O]{K_2Cr_2O_7\ +\ DilH_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$

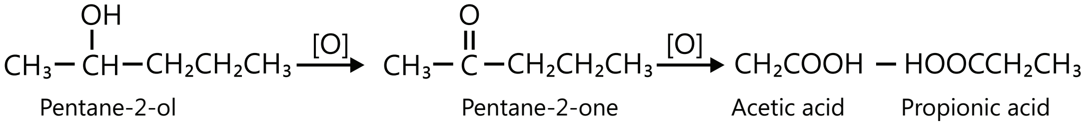
The oxidation can, however, be stopped at the aldehyde stage if Cr(VI) reagent such as Collin's reagent ($CrO_3.2C_5H_5N$, chromium trioxide-pyridine complex), Corey's reagent or pyridinimum chlorochromate (PCC, $CrO_3.C_5H_5N.HCl$ or C_5H_5NH + CrO_3Cl^-) pyridinimum dichromate [PDC, $(C_5H_5NH)_2^{2+}$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



$$\underset{1^\circ\ \text{Alcohol}}{RCH_2OH} \xrightarrow[CH_2Cl_2]{C_5H_5NH^+ CrO_3Cl^- (PCC)} \underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$

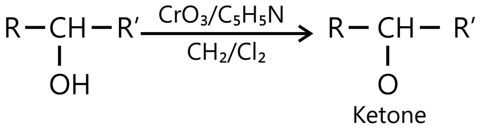
(ii) **Secondary Alcohols** are easily oxidized to ketones with the same number of carbon atoms. However, ketones resist further oxidation but in some conditions, they are oxidized to carboxylic acids containing lesser number of carbon atoms than the original alcohol.





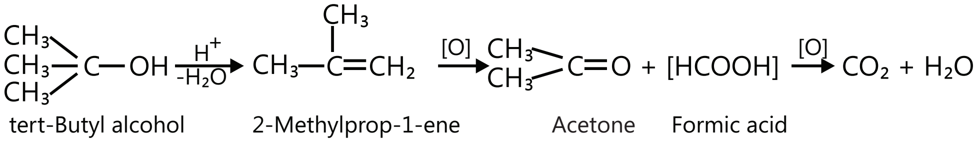
$$\underset{\text{Pentane-2-ol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2CH_2CH_3} \xrightarrow{[O]} \underset{\text{Pentane-2-one}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_3} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_2COOH} - \underset{\text{Propionic acid}}{HOOCCH_2CH_3}$$

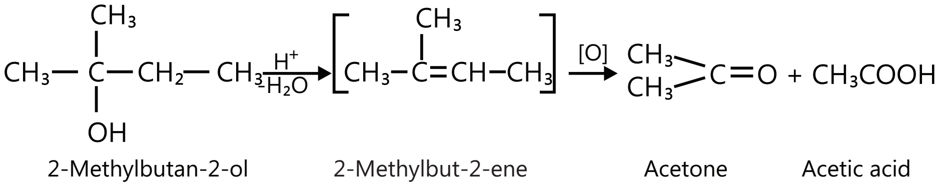
This oxidation be stopped at the ketone stage by using chromic anhydride (CrO_3)



$$R-\underset{\underset{\displaystyle OH}{|}}{CH}-R' \xrightarrow[CH_2/Cl_2]{CrO_3/C_5H_5N} \underset{\text{Ketone}}{R-\underset{\underset{\displaystyle O}{|}}{CH}-R'}$$

(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

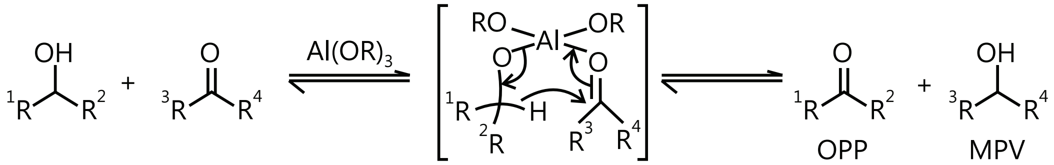




4.14 Oppenauer Oxidation

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 (300º C)

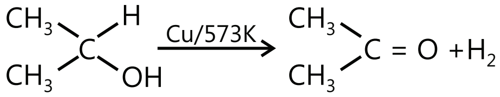
(a) **Primary alcohols** undergo dehydrogenation to give aldehydes.

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

Ethanol
Ethyl alcohol

Ethanal
Acetaldehyde

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

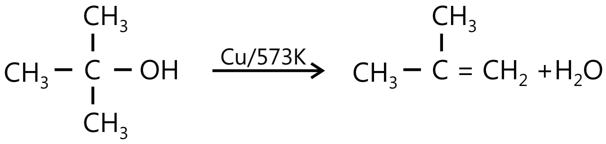


$$(CH_3)_2CH(OH) \xrightarrow{Cu/573K} (CH_3)_2C = O + H_2$$

Propan-2-ol
(Isopropyl alcohol)

Propanone
(Acetone)

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



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

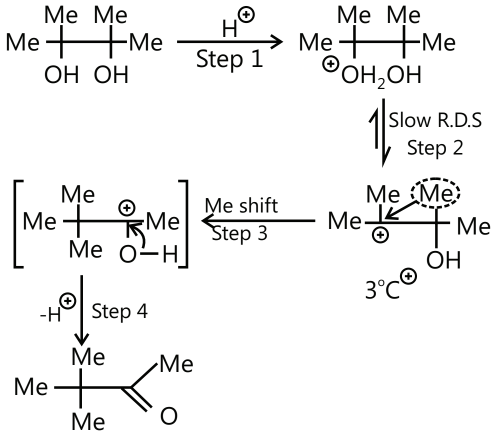
2-Methylpropan-2-ol
(tert-Butyl alcohol)

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:

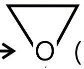


4.16 Dihydric Alcohols

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) $HOCH_2-CH_2OH \xrightarrow[-H_2O]{2HI} [I\text{-}CH_2\text{-}CH_2\text{-}I] \longrightarrow CH_2{=}CH_2 + I_2$

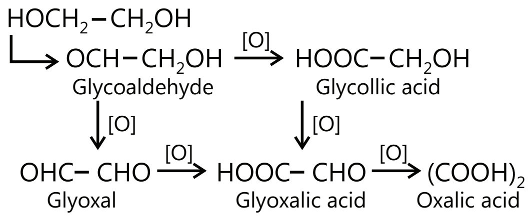
(iii) $HOCH_2-CH_2OH + HNO_3 \xrightarrow{H_2SO_4} \begin{array}{l} CH_2ONO_2 + 2H_2O \\ | \\ CH_2ONO_2 \end{array}$

Ethylene dinitrate

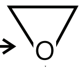
(iv) $HOCH_2-CH_2OH \xrightarrow{CH_3COOH/H_2SO_4} \begin{array}{l} CH_2O\ COCH_3 \\ | \\ CH_2OCOCH_3 \end{array}$

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.



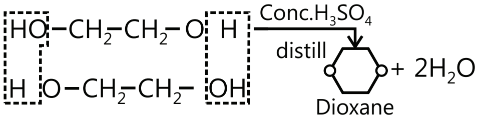
(d) Dehydration:

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

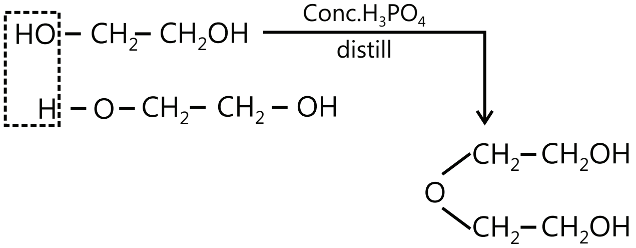
(ii) $HOCH_2-CH_2OH \xrightarrow[-H_2O]{\text{Anhd.}ZnCl_2} [CH_2 = CHOH]$

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

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

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

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

(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:

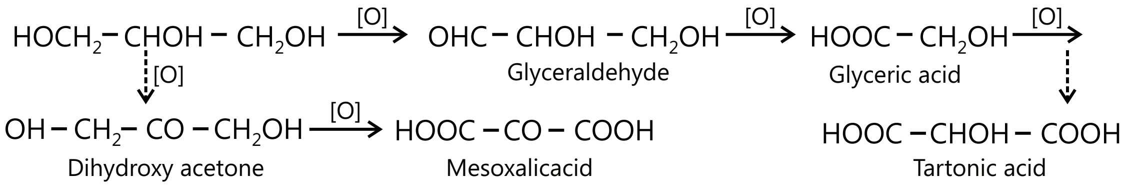
$$HOCH_2-CHOH-CH_2OH \xrightarrow[(283\text{-}298\ K)]{\substack{Conc.HNO_3\\ +Conc.\ H_2SO_4}} \underset{\text{(Glyceryl trinitrate)}\quad\text{(Nitroglycerine)}}{O_2NOCH_2-CHONO_2-CH_2ONO_2}$$

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:

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

(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.

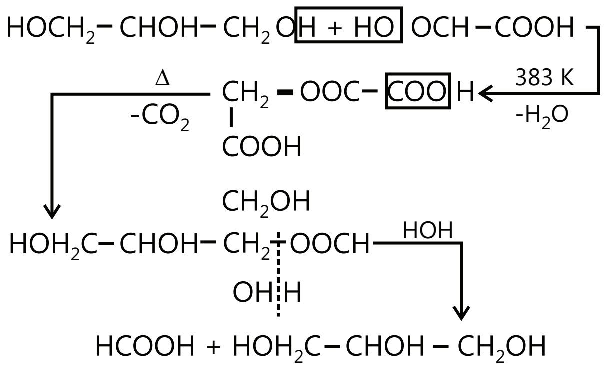
(g) Reaction with HIO_4:

$$HOCH_2-CHOH-CH_2OH + 2HIO_4 \xrightarrow{\Delta} 2HCHO + HCOOH + 2HIO_3 + H_2O$$

(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.

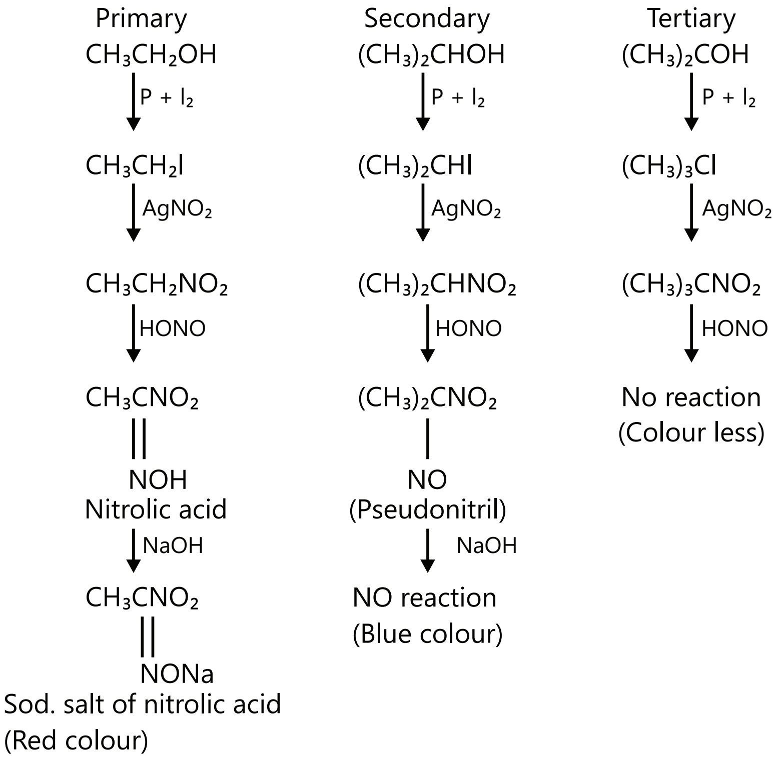
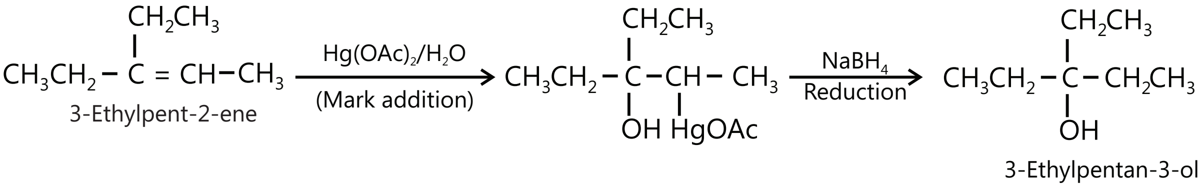


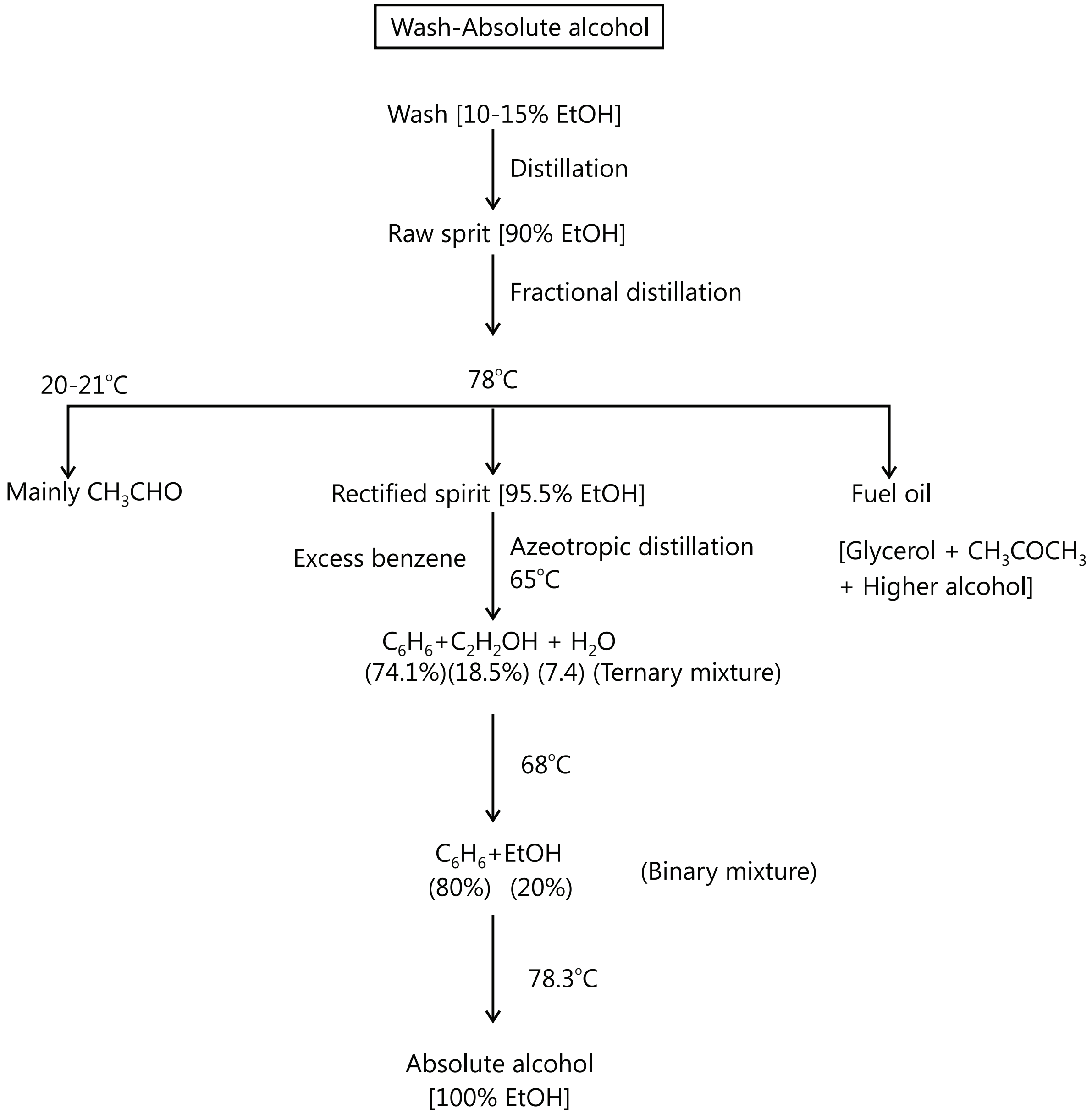
Illustration 5: Give the structure of the major organic product when 3-ethylpent-2-ene is treated with $Hg(OAc)_2$, H_2O, $NaBH_4$. **(JEE MAIN)**

Sol:



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

Absolute alcohol:



Flowchart 22.1 Preparation of absolute alcohol

PLANCESS 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,

p-Anisyl   p-Tolyl   p-Chlorophenyl

  (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?

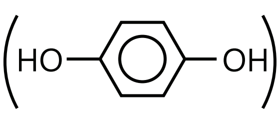
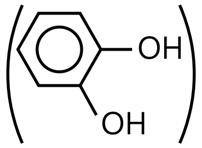
(i) Hydroquinone (ii) Catechol

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

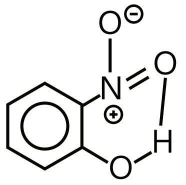
(i) o-Nitrophenol (ii) o-Hydroxy benzaldehyde

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

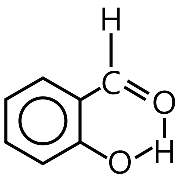
Sol: (a) Although the molecular mass of benzenethiol (Ph – SH) is higher, phenol has high boiling point. It is because there is no H-bonding in PhSH.

(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.

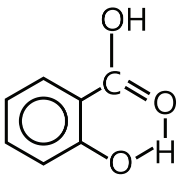
(c) In ortho-isomers of (I), (II) and (III), intramolecular H-bonding (chelation) occurs which inhibits the intermolecular attraction between these molecules and thus, lowers the b.p. and also reduces H-bonding of these molecules with H_2O thereby, decreases water solubility. Intermolecular chelation 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)

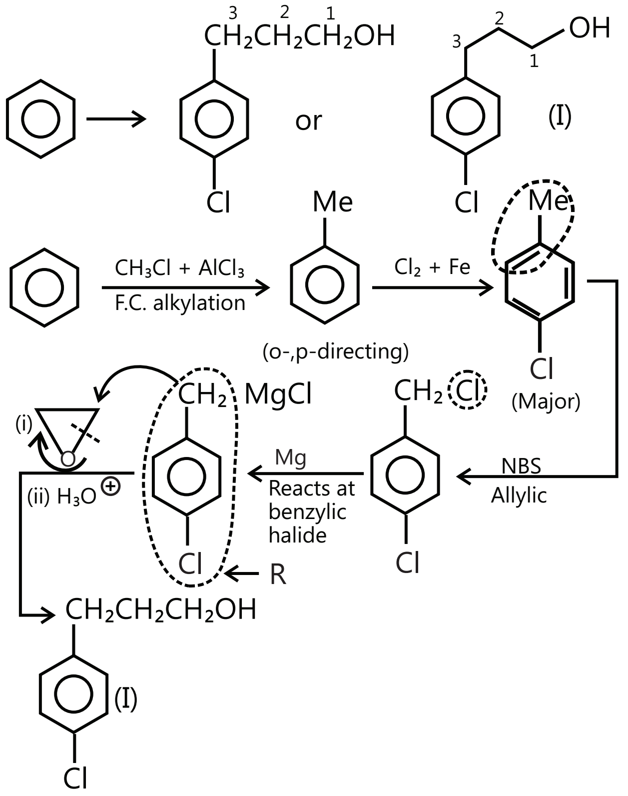
(b) Ethyne to butanol

(c) Propane to allyl alcohol

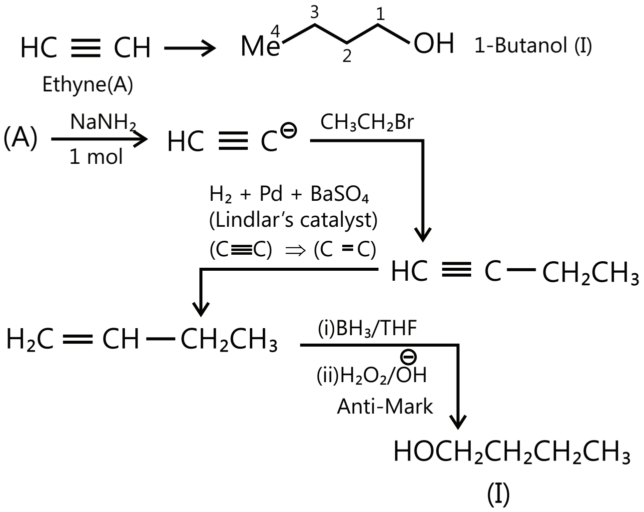
(d) Propane to propanol and propan-2-ol

Synthesis:

(a)

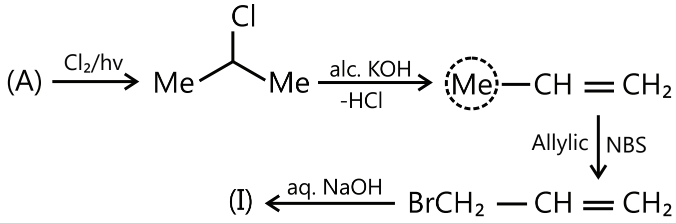


(b)



(c) $MeCH_2Me \longrightarrow H_2C = CH — CH_2\ OH$

Propane (A) Allyl alcohol (I)



(d)

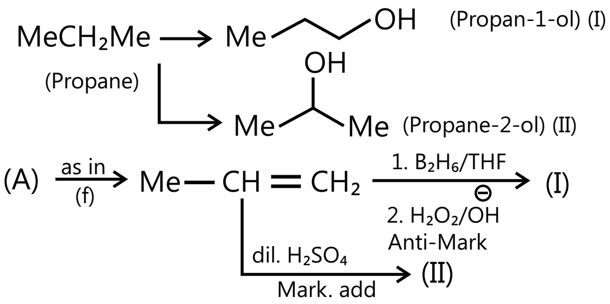
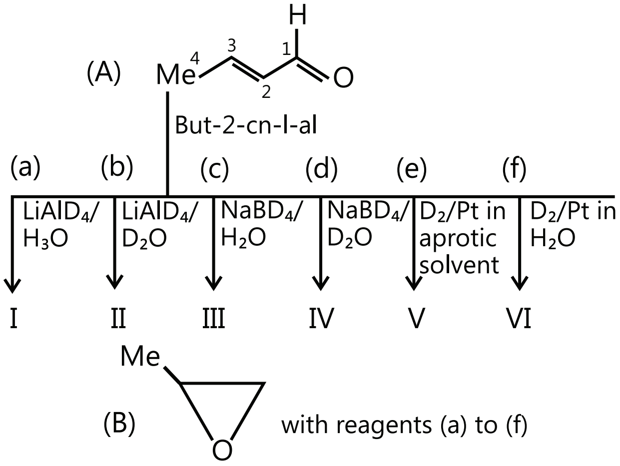


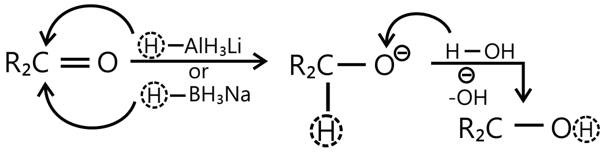
Illustration 9: Complete the following: **(JEE MAIN)**



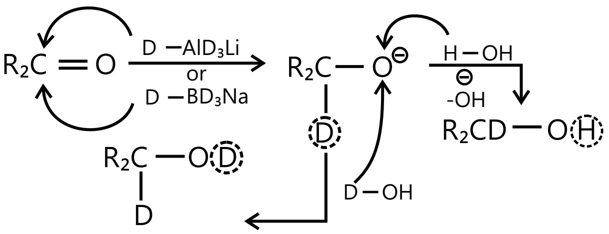
Mechanism:

$$\begin{bmatrix}\text{D form LiAlD}_4\text{ and NaBD}_4\text{ is added to C of (C = O) group}\\ \text{and solvent gives H or D to O atom to form OH or OD, e.g.,}\end{bmatrix}$$

(i)

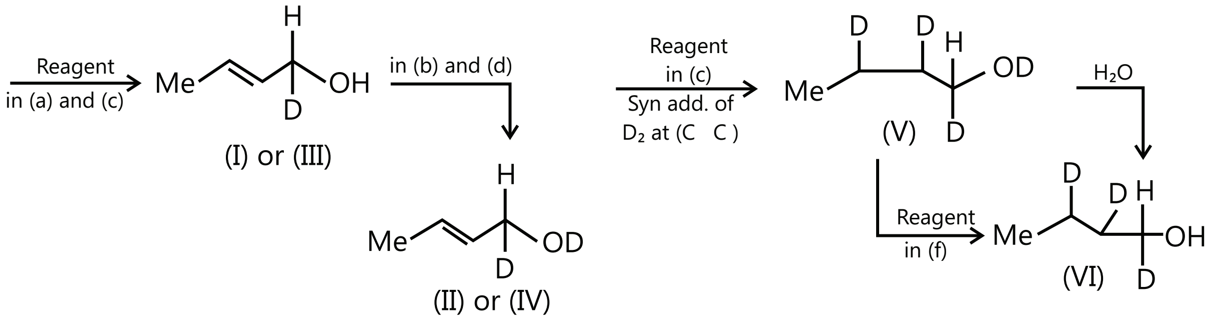


(ii)

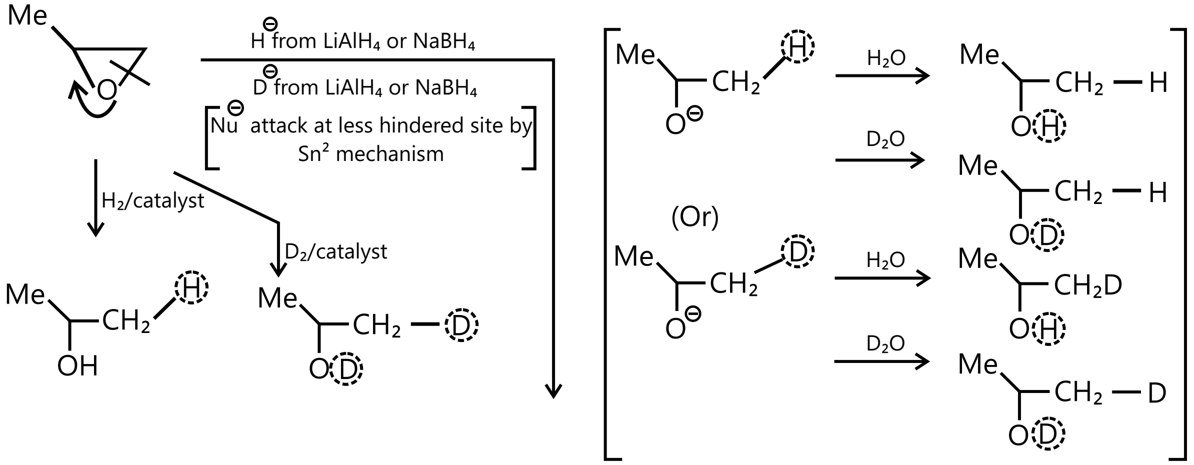


(iii) LAH and $NaBH_4$ do not reduce (C = C) bond whereas catalytic hydrogenation reduces (C = C) bond to (C – C) bond

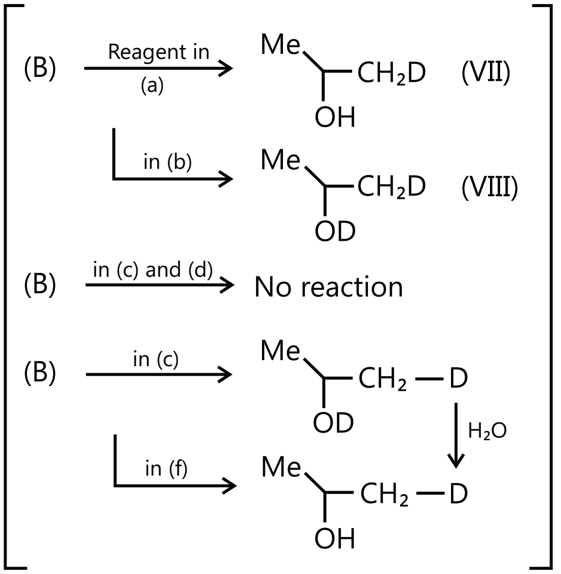
(iv) LAH and catalytic hydrogenation reduce epoxide but $NaBH_4$ does not



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

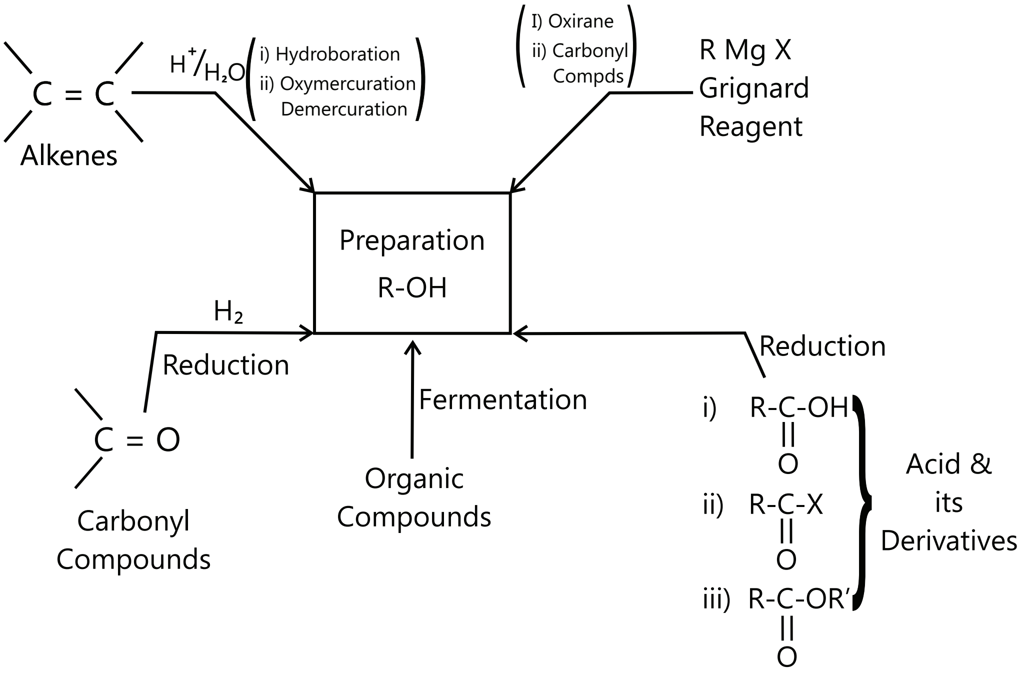


Reaction:

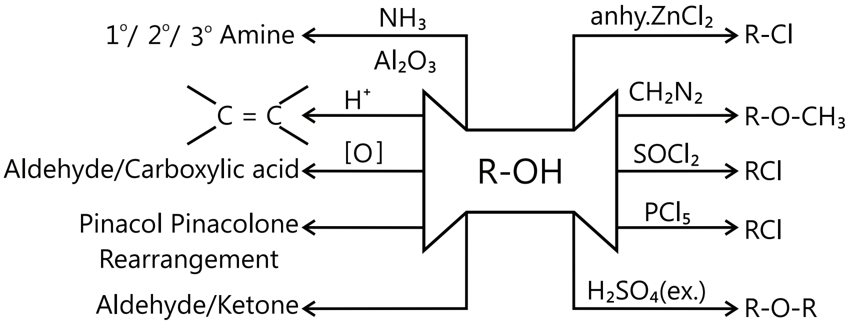


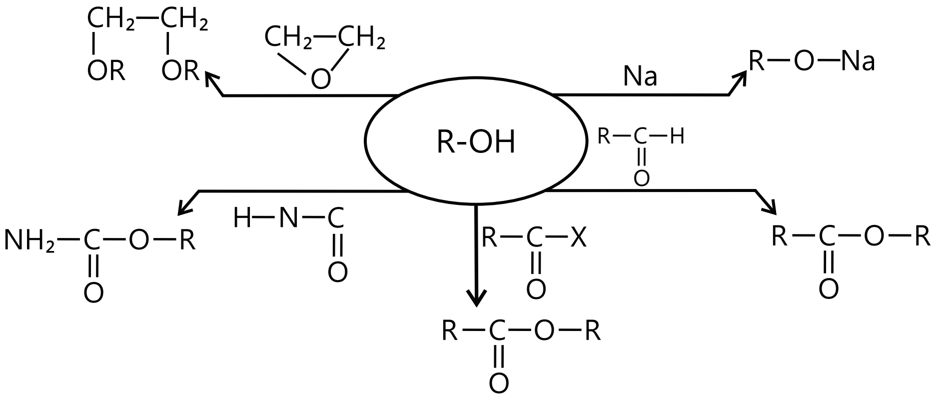
The D of ROD rapidly exchanges for H of H_2O

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.)

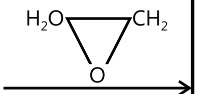
(7) Acid or Acid derivative $\xrightarrow[\text{Bouveault Blanc reduction}]{\text{Na/EtOH}}$

(1° alc.) (2° alc.)

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

(1° alc.) (2° alc.) (3° alc.)

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



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

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

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

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 $\longrightarrow$ Starch $\xrightarrow[\text{HOH}]{\text{Diastase}}$ Maltose $\xrightarrow[\text{Hydrolysis}]{\text{Maltase}}$ Glucose $\xrightarrow[\text{Fermentation}]{\text{Zymase}}$ EtOH

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

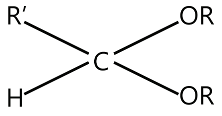
(3) $\xrightarrow{NH_3}$ 1° ,2° ,3° amines

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

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

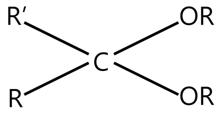
(6) $\xrightarrow{CH_3MgX}$ CH_4

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



Acetal

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



Ketal

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

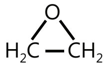
(10) $\xrightarrow{H_2SO_4}$ $ROSO_2OH$(Alkyl hydrogen sulphate)

(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 $\xrightarrow{[O]}$

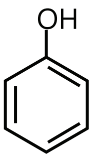
(22) 3°alc. $\xrightarrow{[O]}$

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

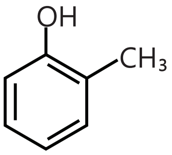
PHENOLS

1. INTRODUCTION

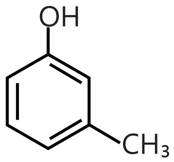
When OH group is attached at benzene ring,the compound is known as phenol



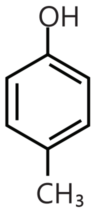
Nomenclature of Phenols



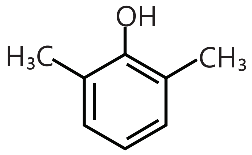
2-Methyl phenol
(o-Cresol)



3-Methyl phenol
(o-Cresol)

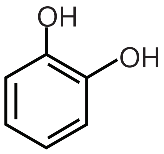


2-Methyl phenol
(o-Cresol)

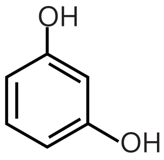


2-6 Dimethyl phenol

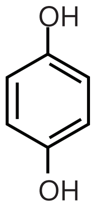
Some dihydric and trihydric phenols are given below:



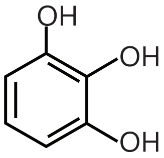
1,2-Benzenediol
(Catechol)



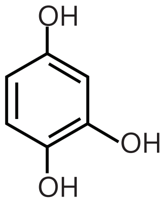
1,3-Benzenediol
(Resorcinol)



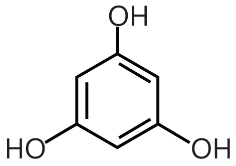
1,4-Benzediol
(Quinol)



1,2,3-Benzenediol
(Pyragallol)



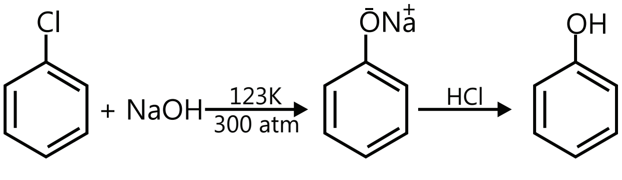
1,3,4-Benzenetriol



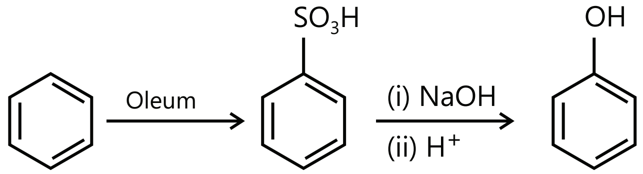
1,3,5-Benzenetriol

2. METHODS OF PREPRATION OF PHENOLS

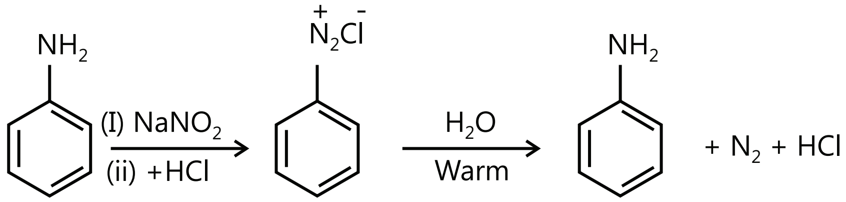
2.1 From Haloarenes



2.2 From Benzenesulphonic Acid



2.3 From Diazonium Salts



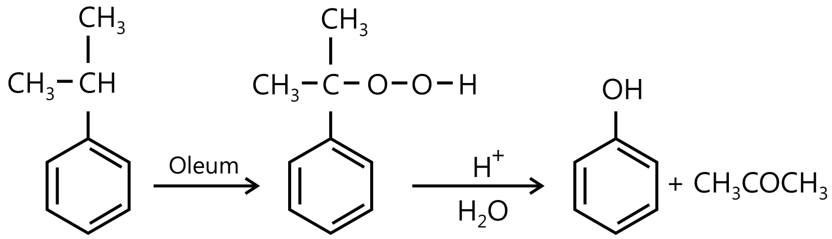
Aniline

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

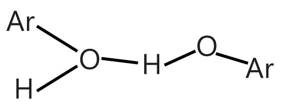
3. PHYSICAL PROPERTIES OF PHENOLS

(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.

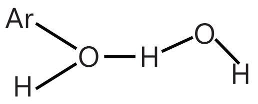
(b) Phenols, generally are insoluble in water; but phenol itself, and polyhydric phenols are fairly soluble in water which is believed to be due to the formation of hydrogen bond with water.

(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 182ºC while toluene (mol. Wt. 92) boils at 110ºC.

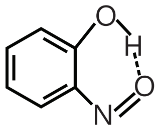
Higher b.p. than alcohols is due to higher polarity of the O-H bond and consequently stronger intermolecular hydrogen bonding in phenols than in alcohols. Appreciable solubilities of the phenol and polyhydric phenols in water is also due to strong hydrogen bonding between phenols and water molecules.



Intermolecular hydrogen bonding phenols

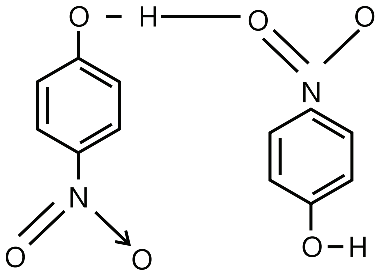


Hydrogen bonding between phenols and water molecules

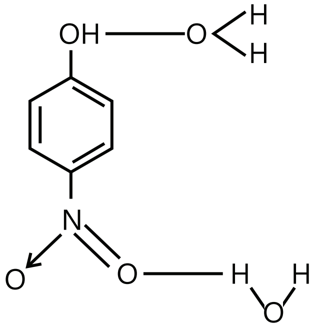


o-Nitro phenol (Intermolecular H-bonding possible due to close mass of NO_2 and -OH groups)

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.



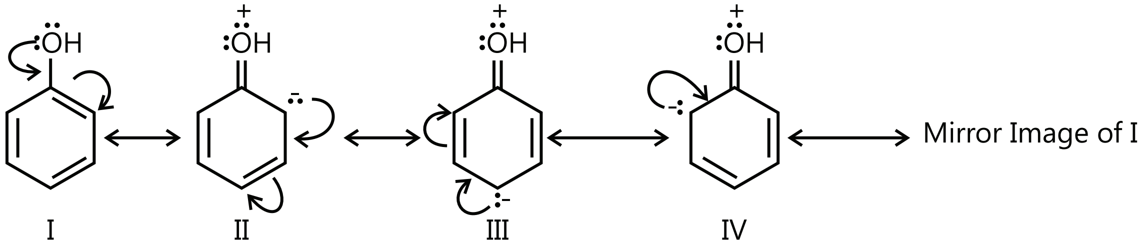
p-Nitro phenol (1 molecules) (intermolecular H-bonding) is not possible due large distance between-NO_2 and -OH occups hence intermolecular H-bonding is possible.



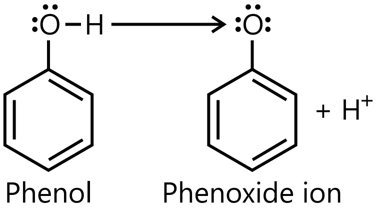
Hydrogen bonding between p-nitro and water

(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.

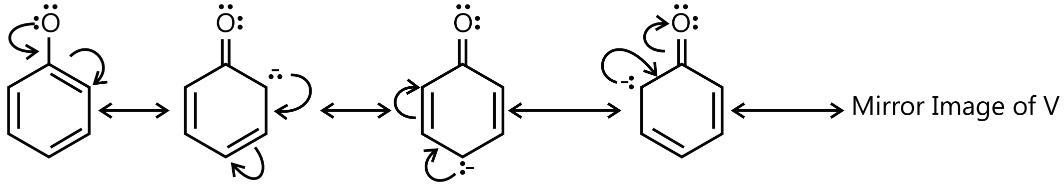


Due to resonance oxygen atom of the –OH group acquires & positive charge (see structures III to V) and hence attract electron pair of the O–H bond leading to the release of hydrogen atom as proton.



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.



V VI VII VIII

Comparison of acidity of phenols and carbonic acid

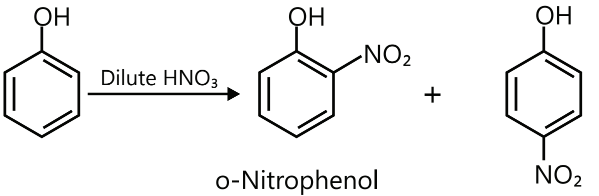
Relative acidity of the various common compounds.

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

4. CHEMICAL PROPERTIES OF PHENOLS

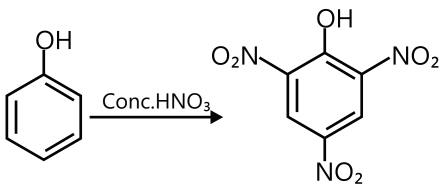
4.1 Nitration

(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

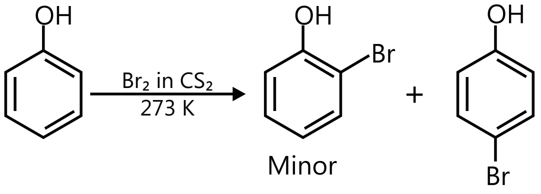
(b) When phenols react with concentrated nitric acid, it gives 2, 4, 6-trinitrophenol.



2,4,6-Trinitrophenol
(Picric acid)

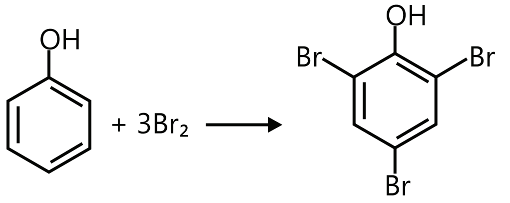
4.2 Halogenation

(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.



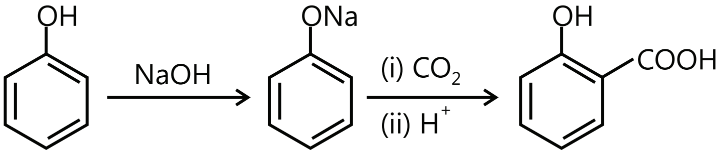
Minor Major

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



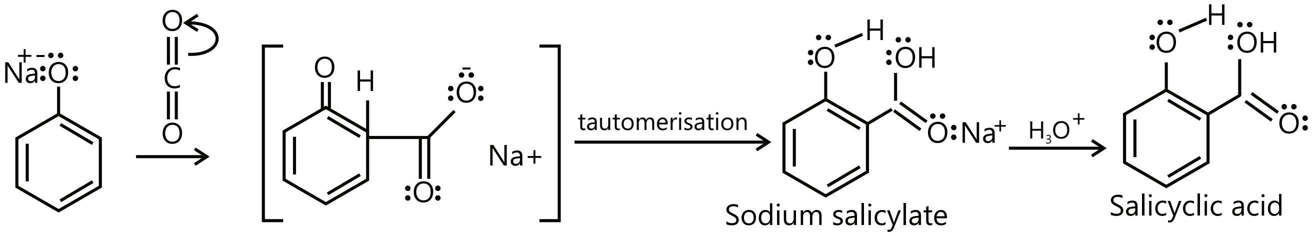
2,4,6-Trinitrophenol

4.3 Kolbe's Reaction



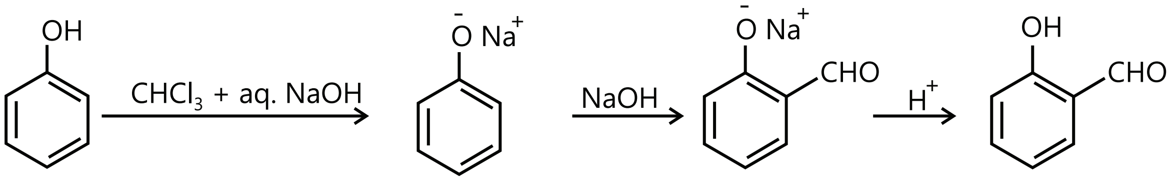
2-Hydroxybenzoic acid
(Salicylic acid)

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.

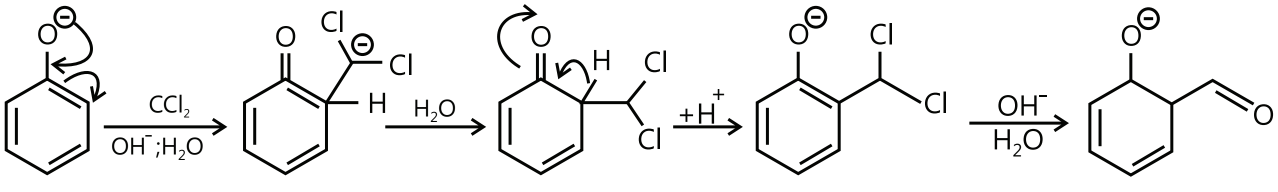


Intermediate

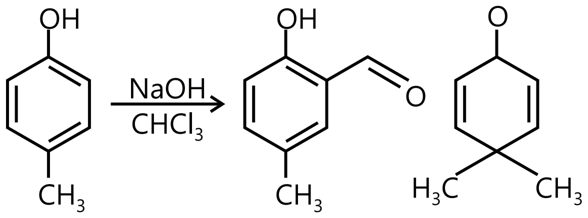
Salicylaldehyde

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

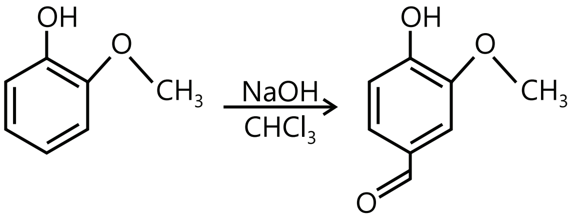
$NaOH + CHCl_3 \rightarrow :CCl_2 + NaCl + H_2O$



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



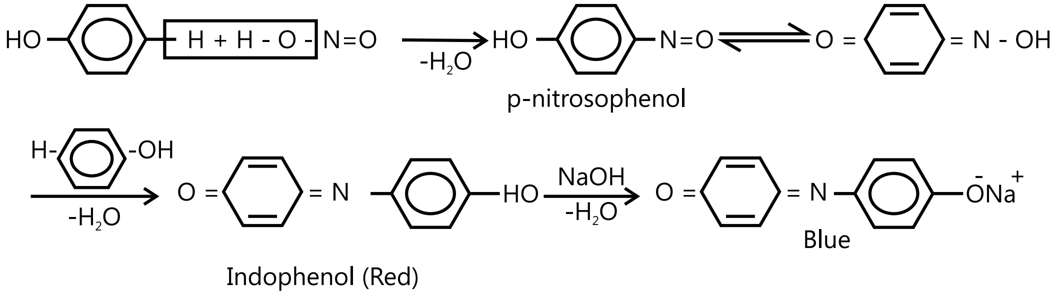
In the Reimer-Tiemann reaction, the o-isomer predominates, but if one of the o-position is occupied the aldehyde group tend to go to the p-positions; e.g. guaiacol forms vanillin



4.5 Libermann's Reaction

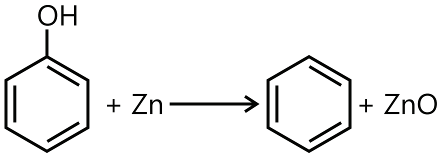
When phenol is treated with sodium dissolved in conc. Sulphuric acid a red colouration appears which changes to blue on adding aqueous NaOH. This reaction is called Libermann's reaction.

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



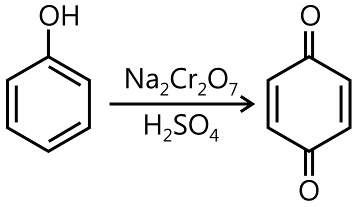
4.6 Reaction of Phenol with Zinc Dust

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.

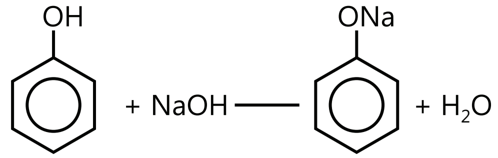


Benzoquinone

5. DISTINCTION BETWEEN ALCOHOL AND PHENOLS

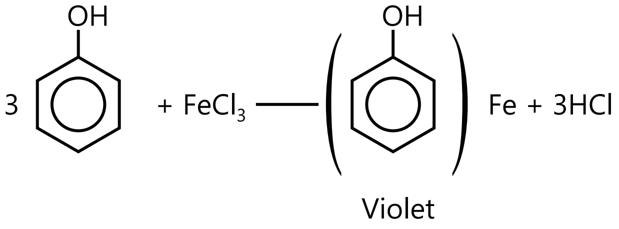
(a) Phenols turns blue litmus red but alcohols do not.

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



R-OH + NaOH —— No reaction

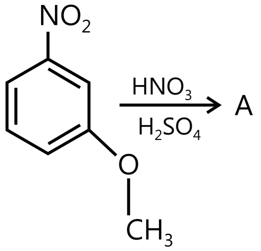
(c) Phenols give violet colour with $FeCl_3$. while alcohols do not.



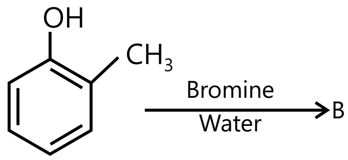
R-OH + $FeCl_3$ —— No reaction

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

(I)



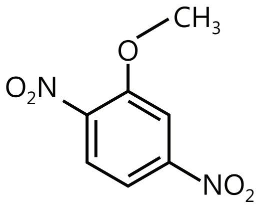
(II)



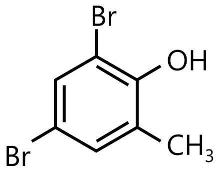
Sol: (I) The nitrating mixture gives the attachment of the nitro group on the ortho position. The presence of methoxy group is an electron-donating groupwhich makes the ortho position more electron-rich enabling the attachment of the electron-withdrawing NO_2 group.

(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 =

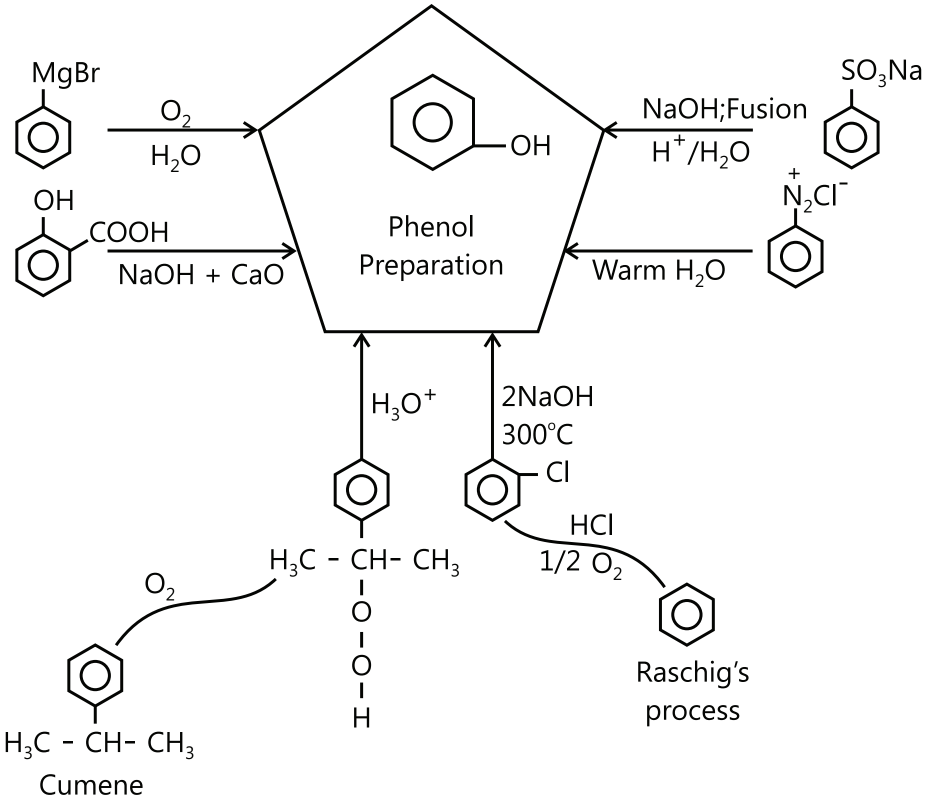


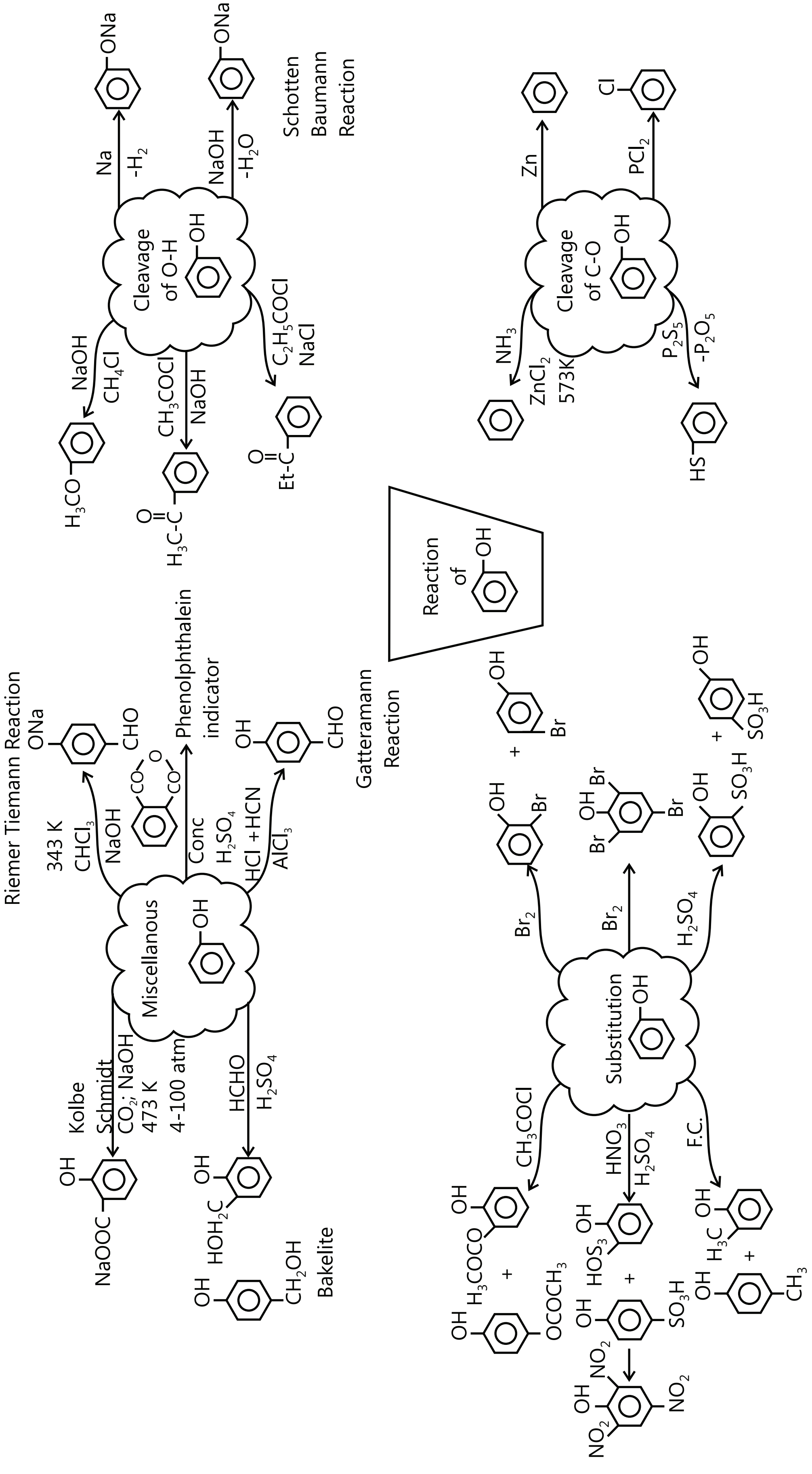
PLANCESS CONCEPTS

- 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



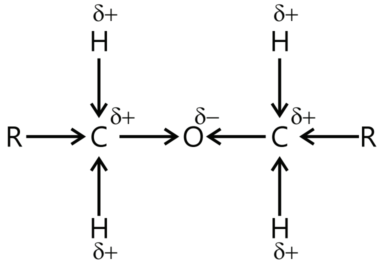

Reaction of
OH
Cleavage of O-H
Na
$-H_2$
ONa
NaOH
$-H_2O$
ONa
Schotten Baumann Reaction
NaOH
CH_4Cl
H_3CO
CH_3COCl
NaOH
H_3C-C
O
C_2H_5COCl
NaCl
Et-C
O
Cleavage of C-O
Zn
PCl_2
Cl
NH_3
$ZnCl_2$
573K
P_2S_5
$-P_2O_5$
HS
Miscellanous
Riemer Tiemann Reaction
343 K
$CHCl_3$
NaOH
ONa
CHO
CO
O
CO
Conc
H_2SO_4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

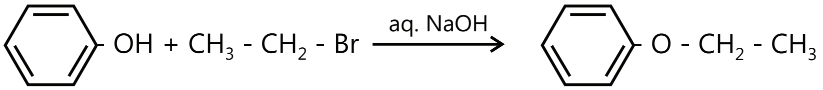
$$R-X+Na-O-R' \xrightarrow{R} R-O-R'+NaX$$

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.

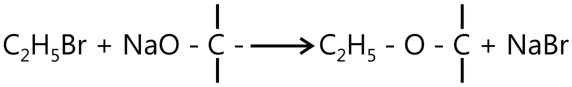
$$R\ \text{-}\ ONa \longrightarrow R\ \text{-}\ O^{-} + Na^{+}$$

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

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



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.



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

(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.

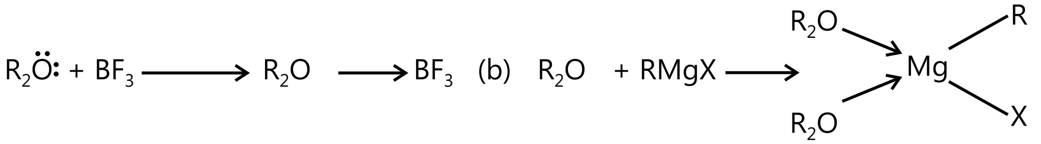
4.2 Basic Nature

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.



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

4.3 Action of Dilute H_2SO_4 (Hydrolysis)

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

4.4 Action of Concentration H_2SO_4

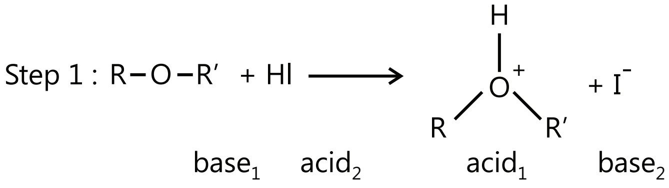
$$C_2H_5\text{-}O\text{-}C_2H_5 + H_2SO_4(\text{conc.}) \xrightarrow{\text{Heat}} C_2H_5OH + C_2H_5HSO_4$$

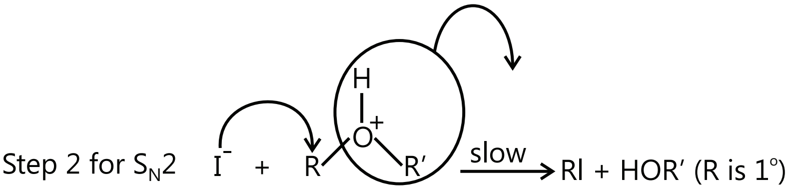
4.5 Action of Conc. HI or HBr.

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

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

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.



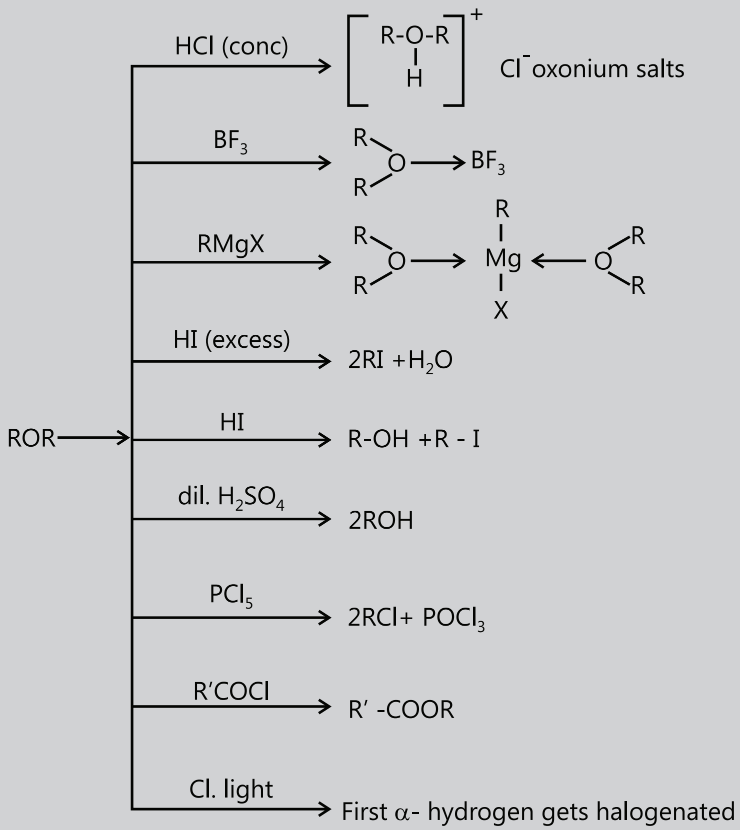


Step 3 for S_N2 $R^+ + I^- \longrightarrow$ RI (R is 3°)

(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.

PLANCESS CONCEPTS

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

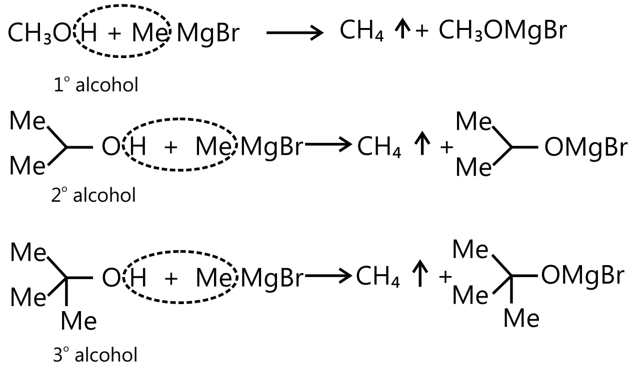


- In reaction with HI, if cold and dilute HI solution is treated with ether, alcohols are formed while in hot and concentrated HI, alkyl halides are formed.
- The reaction mechanism in case of HI depends on the substrate. If the substrates attached to oxygen are 1^0 or 2^0 ,then the mechanism is S_N2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

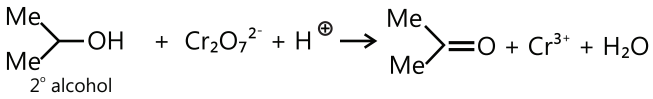
Illustration 1: How are the ethers distinguished from alcohols? **(JEE MAIN)**

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+}.

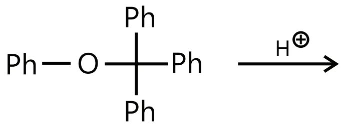
$$\underset{1^\circ\ \text{alcohol}}{MeCH_2OH} + \underset{\left(\text{Orange colour}\right)}{Cr_2O_7^{2-}} + H^{\oplus} \longrightarrow \underset{\text{Acetic acid (blue-green)}}{Me-COOH + Cr^{3+} + H_2O}$$



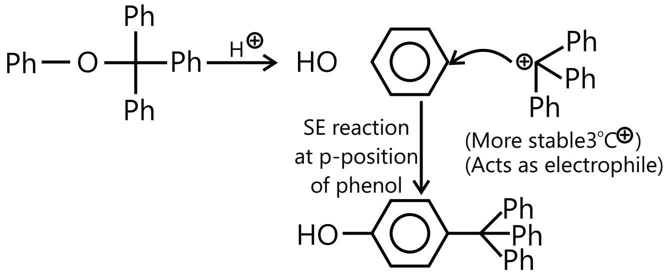
(iii) All alcohols evolve H_2 gas on addition of sodium (Na).

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

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



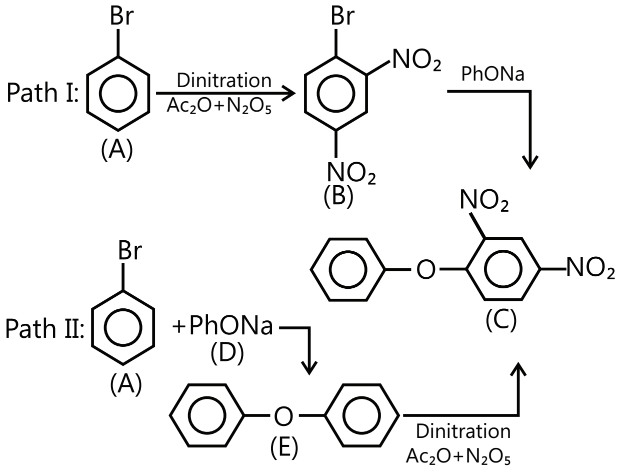
Sol:



[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.

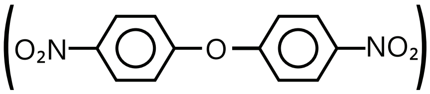
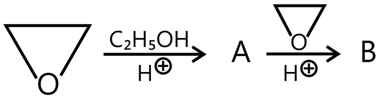
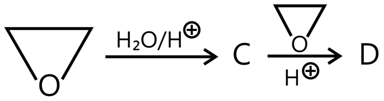
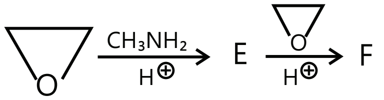


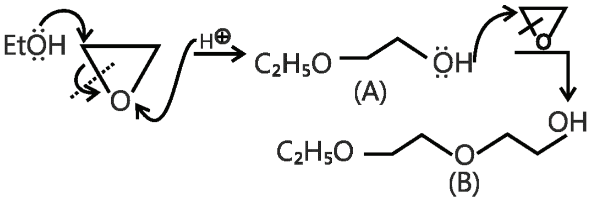
Illustration 4: Complete the following: **(JEE ADVANCED)**

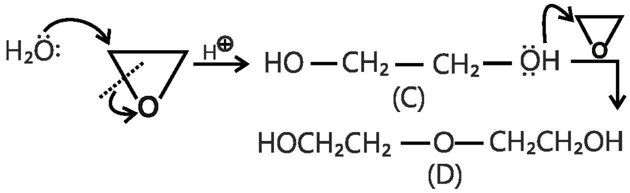
a.


b.


c.


Sol:

a.


b.


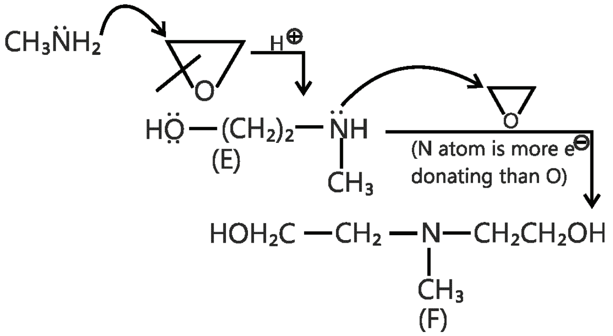
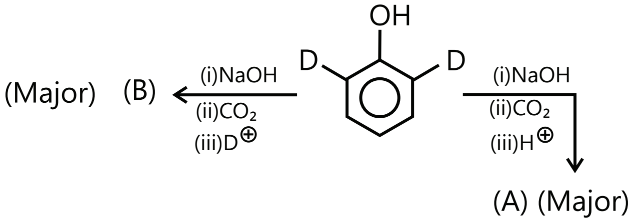
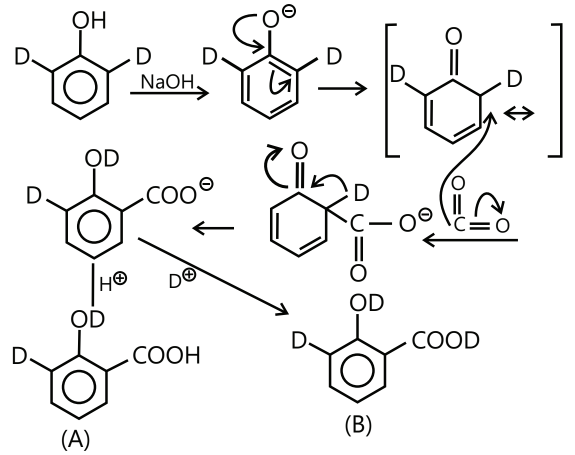
c.


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



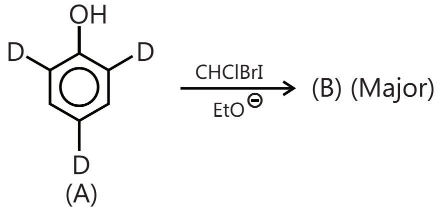
Sol:



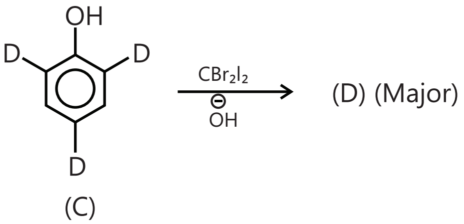
Last image is (A) not (D)

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

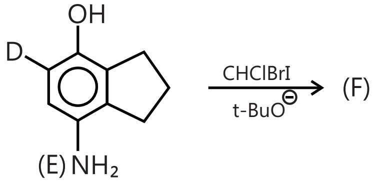
(i)



(ii)



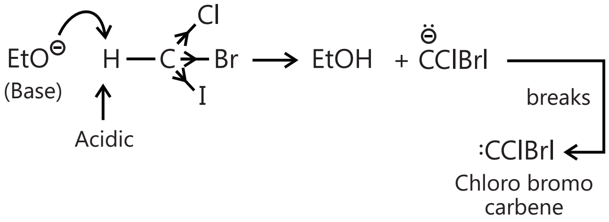
(iii)

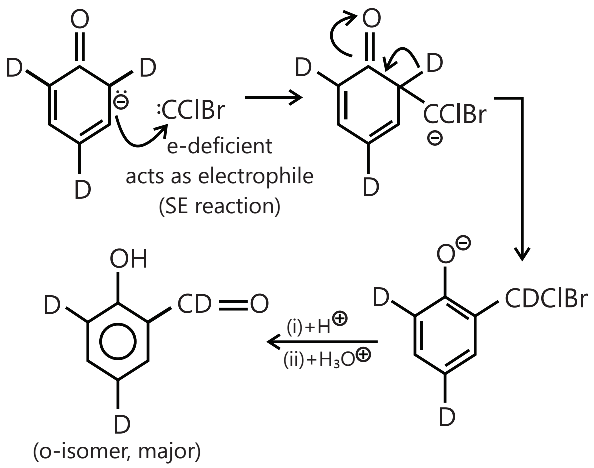


(iv) (E) $\xrightarrow[H_3O^{\oplus}]{CCl_2BrI + \overset{\ominus}{O}H}$ (G)

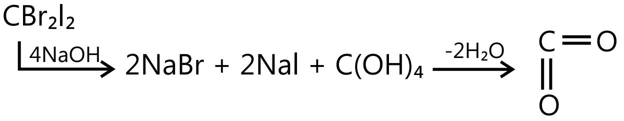
Sol:

(a)



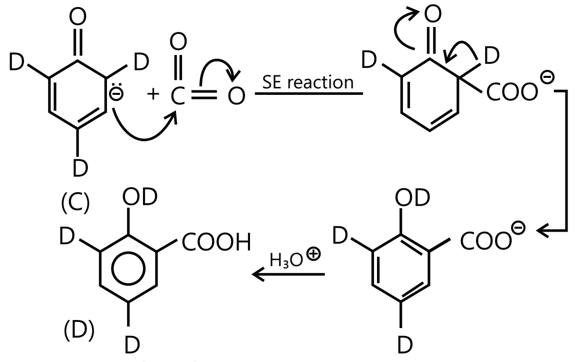


(b)



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

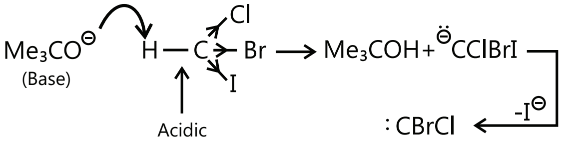
This produces CO_2 ,the reaction is Kolbe reaction.



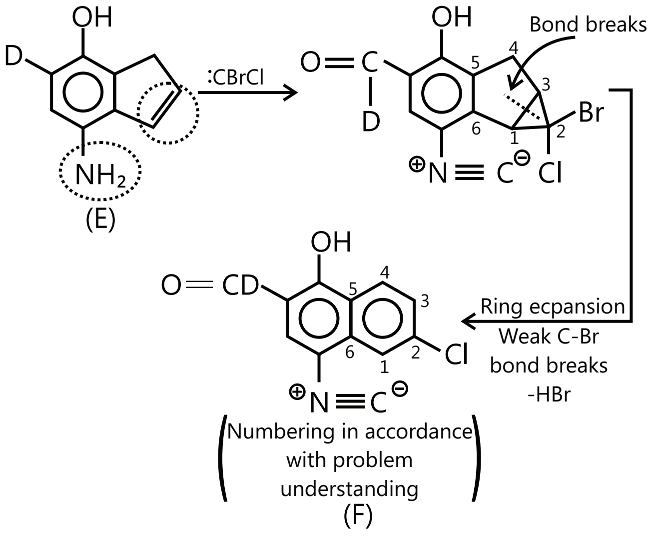
(C)

(D)

(o-Isomer is major)

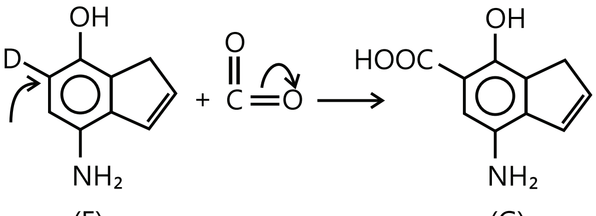


(c) Carbene also converts (– NH_2) group to $(-\overset{+}{N}\equiv\overset{-}{C}-)$ (Carbylamine reaction) and also adds to (C = C) bond of cyclopentane ring and undergoes Reimer-Tiemann reaction at o-position w.r.t. (–OH) group in benzene ring.



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

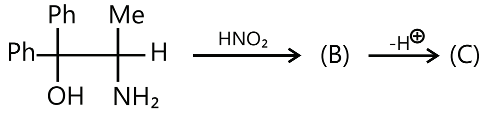
$+C(OH)_4 \xrightarrow{-2H_2O} CO_2$



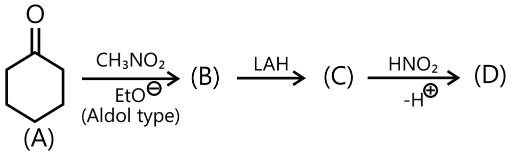
(E) (G)

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

(A)

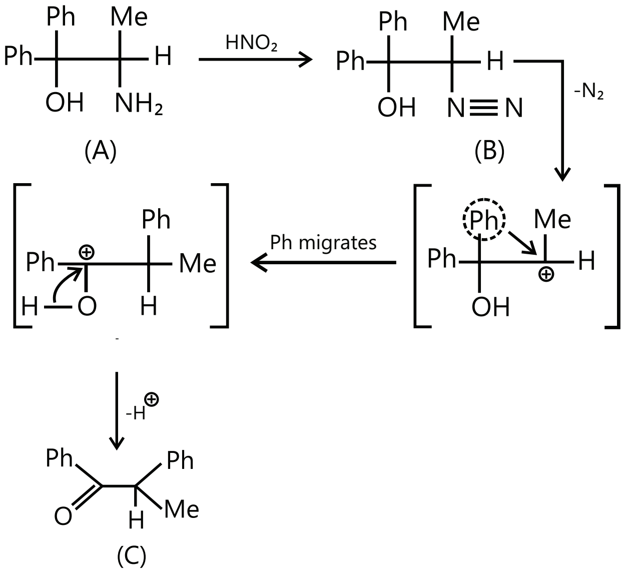


(B)

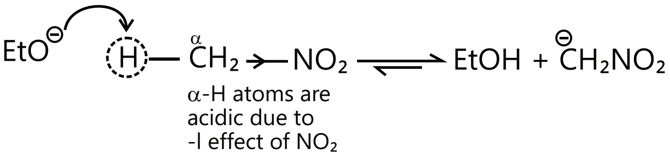


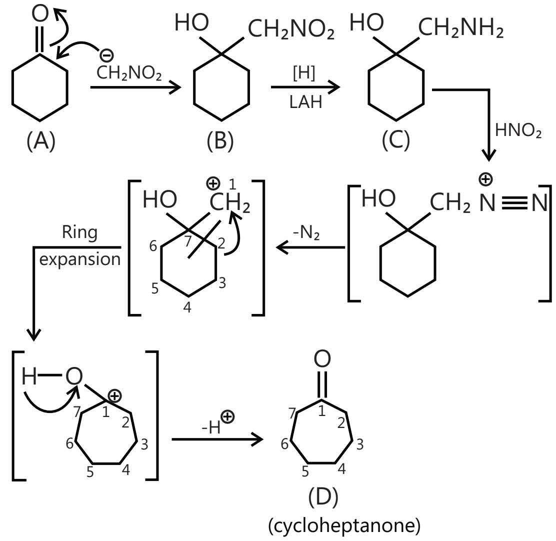
Sol:

(A)

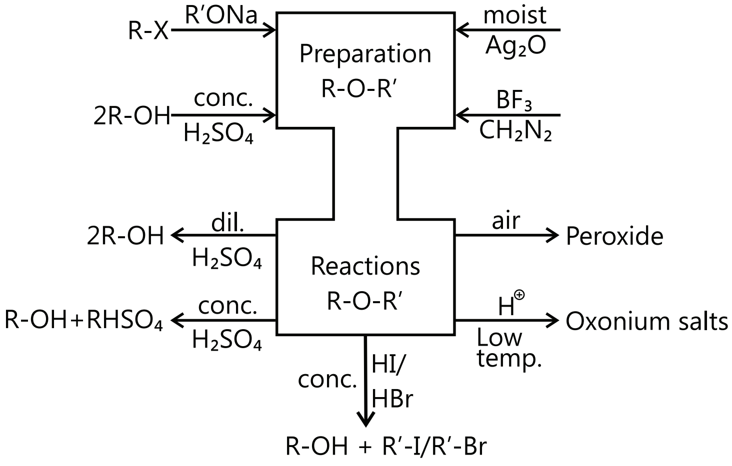


(B)





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

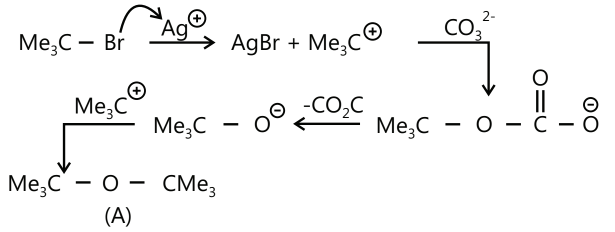
c. $MeOH + H_2C = O + HCl\ (g) \rightarrow (C)$

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

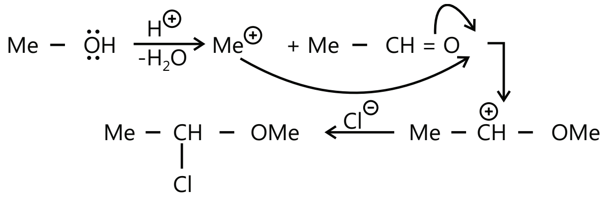
Ag^+ reacts with Br^- leaving $Me_3C^{\ominus}$,which reacts with CO_3^{2-} to give $Me_3C-OCO_2^{\ominus}$. The latter loses CO_2 leaving Me_3COO which reacts with $Me_3C^{\oplus}$ to give the product. Due to steric hindrance, the yield is less.

Mechanism:

a.



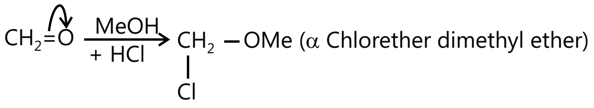
b.



(α Chloroether)

α Chloroethyl methyl ether

c.



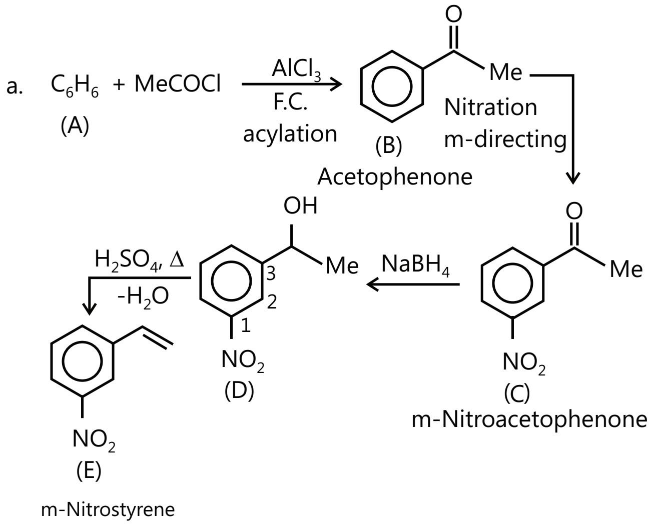
$CH_2=O \xrightarrow[+\ HCl]{MeOH} CH_2(Cl)-OMe$ (α Chlorether dimethyl ether)

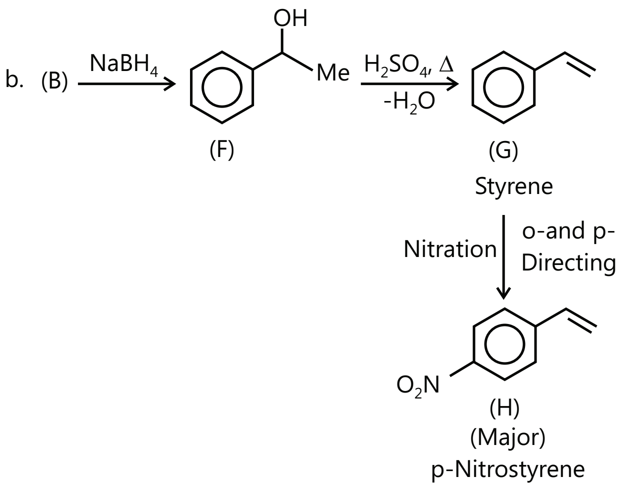
Example 2: Complete the following reactions:

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

Sol:





Example 3: (a) Calculate the depression in freezing point (DT_f) of 0.1 m solution of ROH in cold conc. H_2SO_4. K_f = K kg mol^{-1}.

(b) Calculate the DT_f of 0.2 m soln of Ph_3 C – OH in cold conc. H_2SO_4 . K_f= K kg mol^{-1}.

Sol: (a) ROH reacts with cold conc. H_2SO_4 as follows:

1. $\mathrm{ROH + H_2SO_4 \longrightarrow R\overset{\oplus}{O}H_2 + HSO_4^{\ominus}}$

$$\longrightarrow \mathrm{ROSO_2\,OH} + \cancel{\mathrm{H_2O}}$$

2. $\mathrm{H_2SO_4} + \cancel{\mathrm{H_2O}} \longrightarrow \mathrm{H_3O^{\oplus} + HSO_4^{\ominus}}$

$$\mathrm{ROH + 2H_2SO_4 \longrightarrow ROSO_2OH + H_3O + HSO_4^{\ominus}}$$

Number of moles of particles formed per mole of solute

(i) (van't Hoff factor) = 3 The reaction does not produce $R^{\oplus}$, because $R^{\oplus}$ ion or even $R_3C^{\oplus}$) ion is not stable enough to persist.

∴ $\Delta T_f = i\,K_f \times M$; $3x \times 0.1 = 0.3x$ K

(b) Ph_3C– OH + H_2SO_4 reacts with cold, conc. H_2SO_4 as follows:

1. $\mathrm{Ph_3{+}COH + H_2SO_4 \longrightarrow Ph_3\overset{\oplus}{C}} + \cancel{\mathrm{H_2O}} + \mathrm{HSO_4^{\ominus}}$

2. $\mathrm{H_2SO_4} + \cancel{\mathrm{H_2O}} \longrightarrow \mathrm{H_3O^{\oplus} + HSO_4^{\ominus}}$

$$\mathrm{Ph_3COH + H_2SO_4 \longrightarrow Ph_3C^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}}$$

Number of moles of particles formed per mole solute

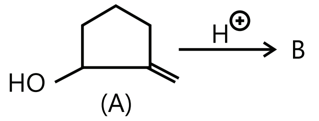
(i) (Van't Hoff factor) = 4

(The reaction produces stable $Ph_3C^{\oplus}$ ion due to resonance stabilization, and $Ph_3C^{\oplus}$ ion, and $Ph_3C^{\oplus}$ persists in the solution.)

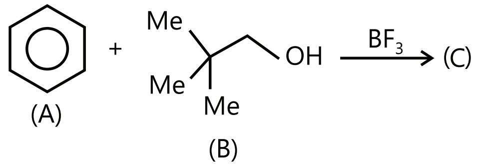
∴ $\Delta T_f = i\,K_f \times M$; $= 4x \times 0.2 = 0.8x$ K

Example 4: Complete the following reactions:

a.

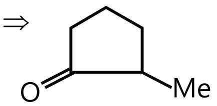


b.

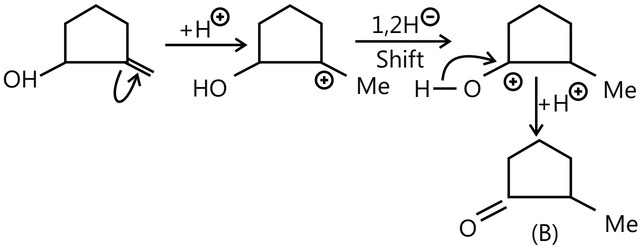


Sol:

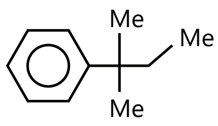
a. B ⇒



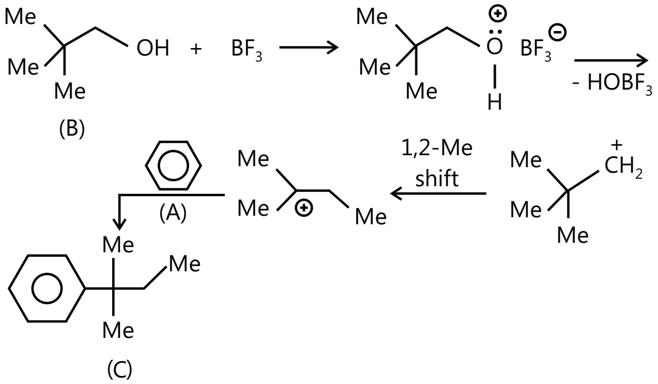
Mechanism:



b. C ⇒

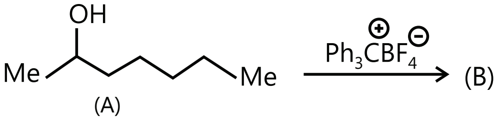


Mechanism:



Example 5: (a) Write the reaction of EtOH with (i) KNH_2 (ii) aq. KOH (iii) Potassium ethynide.

(b) Complete the following reaction:



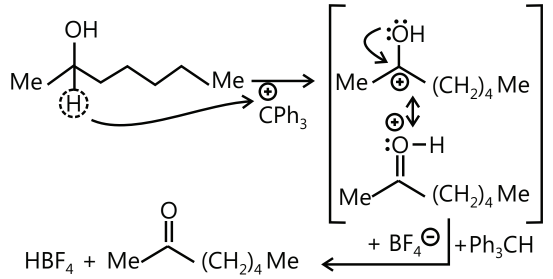
Sol:

a. I. $\overset{\oplus}{K}NH_2^{\ominus} + EtOH \longrightarrow NH_3 + Et\overset{\ominus}{O}\ \overset{\oplus}{K}$

II. $\overset{\oplus}{K}\overset{\ominus}{O}H + EtOH \rightleftharpoons H_2O + Et\overset{\ominus}{O}\ \overset{\oplus}{K}$

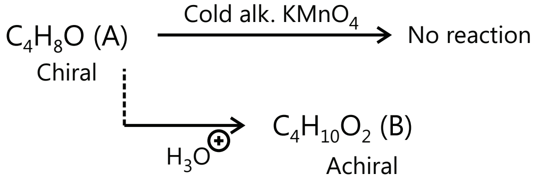
III. $HC \equiv \overset{\ominus}{C}\ \overset{\oplus}{K} + EtOH \longrightarrow HC \equiv CH + Et\overset{\ominus}{O}\ \overset{\oplus}{K}$

b.



Example 6: Identify the following compounds:

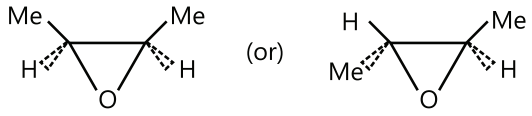
a.



b. $C_5H_{12}O_2$ (C) $\xrightarrow{Na + MeI}$ $C_6H_{14}O_2$ (D)

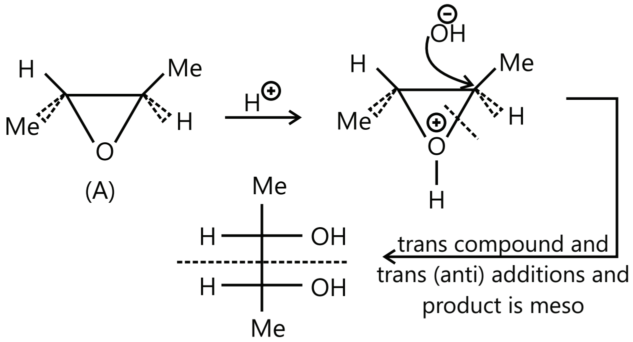
Chiral Achiral

Sol: (a) One Du in (A) and unreactivity with cold alk. $KMnO_4$ (Baeyer's reagent) suggest (A) to be a ring compound. (A) is optically active, suggesting a trans expoxide.



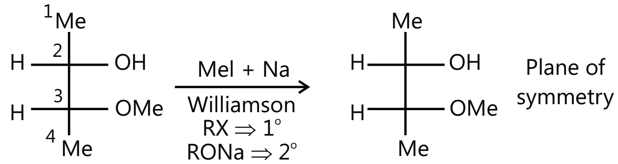
cis-Butene-2-oxide
Achiral (plane of symmetry)

trans-Butene-2-oxide
Chiral (A)



Meso-2,3- Dihydroxy butane
(Achiral) (B)

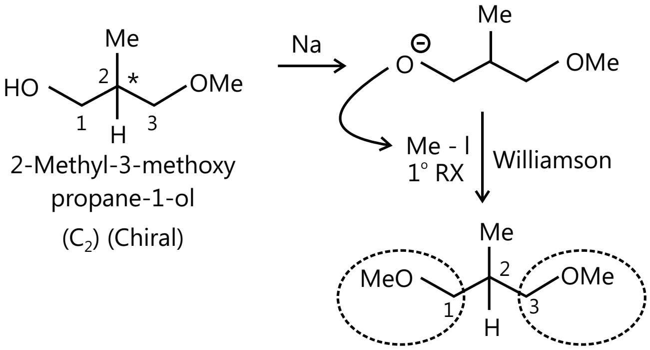
(b) Zero DU is (C) and (D) suggests that both are saturated compounds; (C) can be either diol or containing one (OH) and one (OMe) group since only one mole MeI reacts with (C) (five C atoms) to give (D) (six C atoms). Compound (C) contains one (OH) and one (OMe) given at adjacent positions to make (C) chiral.



Meso-2,3-Dimethoxy butan
Achiral (D)

(C) (Chiral)
(3-Methoxy butan-2-ol)

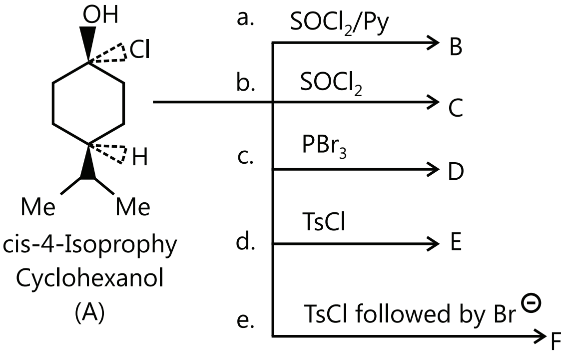
Another possibility is;



2-Methyl-3-methoxy propane-1-ol
(C_2) (Chiral)

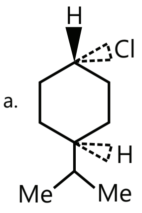
Achiral (D_1)
2-Methyl 1,3-dimethoxy propane

Example 7: Give the stereochemcial product of following reactions:

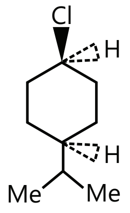


cis-4-Isoprophy Cyclohexanol
(A)

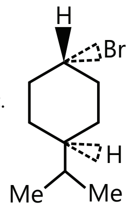
Sol: ROH with $SOCl_2$ gives RCl (with retention configuration) but with $SOCl_2$/pyridine, RCl is found with inversion of configuration (S_N1 reaction)

a.


(B)
trans-(Inversion)

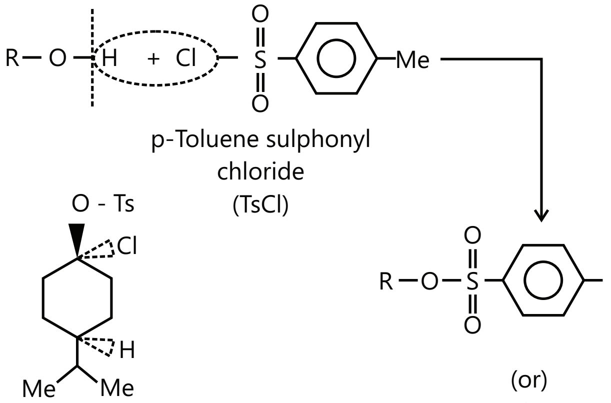
b.


(C)
cis-(Retention)

c.


(D)
trans-(Inversion)
(C-O) bond breaks

d. cis-Tosylate, no change in configuration because none of the (C–O) bonds breaks.

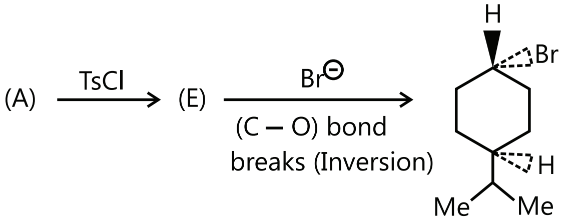


p-Toluene sulphonyl chloride
(TsCl)

(E)
(cis-Tosylate)

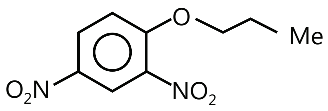
(or)
(R—O—Ts)

e.

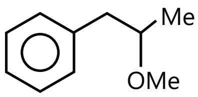


(F)
trans

Example 8: Convert benzene to the following compounds:

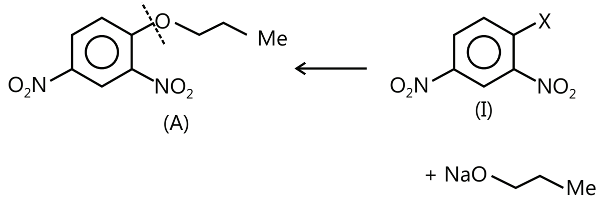
a.


(A)

b.


(B)

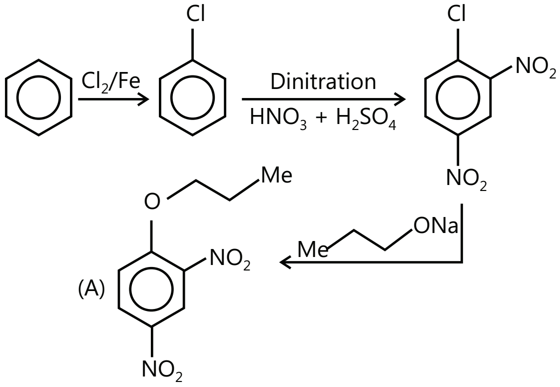
Sol: Williamson's synthesis of (I) and (II) would take place since ArSN is feasible in (I) because (X) is (I) is activated ty two ($-NO_2$) groups. Synthesis (I) from benzene and then react with (II) to obtain the product.

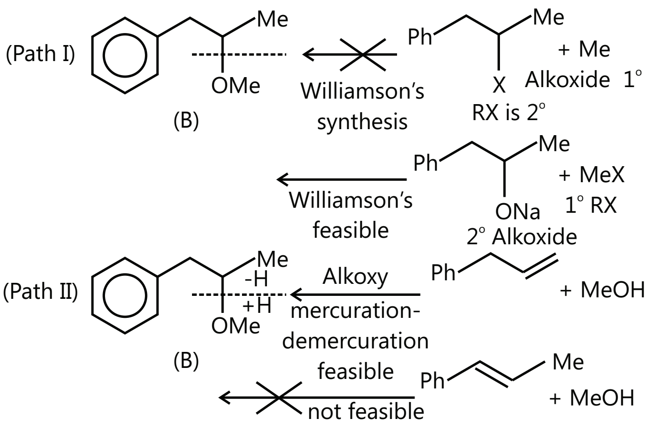
a.


(A)
(I)
(II)

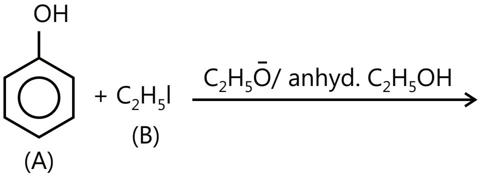
Williamson's synthesis of (I) and (II) would take place since ArSN is feasible in (I) because (X) is (I) is activated ty two ($-NO_2$) groups. Synthesis (I) from benzene and then react with (II) to obtain the product.

(b)





Example 9: Complete the reaction:

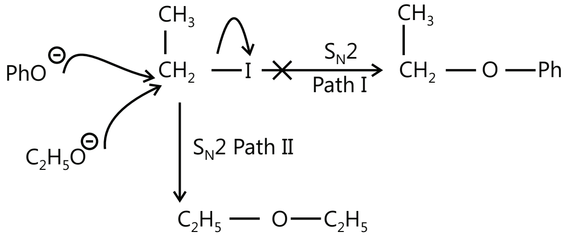


Sol: $C_2H_5O^-$ acts as a base. It abstracts H^+ from phenol to form PhO^- ion.

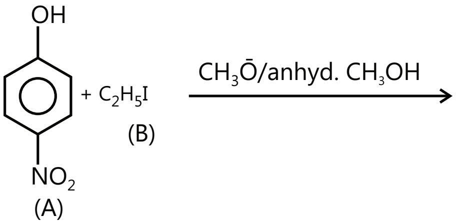
$C_2H_5O^-$ is a stronger nucleophile than PhO^- . Hence, the product is obtained by path II.

(acidic character: $PhOH > C_2H_5OH$)

(Basic and nucleophilic character : $PhO^- < C_2H_5O^-$)



Example 10:



i. $P\text{-}NO_2\text{-}C_6H_4\text{-}OC_2H_2$

ii. $P\text{-}NO_2\text{-}C_6H_4\text{-}O\text{-}NO_2\text{-}P$

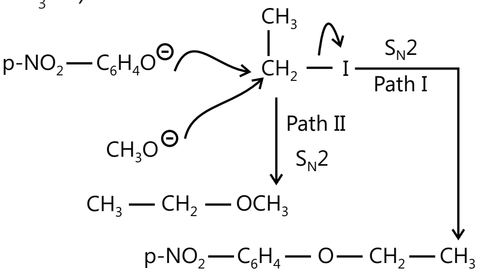
iii. $C_2H_5\text{-}O\text{-}CH_3$

iv. $P\text{-}NO_2\text{-}C_2H_5\text{-}I$

Sol: (iii) CH_3O^- acts as a base. It abstracts $H^{\oplus}$ from p-nitrophenol to form $p\text{-}NO_2 - C_6H_4O^-$

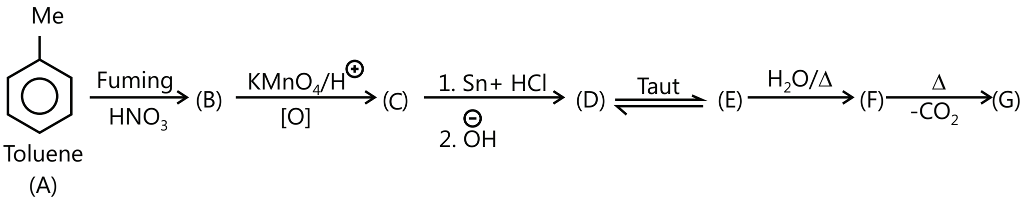
$CH_3O^{\ominus}$ is a stronger nucleophile than $p\text{–}NO_2 - C_6H_4O^{\ominus}$, hence the product is obtained by path II.

(Basic and nucleophilic character : $p\text{–}NO_2 - C_6H_4H^{\ominus} < CH_3O^{\ominus}$)

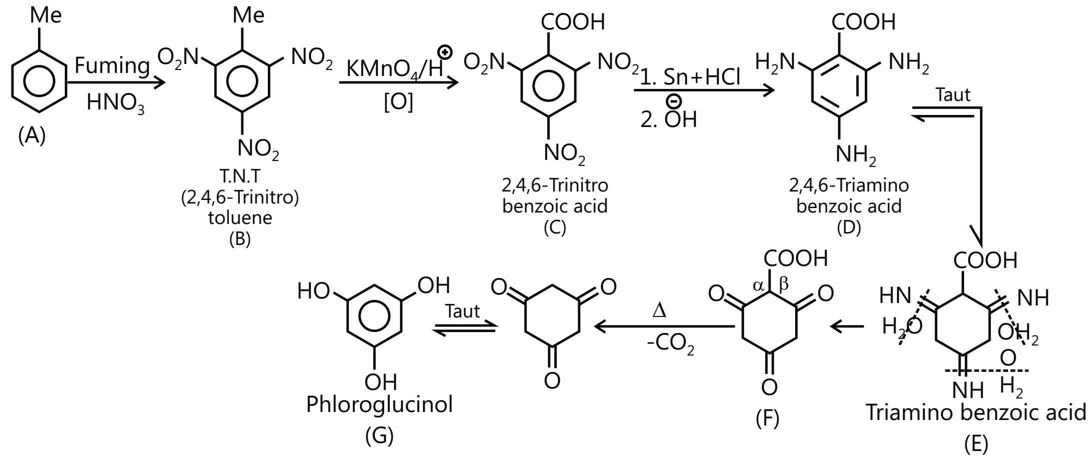


JEE Advanced/Boards

Example 1: Complete the following reactions:

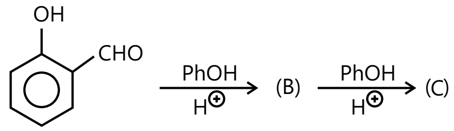


Sol:



Example 2: Complete the following reactions:

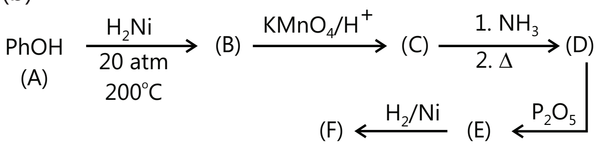
(a)



Salicyaldehyde

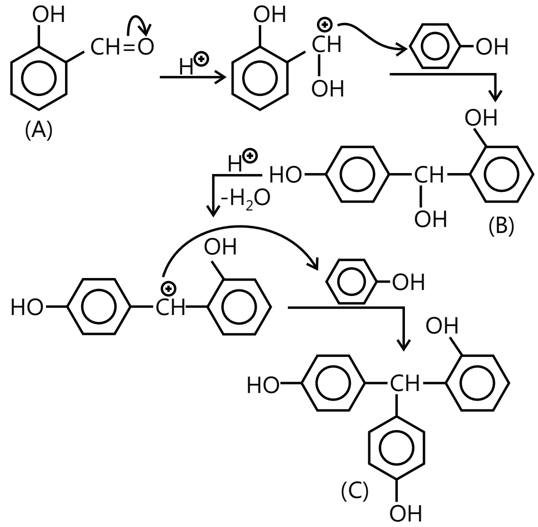
o-Hydroxy benzaldehyde
(A)

(b)

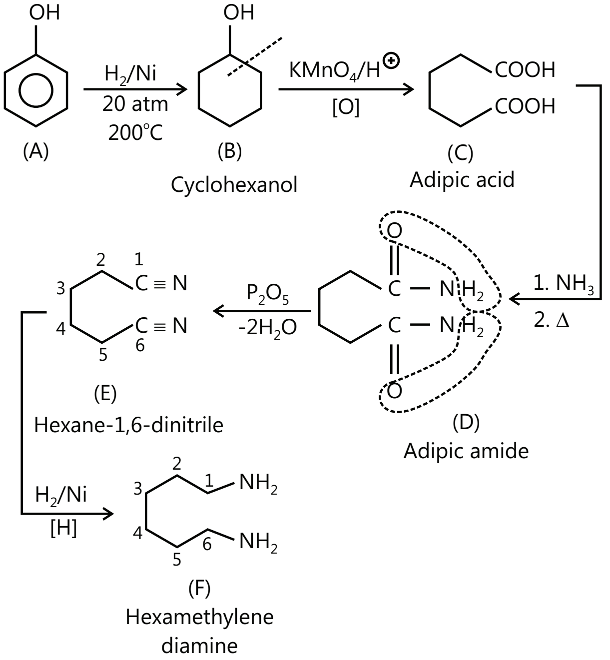


Sol:

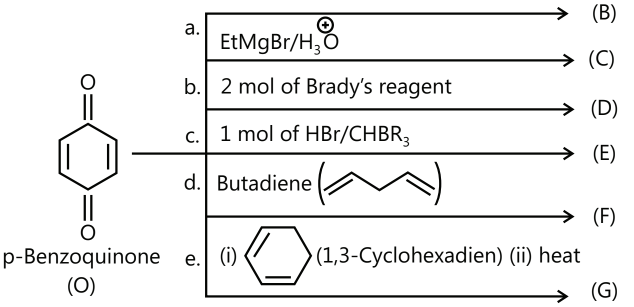
(a)



(b)

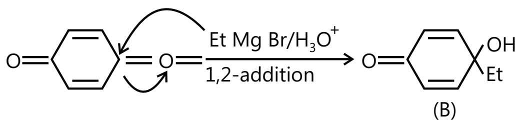


Example 3: Complete the following reactions:

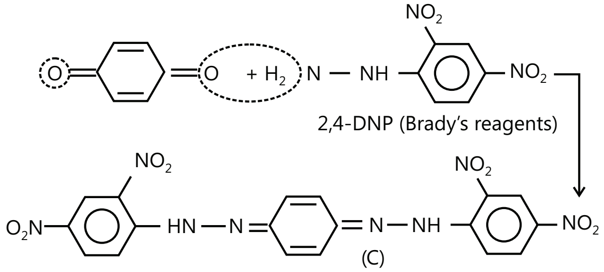


Sol: The reaction of quinones is that of α,β-unsaturated ketone.

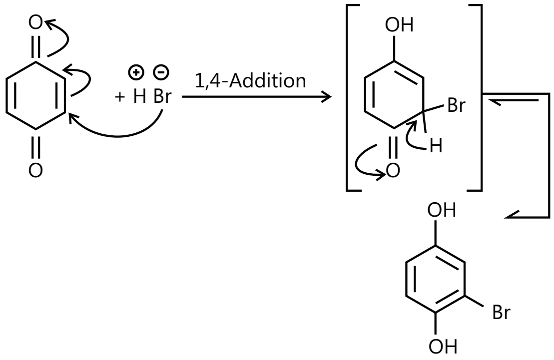
(A)



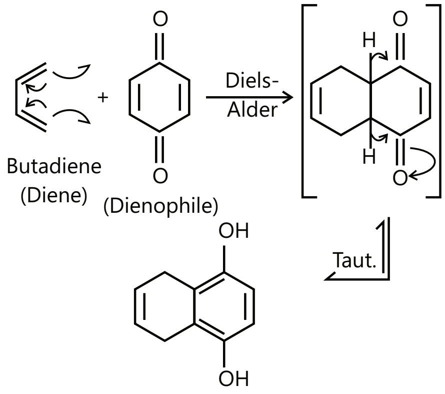
(B)



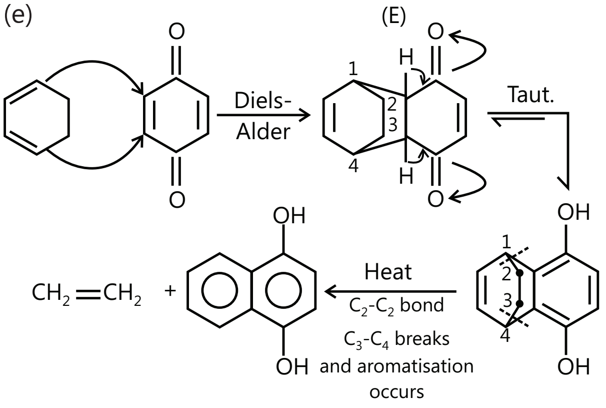
(C)



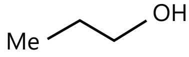
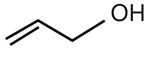
(d) It is an example of Diels-Alder reaction.

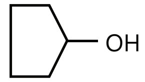
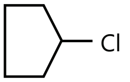


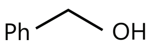
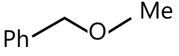
(e)



Example 4: Distinguish between the following pairs:

(A) (I)  and (II) 

(B) (I)  and (II) 

(C) (I)  and (II) 

Sol: (a) (II) is unsaturated alcohols (allyl alcohol). When Br_2/CCl_4 solution is added to it, orange colour of Br_2/CCl_4 disappears. However, (I) (propyl alcohol) does not react with Br_2/CCl_4 and orange colour persists.

(b) (I) (cyclopentanol) dissolves in conc. H_2SO_4 and forms one layer, while (II) (cyclopentyl chloride) does not dissolve in conc. H_2SO_4 and two distinct layers appear.

(c) (I) (benzyl alcohol) (1° ROH) is oxidized by acid $Cr_2O_7^{2-}$ and orange colour of $Cr_2O_7^{2-}$ changes to green (Cr^{3+}), whereas (II) (benzyl methyl ether) does not react.

Example 5: Explain which of the following reactions will occur.

a. $\underbrace{RCOOH}_{pK_a=5} + \underbrace{HCO_3^-}_{pK_a=10.3} \rightarrow$

b. $RCOOH + CO_3^{2-} \rightarrow$

c. $\underbrace{PhOH}_{pK_a=10} + HCO_3^- \rightarrow$

d. $PhOH + CO_3^{2-} \rightarrow$

Sol: (a) The reaction is ;

$$\underbrace{RCOOH}_{pK_a=5} + \underbrace{HCO_3^-}_{pK_a=10.3} \rightarrow \underbrace{RCOO^-}_{\text{Weaker conjugate base}(C_B)} + \underbrace{H_2O + CO_2}_{W_A\,(pK_a=6.4)}$$

(b) Reaction occurs

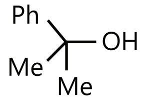
$$RCOOH + CO_3^{2-} \rightarrow \underbrace{RCOO^-}_{(W_{C_B})} + \underbrace{HCO_3^-}_{\substack{pK_a=10.3 \\ W_A}}$$

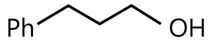
(c) Reverse reaction occurs.

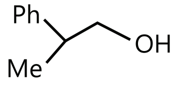
$$\underbrace{PhOH}_{pK_a=10} + HCO_3^- \not\rightleftharpoons \underbrace{PhO^-}_{\text{Weaker } C_B} + \underbrace{H_2CO_3}_{S_A}$$

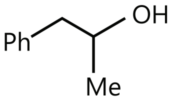
(d) $$PhOH + CO_3^{2-} \rightleftharpoons \underbrace{PhO^-}_{\text{Weaker } C_B} + \underbrace{HCO_3^-}_{\substack{pK_a=10.3 \\ W_A}}$$

Example 6: How will you synthesize the following alcohol using grignard reagent

(A) 

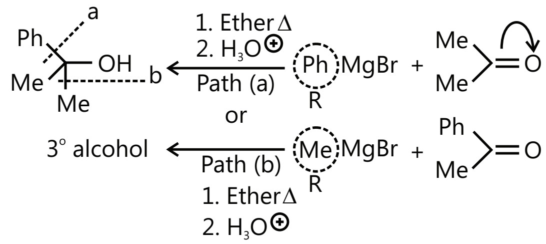
(B) 

(C) 

(D) 

Sol:

(A)



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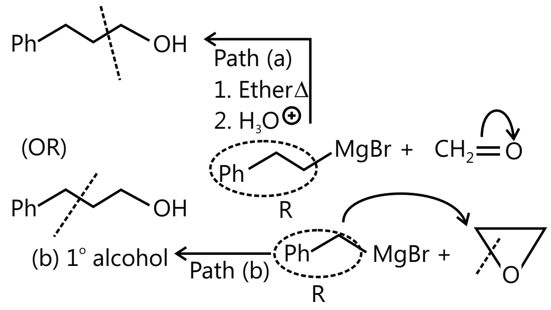

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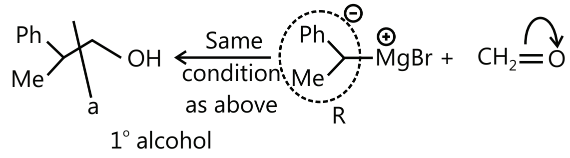

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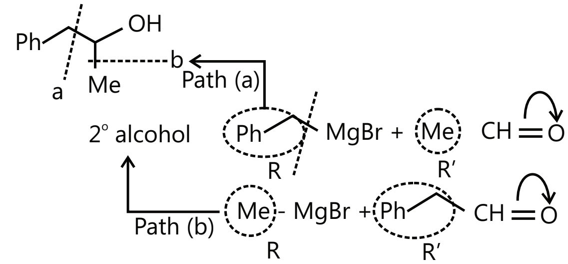
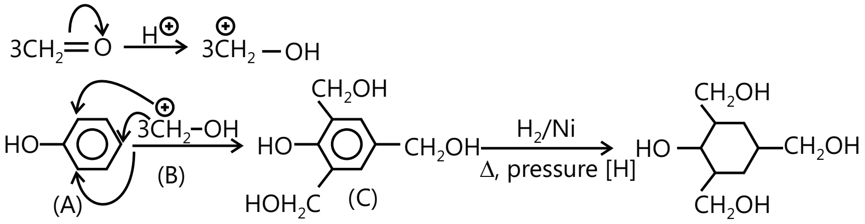


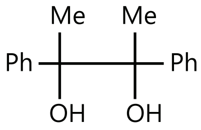
Example 7: Complete the following reaction

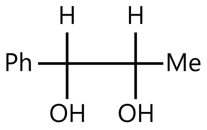
$$\underset{(A)}{PhOH} + \underset{(B)}{3CH_2 = O} \xrightarrow{H^{\oplus}} (C) + \xrightarrow[\Delta,\ \text{pressure}]{H_2/Ni} (D)$$

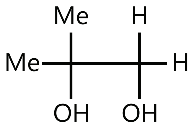
Sol:



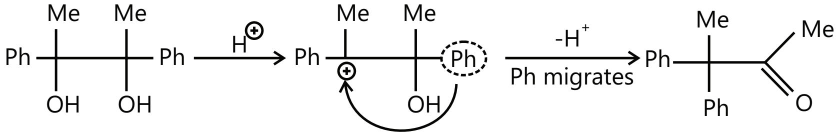
Example 8: Give the products of the pinacol rearrangement of the following glycols in acids.

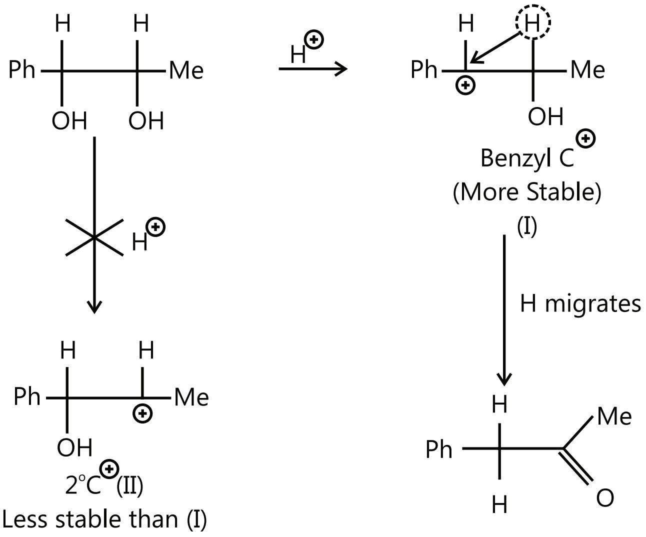
(A)


(B)


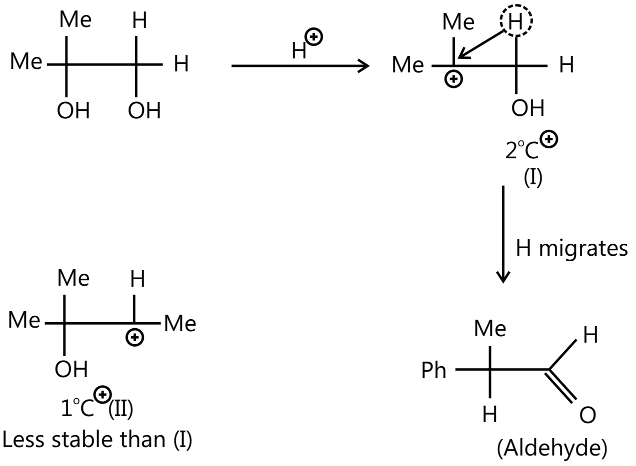
(C)


Sol:

(a)


(b)


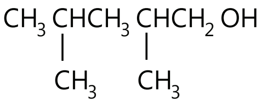
(c)

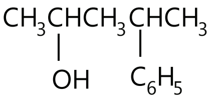


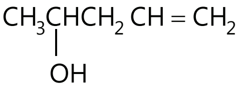
JEE Main/Boards

Exercise 1

Q.1 Give IUPAC substitutive names for the following alcohols:

(a) 
$CH_3\underset{CH_3}{\underset{|}{C}H}CH_3\underset{CH_3}{\underset{|}{C}H}CH_2OH$

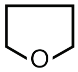
(b) 
$CH_3\underset{OH}{\underset{|}{C}H}CH_3\underset{C_6H_5}{\underset{|}{C}H}CH_3$

(c) 
$CH_3\underset{OH}{\underset{|}{C}H}CH_2CH=CH_2$

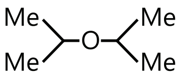
Q.2 How will you convert ethanol into the following compounds?

(i) Butane-1, 3-diol (ii) But-2-enal (iii) But-2-enoic acid

Q.3 Write all the stereoisomers of 2-isoproyl-5-methyl cyclohexanol and give the decreasing order of their stabilities.

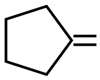
(I) 
THF (Tetraphydrofuran)

(II) $C_2H_5-O-C_2H_5$
Diethyl ether

(III) 
Diisopropyl ether

Q.4 How will you prepare the following:

(1) 3-phenyl but-1-ene to 2-phenyl butan-2-ol

(2)  CH_2 to cyclopentyl methanol

Q.5 Arrange the following compounds in the decreasing order of their boiling points and solubility in H_2O.

a. (I) Methanol (II) Ethanol
(III) Propan-1-ol (IV) Butane-1-ol
(V) Butane-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

Q.6 Explain the less solubility and lower boiling point of:

(I) o-Nitrophenol

(II) o-Hydroxy benzaldehyde

(III) o-Hydroxybenzoic acid (salicyclic acid) compared with their p-and m-isomers.

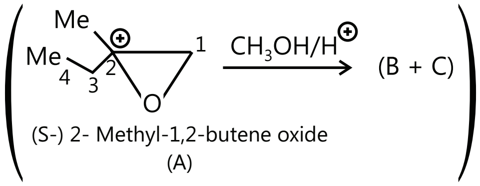
Q.7 Which isomer (o, m, or p) of hydroxy acetophenone is steam volatile?

Q.8

Cyclobutyl ethene $\xrightarrow{Dil.H_2SO_4}$ (B) $\begin{pmatrix}\text{Number of}\\ \text{isomeric products}\\ \text{including stereoisomers}\end{pmatrix}$

Q.9 Give the decreasing order of Lewis basicities of the following:

Q.10 Explain the formation of B and C, optically pure different isomers from (A) with little racemisation.



Q.11 Show how will you synthesize

(a) 1-phenylethanol from a suitable alkene,

(b) Cyclohexylemethanol using an alkyl halide by an S_N2 reaction,

(c) Pentan-1-ol using a suitable alkyl halide?

Q.12 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

Q.13 Compound (D), an isomer of (A) in Problem 4, reacts with BH_3. THF and then $H_2O_2 / \overset{\ominus}{O}H$ to give chiral (E). Oxidation of (E) with $KMnO_4$ or acid dichromate affords a chiral carboxylic acid, (F). Ozonolysis of (D) after reduction with Zn gives the same compound (G) obtained by oxidation of 2-methyl pentan-3-ol with $KMnO_4$. Identify (D), (E), (F), and (G).

Q.14 An organic compound (A) $(C_8H_8O_3)$ was insoluble in water, dilute HCl, and $NaHCO_3$. It was soluble in NaOH. A solution of (A) in dilute NaOH was boiled and steam distilled and distillate was reacted with NaOH to give a yellow precipitate was reacted with NaOH to give a yellow precipitate. The alkaline residue is acidified to give a solid (B) $(C_7H_6O_3)$. (B) dissolved in aqueous $NaHCO_3$ with the evolution of gas. Identify (A) and (B).

Q.15 Neutralisation of 30 gm of a mixture of acetic acid and phenol solutions required 100 ml of 2M sodium hydroxide solution. When the same mixture was treated with bromine water, 33.1 gm of precipitate was formed. Determine the mass percentage of acetic acid and phenol in the given solution.

Q.16 Find the structure of (A), $C_{10}H_{10}O_2$, a sweet-smelling liquid that has the following properties. It does not dissolve in NaOH or give a colour with $FeCl_3$; it adds one equivalent of H_2 on catalytic hydrogenation. Reductive ozonolysis affords $H_2C=O$ and $C_9H_8O_3$ (B) that gives a positive Tollens test. Oxidation of (A) with $KMnO_4$ gives an acid (C) (MW=166) which gives no colour with $FeCl_3$. When (C) is refluxed with concentrated $HI, H_2C=O$ and 3,4-dihydroxybenzoic acid are isolated and identified.

Exercise 2

Q.1 An organic compound (A) with molecular formula C_7H_8O dissolves in NaOH and gives characteristic colour with $FeCl_3$. On treatment with Br_2, it gives a tribromo product $C_7H_5OBr_3$. The compound is:

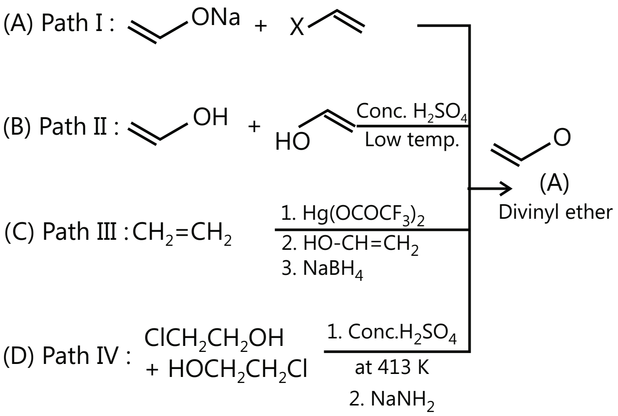
(A) p-Hydroxybenzene

(B) 2-Methoxy-2-phenyl propane

(C) m-Cresol

(D) p-Cresol

Q.2 Which of the following paths is/are feasible for the preparation of ether (A)?



Q.3 Which of the following statement is correct?

i. Glycerol on reaction with oxalic acid at 110°C (383 K) and followed by heating and hydrolysis gives formic acid and glycerol.

ii. Glycerol on reaction with oxalic acid at 230°C (503 K) and followed by heating gives allyl alcohol.

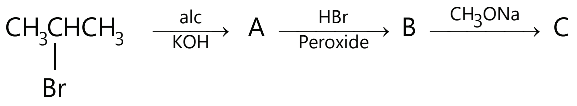
iii. Glycerol on oxidation with dil.HNO_3 gives a mixture of glyceric and tartonic acid.

iv. Glycerol on oxidation with conc. HNO_3 gives glycerol acid.

(A) i and ii (B) i and iii

(C) iii and iv (D) i, ii, iii, iv

Q.4 In the reaction



$$\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_3} \xrightarrow[KOH]{alc} A \xrightarrow[Peroxide]{HBr} B \xrightarrow{CH_3ONa} C$$

(A) Diethyl ether (B) 1-Methoxypropane

(C) Isopropyl alcohol (D) Propylene glycol.

Q.5 The compound which is not isomeric with diethyl ether is:

(A) n-propyl methyl ether (B) 2-methyl propan-2-ol

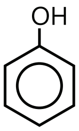
(C) Butanone (D) Butan-1-ol

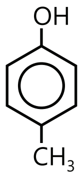
Q.6 Phenol reacts with bromine water is CS_2 at low temperature to give:

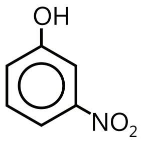
(A) o-Bromophenol (B) o-and p-Bromophenol

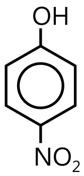
(C) p-Bromophenol (D) 2,4, 6-Tribromphenol

Q.7 In the following compounds:


(I)


(II)


(III)

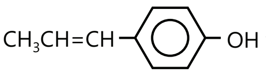

(IV)

The order of acidity is

(A) (III) > (IV) > (I) > (II) (B) (I) > (IV) > (III) > (II)

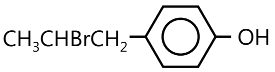
(C) (II) > (I) > (III) > (IV) (D) (IV) > (III) > (I) > (II)

Q.8 The reaction of

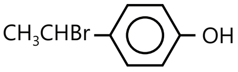


with HBr gives

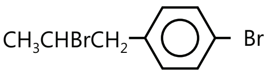
(A)



(B)



(C)



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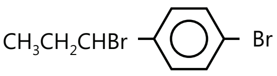


Q.9 Reaction involving anti addition is:

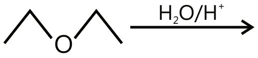
(A) $CH_2 = CH_2 \xrightarrow{H^+/H_2O}$

(B) $CH_3CH = CH_2 \xrightarrow{HX}$

(C) $CH_3CH = CH_2 \xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O}$

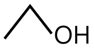
(D) $CH_2 = CH_2 \xrightarrow[H_2O_2/OH^-]{B_2H_6/THF}$

Q.10

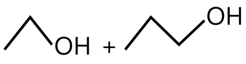


? Product/(s) will be:

(A)



(B)



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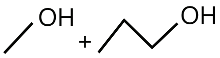
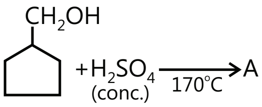


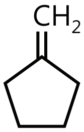
(D)

Q.11



What is the major product A?

(A)



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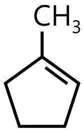
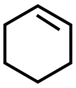
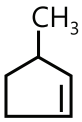


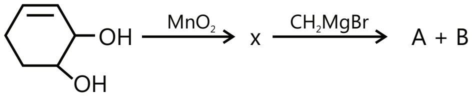
(C)



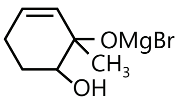
(D)



Q.12



(A)



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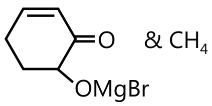
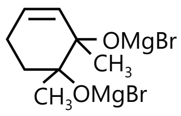


(C)



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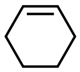
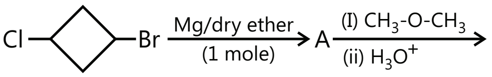
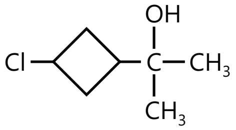
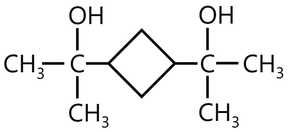
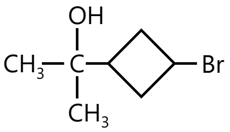


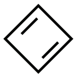
Q.13 

What is B?

(A) 

(B) 

(C) 

(D) 

Q.14 When 3, 3-dimethyl 2-butanol is heated with H_2SO_4 the major product obtained is

(A) 2, 3-dimethyl 2-butene

(B) cis and trans isomers of 2, 3-dimethyl 2-butene

(C) 2, 3-dimethyl 1-butene

(D) 3, 3-dimethyl 1-butene

Q.15 Consider the following reaction

Phenol

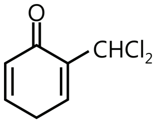
$$\xrightarrow[\text{Zn dust}]{} X \xrightarrow[\text{Anhydrous AlCl}_3]{CH_2Cl} Y \xrightarrow[H_2O/H^+]{\text{Alkaline KMnO}_4} Z$$

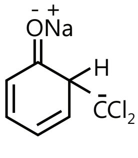
The product Z is

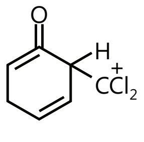
(A) Benzene (B) Toluene

(C) Benzaldehyde (D) Benzoic acid

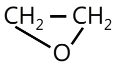
Q.16 In Reimer-Tiemann reaction, the intermediate which does not form is

(A) 

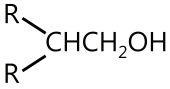
(B) 

(C) 

(D) All of these

Q.17 Reaction of  with RMgX leads to formation of

(A) RCH_2CH_2OH (B) $RCHOHCH_3$

(C) RCHOHR (D) 

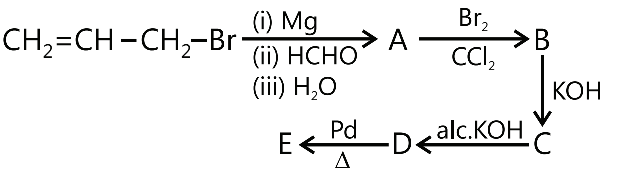
R_2CHCH_2OH

Q.18 Ethyl chloride is converted into diethyl ether by

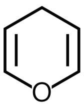
(A) Perkin's reaction (B) Grignard reaction

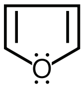
(C) Wurtz synthesis (D) Williamson's synthesis

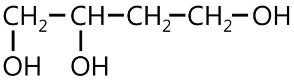
Q.19



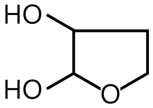
Product (E) is

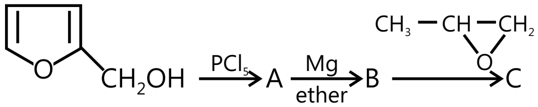
(A) 

(B) 

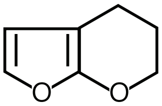
(C) 

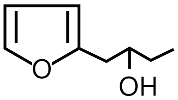
$CH_2(OH)-CH(OH)-CH_2-CH_2-OH$

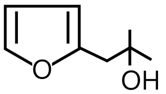
(D) 

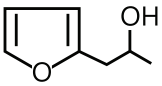
Q.20 

Product (C) is

(A) 

(B) 

(C) 

(D) 

Previous Years Questions

Q.1 Hydrogen bonding is maximum in ***(1987)***

(A) Ethanol (B) Diethyl ether

(C) Ethyl chloride (D) Triethyl amine

Q.2 Hydrogen bonding is maximum in ***(1987)***

(A) Ethanol (B) Diethyl ether

(C) Ethyl chloride (D) Triethyl amine

Q.3 In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is ***(1988)***

(A) C – C (B) C – O (C) C – H (D) O – H

Q.4 The products of combustin of an aliphatic thiol (RSH) at 298 K are ***(1992)***

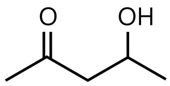
(A) $CO_2(g)$, $H_2O(g)$ and $SO_2(g)$

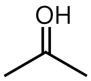
(B) $CO_2(g)$, $H_2O(l)$ and $SO_2(g)$

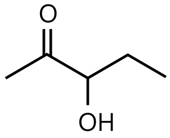
(C) $CO_2(l)$, $H_2O(l)$ and $SO_2(g)$

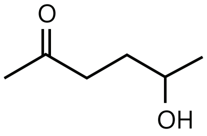
(D) $CO_2(g)$, $H_2O(l)$ and $SO_2(l)$

Q.5 Which one of the following will most readily be dehydrated in acidic condition? ***(2000)***

(A) 

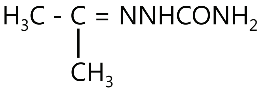
(B) 

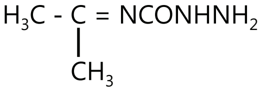
(C) 

(D) 

Q.6 Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O) 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous solution of $H_2NCONHNH_2$ and sodium acetate gives a product 'C'. Identify the structure of 'C' ***(2002)***

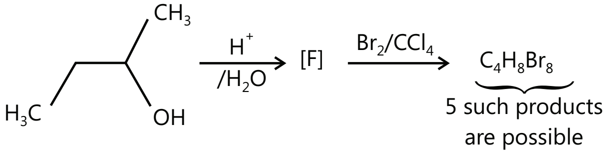
(A) $CH_3CH_2CH = NNHCONH_2$

(B) 
$H_3C - \underset{\underset{CH_3}{|}}{C} = NNHCONH_2$

(C) 
$H_3C - \underset{\underset{CH_3}{|}}{C} = NCONHNH_2$

(D) $CH_3CH_2OH + NCONHNH_2$

Q.7 How many structures of F is possible? ***(2003)***



(A) 2 (B) 5 (C) 6 (D) 3

Q.8 Read the following question and answer as per the direction given below:

(A) Statement-I is true ; statement-II is true; statement-II is a correct explanation of statement-I.

(B) Statement is true; statement-II s true; statement-I is not the correct explanation of statement-I.

(C) Statement-I is true; statement-II is false.

(D) Statement-I is false ; statement-II is true.

Statement-I: Solubility of n-alcohol is water decreases with increase in molecular weight.

Statement-II: The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permit enhanced hydrogen bonding with water ***(1988)***

Q.9 The yield of a ketone when a secondary alcohol is oxidized is more than the yield of aldehyde when a primary alcohol is oxidized. ***(1983)***

Q.10 Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. ***(1985)***

Q.11 A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was: ***(2009)***

(A) CH_3OH (B) HCHO

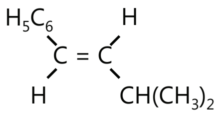
(C) CH_3COCH_3 (D) CH_3COOH

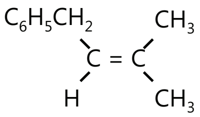
Q.12 The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is: ***(2009)***

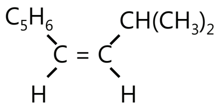
(A) Benzoic acid (B) Salicylaldehyde

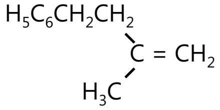
(C) Salicylic acid (D) Phthalic acid

Q.13 The main product of the following reaction is $C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{conc. } H_2SO_4} ?$ ***(2010)***

(A) 

(B) 

(C) 

(D) 

Q.14 Ortho–Nitrophenol is less soluble in water than p– and m– Nitrophenols because: ***(2012)***

(A) o–Nitrophenol is more volatile in steam than those of m – and p–isomers

(B) o–Nitrophenol shows Intramolecular H–bonding

(C) o–Nitrophenol shows Intermolecular H–bonding

(D) Melting point of o–Nitrophenol is lower than those of m–and p–isomers.

Q.15 Iodoform can be prepared from all except: ***(2012)***

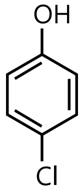
(A) Ethyl methyl ketone

(B) Isopropyl alcohol

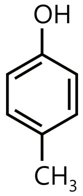
(C) 3–Methyl – 2– butanone

(D) Isobutyl alcohol

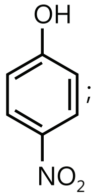
Q.16 Arrange the following compounds in order of decreasing acidity: ***(2013)***



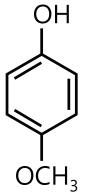
(I) ;



(II) ;



(III) ;



(IV) ;

(A) II > IV > I > III (B) I > II > III > IV

(C) III > I > II > IV (D) IV > III > I > II

Q.17 An unknown alochol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism: ***(2013)***

(A) Secondary alcohol by S_N1

(B) Tertiary alcohol by S_N1

(C) Secondary alcohol by S_N2

(D) Tertiary alcohol by S_N2

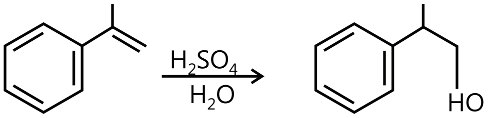
JEE Advanced/Boards

Exercise 1

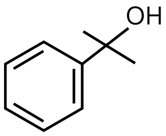
Q.1 Calculate the depression in freezing point (ΔT_f) of 0.1 m solution of ROH in cold conc. H_2SO_4. K_f = x K kg mol^{-1}

Q.2 0.218 gm of the acetyl derivative of a polyhdric alcohol (molecular mass = 92) requires 0.168 gm of KOH for hydrolysis. Calculate the number of (-oH) groups in the alcohol.

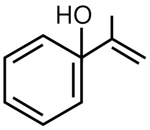
Q.3 Consider the following reaction:



(A)



(B)

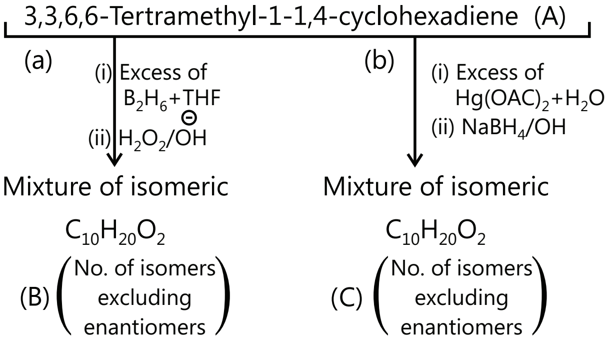


(C)

(i) Provide a complete mechanism for the formation of the major product

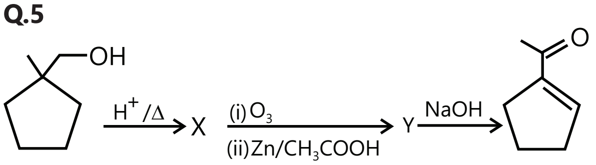
(ii) Briefly explain the choice of major product.

Q.4



What are the numerical values of (B) and (C)?

Q.5



Q.6 Compound X (molecular formula, C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate with excess of MeMgBr, 0.42 g of X gives 224 mL of CH_4 at STP. Treatment of X with H_2 in presence of Pt catalyst followed by boiling with excess HI, gives n-pentane. Suggest structure for X and write the equation involved.

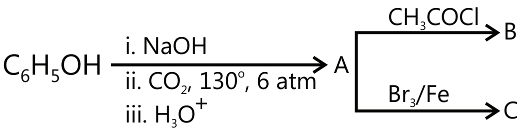
Q.7 An organic compound (A) gives positive Liebermann reaction and on treatment with $CHCl_3$ / KOH followed by hydrolysis gives (B) and (C). Compound (B) gives colour with Schiff's reagent but not (C), which is steam volatile. (C) on treatment with $LiAlH_4$ gives (D), $C_7H_8O_2$, which on oxidation gives (E). Compound (E) reacts with $(CH_3CO)_2O/CH_3COOH$ to give a pain reliever (F). Give the structures of (A) to (F) with proper reasoning.

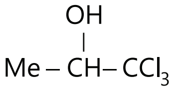
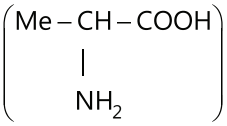
Q.8 Two isomeric compound, (A) and (B), have the same formula $C_{11}H_{13}OCl$. Both are unsaturated, yield the same compound (C) on catalytic hydrogenation, and produce 4-chloro-3-ethoxybenzoic acid on vigorous oxidation. (A) exists in geometrical isomers, (D) and (E), but not (B). give structures of (A) to (E) with proper reasoning.

Q.9 15 Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon: 42.86%, hydrogen: 2.40%, nitrogen: 16.67%, and oxygen: 38.07%.
(i) Calculate the empirical formula of the minor product.
(ii) When 5.5 gm of the minor product is dissolved in 45 gm of benzene, the boiling point of the solution is 1.84°C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula.

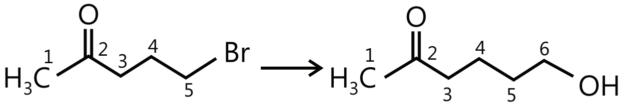
(Molal boiling point elevation constant of benzene is 2.53 K kg mol^{-1}.)

Q.10 Identify A, B and C in the following reaction.

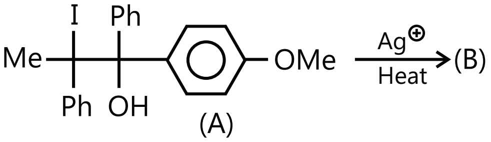


Q.11 20 If  $Me-\overset{\overset{\large OH}{|}}{C}H-CCl_3$ is treated with alkaline NaN_3 and followed by reduction with H_2 / Pd it gives an α -amino acid alanine  $\left(\begin{array}{c} Me-CH-COOH \\ | \\ NH_2 \end{array}\right)$. Explain the reaction.

Q.12 Convert

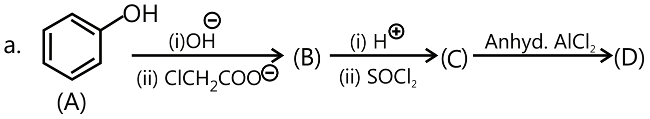


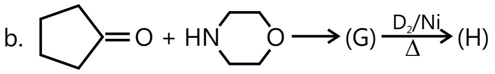
Q.13 Assign the structure of (B), the principal organic product of the following reaction:



Q.14 When a mixture of t-butyl alcohol and ethyl alcohol is heated with conc. H_2SO_4, a single ether product is obtained. Identify the product giving proper reasons.

Q.15 Identify the major products (B) to (H).





Q.16 When pent-4-en-1-ol is treated with aqueous Br_2 / OH, a cyclic bromo ether is formed rather than the expected bromohydrin. Propose a suitable mechanism for the above.

Exercise 2

Single Correct Choice Type

Q.1 Select the correct statement.

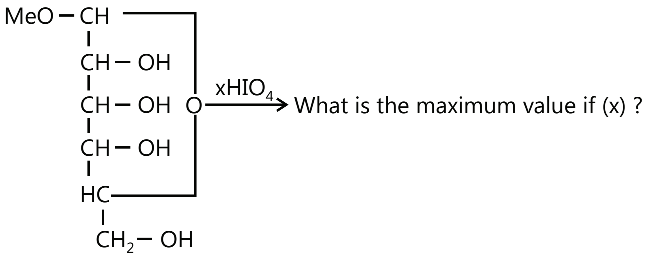
(A) Solvolysis of $(CH_3)_2C=CH-CH_2Cl$ in ethanol is over 6000 times than alkyl chloride (25°C)

(B) CH_3-CH=CH-CH_2-OH when reacts with HBr give a mixture of 1-bromo-2-butene and 3-bromo 1-butene

(C) When solution of 3-buten 2-ol in aqueous sulphuric acid is allowed to stand for one week, it was found to contain both 3-buten 2-ol and 2-buten-1-ol

(D) All of these

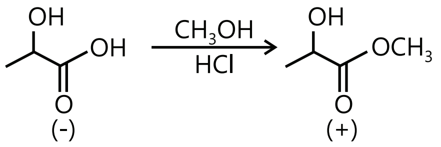
Q.2



What is the maximum value if (x) ?

(A) 1 (B) 2 (C) 3 (D) 4

Q.3 Esterification (shown below) is a reaction converting a carboxylic acid to its ester. It involves only the carbonyl carbon. Esterification of (-) lactic acid with methanol yields (+) methyl lactate. Assuming that there are no side reactions, what is true about this reaction?



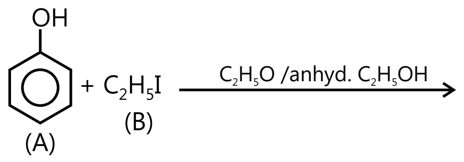
(A) An S_N2 process has occurred, inverting the absolute configuration of the chiral center.

(B) An S_N1 reaction at the chiral center has inverted the optical rotation.

(C) A diastereomer has been produced; diastereomers have different physical properties including optical rotation

(D) Optical rotation is not directly related to absolute configuration, so the change in sign of rotation is merely a coincidence

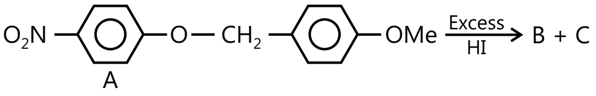
Q.4

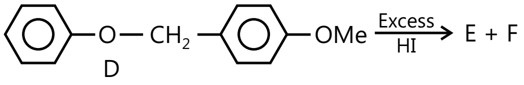


(A) $PhOC_2H_5$ (B) PH – O – Ph

(C) PhI (D) $C_2H_5OC_2H_5$

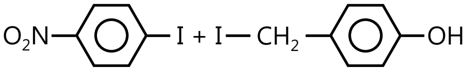
Q.5

(I) 

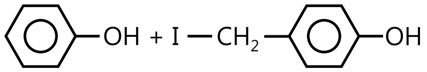
(II) 

Which of the following statements is/are correct about the above reaction?

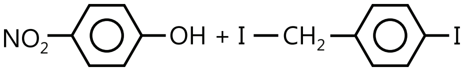
(A) The compounds (B) and (C), respectively, are:



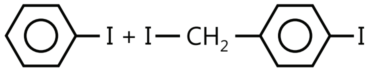
(B) The compound (D) and (E), respectively, are:



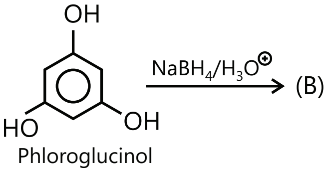
(C) The compound (B) and (C), respectively, are:

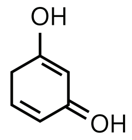


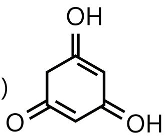
(D) The compounds (E) and (F), respectively, are:

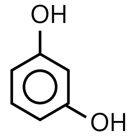


Q.6 Phenols are generally not changed with $NaBH_4/H_3O^\oplus$ 1, 3-and 1, 4-benzenediols and 1, 3, 5-benzenetriols are unchanged under these conditions. However, 1, 3, 5- benzenetriol (phloroglucinol) gives a high yield of product (B).



(A) 

(B) 

(C) 

Q.7 Diethyl ether on heating with conc. HI gives two moles of

(A) Ethanol (B) Iodoform

(C) Ethyl iodide (D) Methyl iodide

Q.8 An industrial method of preparation of methanol is

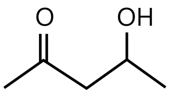
(A) catalytic reduction of carbon monoxide in presence of $ZnO-Cr_2O_3$

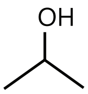
(B) by reacting methane with stem at 900°C with nickel catalyst

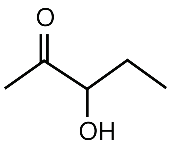
(C) by reducing formaldehyde with $LiAlH_4$

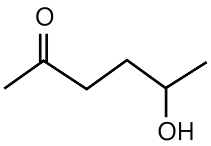
(D) by reacting formaldehyde with aqueous sodium hydroxide solution

Q.9 Which one of the following will most readily be dehydrated in acidic condition?

(A) 

(B) 

(C) 

(D) 

Q.10

$C_3H_7-OH+Er_3O^{+}BF_4^{-}\rightarrow C_3H_7-O-Et+EtOEt$

Which of the following statements is wrong?

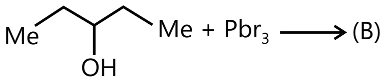
(A) The nucleophile in the reaction is C_3H_7OH.

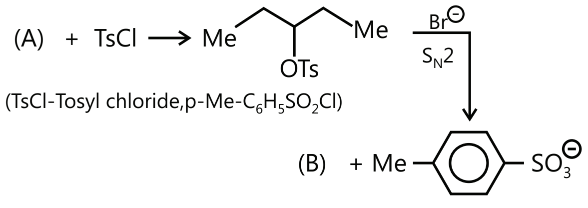
(B) The nucleophile in the reaction is $Bf_4^{\ominus}$

(C) The leaving group is Et_2O.

(D) S_N2 reaction occurs

Q.11 Which of the best method for the conversation of (A) pantan-3-ol to 3-bromopentane (B)?

(A) 

(B) 

(Tosylate ion)

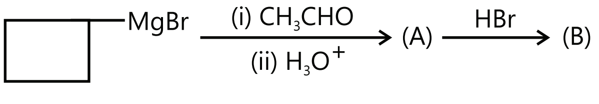
(C) (A) $\xrightarrow{HBr}$ (B)

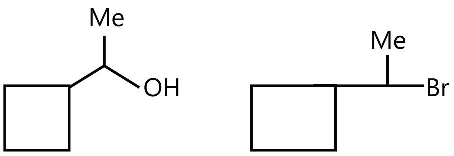
(D) Both (A) and (B)

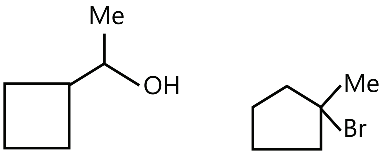
Q.12 In Zeisel's method for the determination of methoxyl groups, a sample of 2.68 gm of a compound (A) gave 14.08 gm of AgI. If the molecular weight of compound (A) is 134, the number of $(-OCH_3)$ group(s) in the compound (A) is:

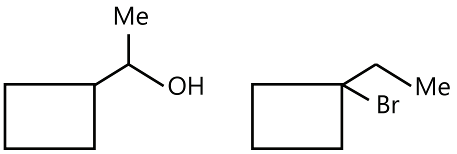
(A) 1 (B) 2 (C) 3 (D) 4

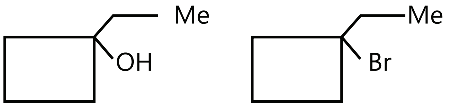
Q.13



(A) 

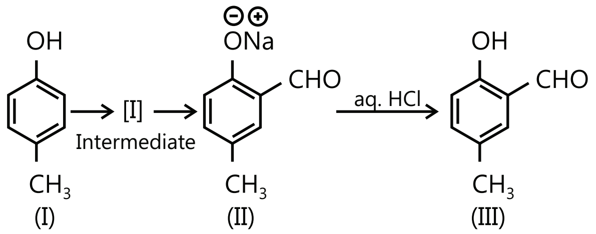
(B) 

(C) 

(D) 

Comprehension Type

Reimer-Tiemann reaction introduces an aldehyde group on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. It is a general method for the synthesis of substituted salicyaldehydes as depicted below:



Q.14 Which one of the following reagents is used in the above reaction?

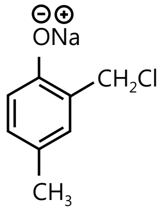
(a) aq. NaOH + CH_3Cl (b) aq.NaOH + CH_2Cl_2

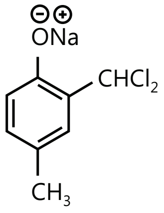
(c) aq.NaOH+$CHCl_3$ (d) aq.NaOH+CCl_4

Q.15 The electrophile in this reaction is:

(A) :CHCl (B) ${}^{\oplus}CHCl_2$ (C) :CCl_2 (D) •CCl_3

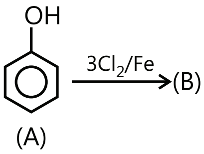
Q.16 The structure of the intermediate (I) is:

(A) 

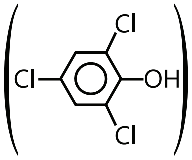
(B) 

Assertion Reasoning Type

Q.17 Assertion:



The product (B) is

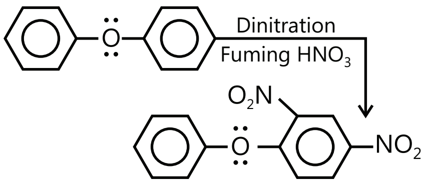


Reason (R): Phenol cannot be chlorinated because the ring is susceptible to oxidation by Cl_2.

Q.18 Assertion: 2, 6-Dimethyl-4-nitrophenol (I) is more acidic than 3, 5-dimethyl-4-nitrophenol (II).

Reason: It is due to steric inhibition of the resonance of ($-NO_2$) group with two (Me) groups in (II).

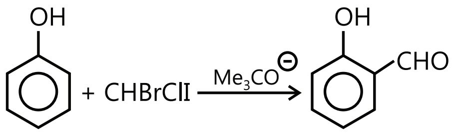
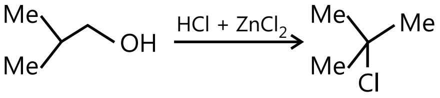
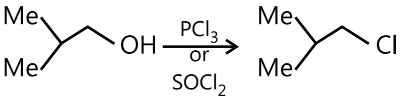
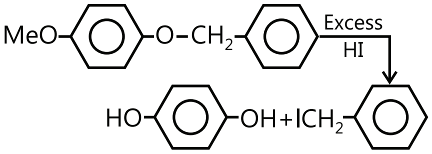
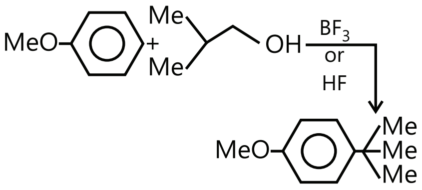
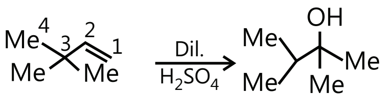
Q.19 Assertion: Diphenyl ether (I) on dinitration gives the product (II).



Reason: The ring with first nitro group is deactivated by $\bar{e}$ withdrawing NO_2 group, so the second nitro group enters the other ring.

Match the Columns

Q.20 Match the reactions of column I with the Mechanism of column II.

	Column I		**Column II**
	Reactions		**Mechanism**
(A)		(p)	Carbocation intermediate
(B)		(q)	Bromochloro carbine intermediate
(C)		(r)	SE reaction
(D)		(s)	Rearrangement of carbocation intermediate
(E)		(t)	S_N1 mechanism
(F)		(u)	No rearrangement

Previous Years' Questions

Q.1 When phenyl magnesium bromide reacts with tert-butanol, which of the following is formed? ***(2005)***

(A) Tert-butyl methyl ether (B) Benzene

(C) Tert-butyl benzene (D) Phenol

Q.2 The best method to prepare cyclohexene from cyclohexanol is by using ***(2005)***

(A) conc. HCl + $ZnCl_2$ (B) conc. H_3PO_4

(C) HBr (D) conc. HCl

Q.3 (I) 1, 2-dihydroxy benzene

(II) 1, 3-dihydroxy benzene

(III) 1, 4-dihydroxy benzene

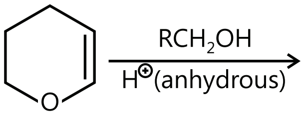
(IV) Hydroxy benzene

The increasing order of boiling points of above mentioned alcohols is ***(2006)***

(A) I < II < III < IV (B) I < II < IV < III

(C) IV < I < II < III (D) IV < II < I < III

Q.4 The major product of the following reaction is ***(2011)***



(A) A hemiacetal (B) An acetal

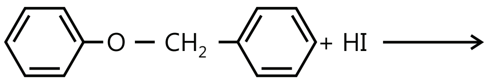
(C) An ether (D) An ester

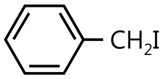
Q.5 The products of reaction of alcoholic silver nitrate with ethyl bromide are ***(1998)***

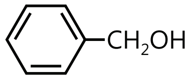
(A) Ethane (B) Ethene

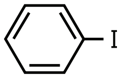
(C) Nitroethane (D) Ethyl alcohol

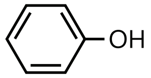
Q.6 The following ether, when treated with HI produces ***(1999)***



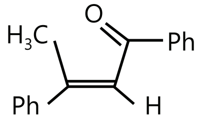
(A) 

(B) 

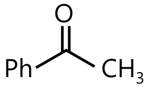
(C) 

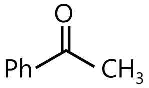
(D) 

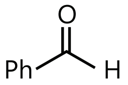
Paragraph 1: A tertiary alcohol H upon acid catalysed dehydration gives product I. Ozonolysis of I leads to compounds J and K. Compound J upon reaction with KOH gives benzyl alcohol and a compound L, whereas K on reaction with KOH gives only M. ***(2008)***

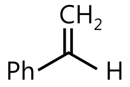
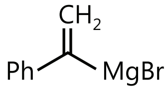
M = 

Q.7 Compound H is formed by the reaction of

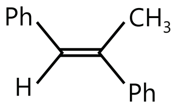
(A)  ; PhMgBr

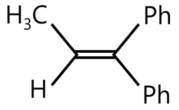
(B)  ; $PhCH_2MgBr$

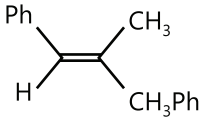
(C)  ; $PhCH_2MgBr$

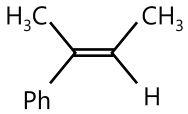
(D)  ; 

Q.8 The structure of compound I is

(A) 

(B) 

(C) 

(D) 

Q.9 The structures of compound J, K and L respectively, are

(A) $PhCOCH_3$, $PhCH_2COCH_3$ and $PhCH_2COO^- K^+$

(B) PhCHO, $PhCH_2CHO$ and $PhCOO^- K^+$

(C) $PhCOCH_3$, $PhCH_2CHO$ and $CH_3COO^-K^+$

(D) PhCHO, $PhCOCH_3$ and $PhCOO^-K^+$

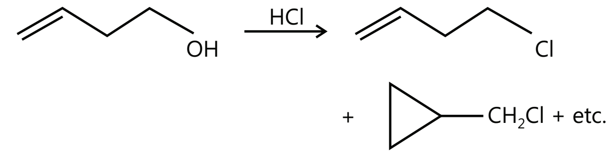
Q.10 Give reasons for the following in one or two sentences. "Acid catalysed dehydration of t-butanol is faster than that of n-butanol. ***(1998)***

Q.11 Write the structures of the products: ***(1998)***

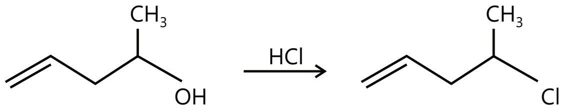
$(CH_3)_2\,CHOCH_3 \xrightarrow[\text{Heat}]{\text{HI,Excess}} \text{Product}$

Q.12 Explain briefly the formation of products giving the structures of the intermediates. ***(1999)***

(i)

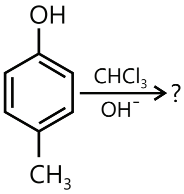


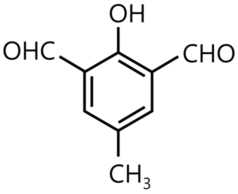
(ii)



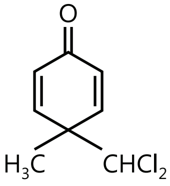
Q.13 Cyclobutylbromide on treatment with magnesium in dry ether forms an organometallic compound (A). The organometallic reacts with ethanol to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1–bromo-1-methylcyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B). ***(2001)***

Q.14. In the following reaction, the product(s) formed is (are) ***(2013)***

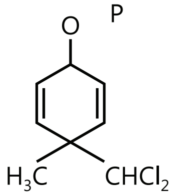




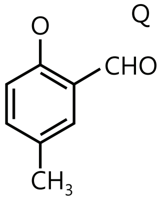
P



Q



R



S

(A) P(major) (B) Q(minor)

(C) R(minor) (D) S(major)

Q.15 The correct statement(s) about O_3 is (are) ***(2013)***

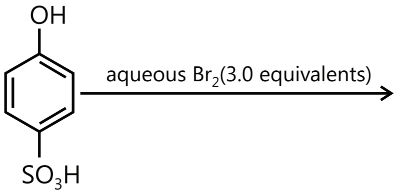
(A) O–O bond lengths are equal

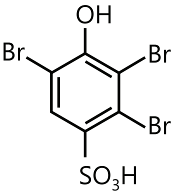
(B) Thermal decomposition of O_3 is endothermic

(C) O_3 is diamagnetic in nature

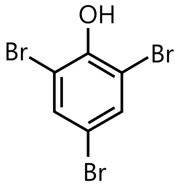
(D) O_3 has a bent structure

Q.16 The major product(s) of the following reaction is (are) ***(2013)***

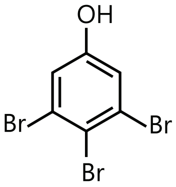




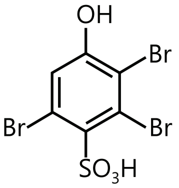
P



Q



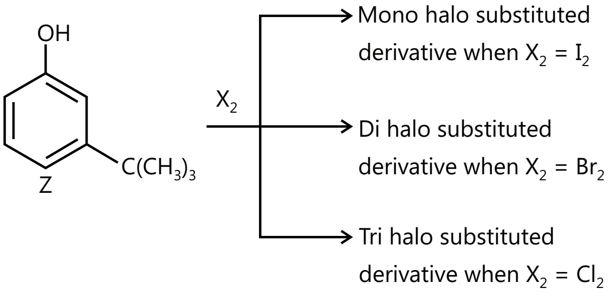
R



S

(A) P (B) Q (C) R (D) S

Q.17 The reactivity of compound Z with different halogens under appropriate conditions is given below: ***(2014)***



The observed pattern of electrophilic substitution can be explained by

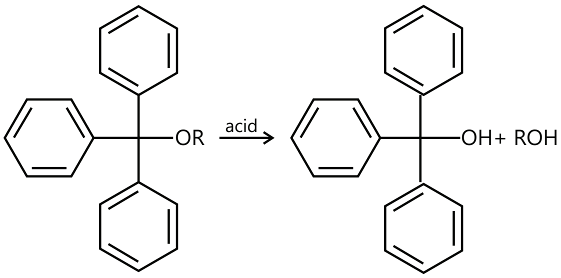
(A) The steric effect of the halogen

(B) The steric effect of the tert-butyl group

(C) The electronic effect of the phenolic group

(D) The electronic effect of the tert-butyl group

Q.18 The acidic hydrolysis of ether (X) shown below is fastest when ***(2014)***



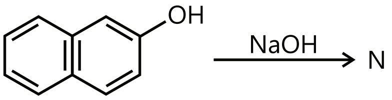
(A) One phenyl group is replaced by a methyl group.

(B) One phenyl group is replaced by a para-methoxyphenyl group.

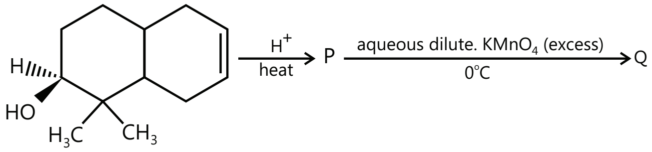
(C) Two phenyl groups are replaced by two para-methoxyphenyl groups.

(D) No structural change is made to X.

Q.19 The number of resonance structures for N is ***(2015)***



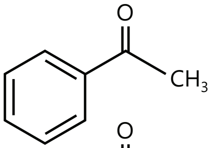
Q.20 The number of hydroxyl group(s) in Q is ***(2015)***

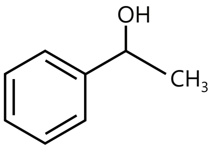


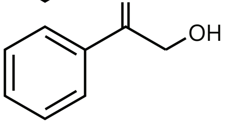
Paragraph 2: In the following reactions

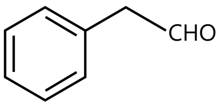
$$\begin{tikzcd}
C_8H_6 \arrow[r, "Pd\text{-}BaSO_4", "H_2"'] \arrow[d, "H_2O\ \ HgSO_4,\ H_2SO_4"] & C_8H_8 \arrow[r, "i)\ B_2H_4", "ii)\ H_2O_4,\ NaOH,\ H_2O"'] & X \\
C_8H_8O \arrow[r, "i)\ EtMgBr,\ H_2O", "ii)\ H^+,\ heat"'] & Y
\end{tikzcd}$$

Q.21 Compound X is ***(2015)***

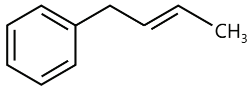
(A)


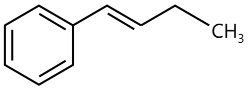
(B)


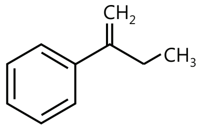
(C)


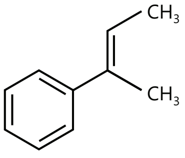
(D)


Q.22 The major compound Y is ***(2015)***

(A)


(B)


(C)


(D)


Q.23 The correct statement(s) about the following reaction sequence is(are) ***(2016)***

$$\text{Cumene}\ (C_9H_{12}) \xrightarrow[ii) H_3O^+]{i)\ O_2} P \xrightarrow{CHCl_3/NaOH} Q\ (\text{major}) + R\ (\text{minor})\ Q \xrightarrow[PhCH_2Br]{NaOH} S$$

(A) R is steam volatile

(B) Q gives dark violet coloration with 1% aqueous $FeCl_3$ solution

(C) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine

(D) S gives dark violet coloration with 1% aqueous $FeCl_3$ solution

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.1 Q.5 Q.8
Q.10

Exercise 2

Q.2 Q.3 Q.7
Q.14 Q.15 Q.16

Previous Years' Questions

Q.3 Q.4 Q.6

JEE Advanced/Boards

Exercise 1

Q.1 Q.8 Q.11
Q.15

Exercise 2

Q.2 Q.5 Q.7
Q.10 Q.12 Q.15
Q.18

Previous Years' Questions

Q.3 Q.6 Q.8
Q.12

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 C **Q.2** D **Q.3** D **Q.4** B **Q.5** B **Q.6** B
Q.7 D **Q.8** B **Q.9** C **Q.10** A **Q.11** C **Q.12** B
Q.13 A **Q.14** A **Q.15** D **Q.16** D **Q.17** A **Q.18** D
Q.19 B **Q.20** C

Previous Years' Questions

Q.1 A **Q.2** A **Q.3** D **Q.4** B **Q.5** A **Q.6** A
Q.7 D **Q.8** C **Q.9** F **Q.10** F **Q.11** D **Q.12** D
Q.13 A **Q.14** B **Q.15** D **Q.16** C **Q.17** B

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

Q.1 D **Q.2** B **Q.3** D **Q.4** A **Q.5** A **Q.6** C
Q.7 C **Q.8** A **Q.9** A **Q.10** B **Q.11** B **Q.12** C
Q.13 B

Comprehension Type

Q.14 C **Q.15** C **Q.16** B

Assertion Reasoning Type

Q.17 D **Q.18** A **Q.19** D

Match the Columns

Q.20 A → q, r; B → p, s; C → u; D → p, t; E → p, r, s; F → p, s

Previous Years' Questions

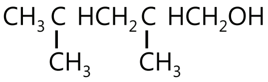
Q.1 B **Q.2** B **Q.3** C **Q.4** A **Q.5** C, E **Q.6** A, D
Q.7 B **Q.8** A **Q.9** D **Q.14** B,D **Q.15** A, C, D **Q.16** B
Q.17 A, B, C **Q.18** C **Q.19** 9 **Q.20** D **Q.21** C **Q.22** D
Q.23 B, C

Solutions

JEE Main/Boards

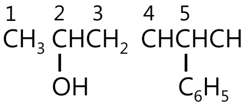
Exercise 1

Sol 1: The longest chain to which the hydroxyl group is attached gives us the base name. The ending is ol. We then number the longest chain from the end that gives the carbon bearing the hydroxyl group the lower number. Thus, the names, in both of the accepted IUPAC formats, are

(A) 

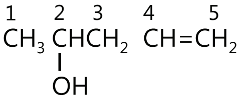
$CH_3CH(CH_3)CH_2CH(CH_3)CH_2OH$

2,4-Dimethylpentan-1-ol

(B) 

$\overset{1}{C}H_3\overset{2}{C}H(OH)\overset{3}{C}H_2\overset{4}{C}H(C_6H_5)\overset{5}{C}H$

4-Phenyl-2-pentanol
(or 4-phenylpentan-ol)

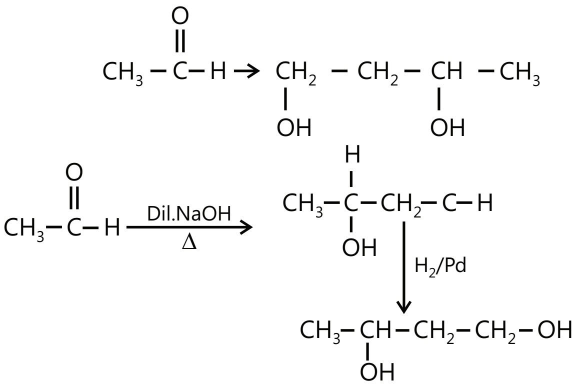
(C) 

$\overset{1}{C}H_3\overset{2}{C}H(OH)\overset{3}{C}H_2\overset{4}{C}H=\overset{5}{C}H_2$

4-Penten-2-ol
(or pent-4-en-2-ol)

Sol 2:

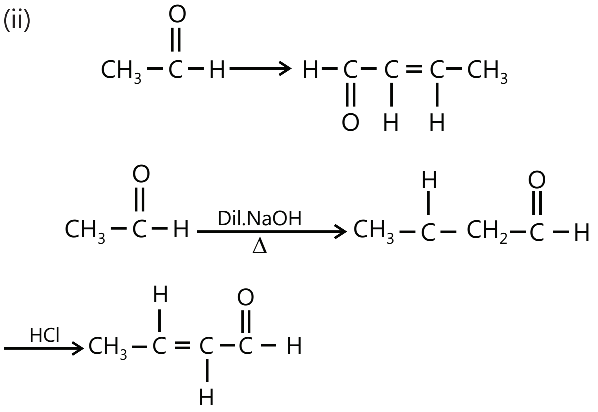
(i)



$$CH_3-\overset{\overset{O}{\|}}{C}-H \rightarrow \underset{\underset{OH}{|}}{CH_2}-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$$

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\Delta]{Dil.NaOH} CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-C-H \xrightarrow{H_2/Pd} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-OH$$

(ii)

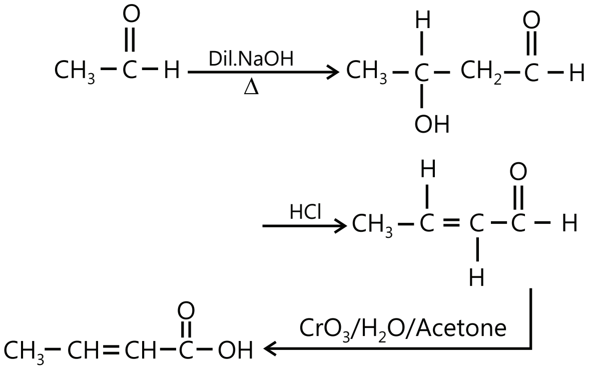


$$CH_3-\overset{\overset{O}{\|}}{C}-H \longrightarrow H-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_3$$

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\Delta]{Dil.NaOH} CH_3-\overset{\overset{H}{|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-H$$

$$\xrightarrow{HCl} CH_3-\overset{\overset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-\overset{\overset{O}{\|}}{C}-H$$

(iii)

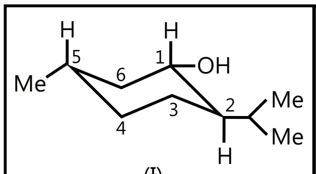
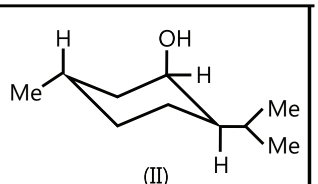
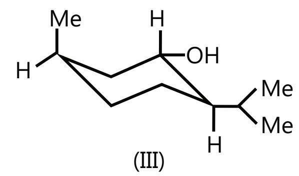
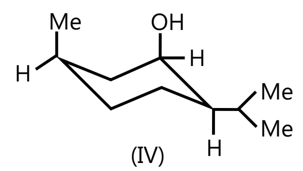


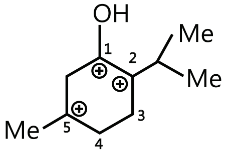
$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\Delta]{Dil.NaOH} CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-H$$

$$\xrightarrow{HCl} CH_3-\overset{\overset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-\overset{\overset{O}{\|}}{C}-H$$

$$\xrightarrow{CrO_3/H_2O/Acetone} CH_3-CH=CH-\overset{\overset{O}{\|}}{C}-OH$$

Sol 3: There are three chiral C atoms and there are four diastereomers, each with a pair of enantiomers. Thus total stereoisomers are 8.

 (I)	 (II)	 (III)	 (IV)
(OH⇒e. i – Pr⇒e Me⇒e) All equatorial (most stable) Three (e)	(OH⇒a. i – Pr⇒e Me⇒e) Two (e) Me is bulky, so in e-position; more stable	(OH⇒e. i – Pr⇒e Me⇒a) Two (e) Me is in (a)-position, so less stable	(OH ⇒ a. i Pr ⇒ e Me ⇒ a) One (e) least stable

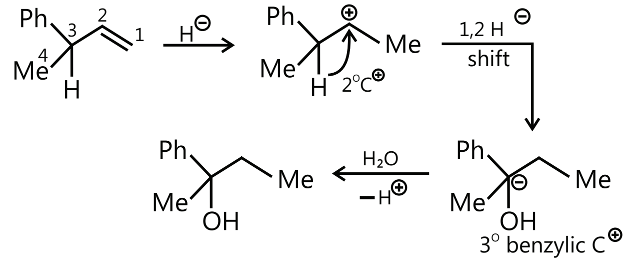


(Chiral C aloms at C-1, C-2 and C-5)

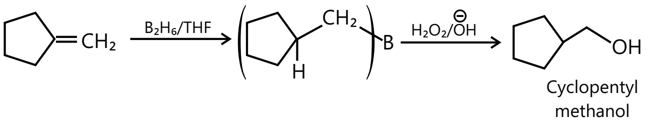
Stability order is: I > II > III> IV

Sol 4:

(1)



(2)



Sol 5: a. Boiling point order: VI > IV > V > III > II > I

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

Explanation: All of them ate alcohols, so all have H-bonding. As the molecular mas and surface area increases, the boiling point increases and solubility decreases.

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

b. Boiling point order: I > III > IV > II

Solubility order: I > III > IV > II

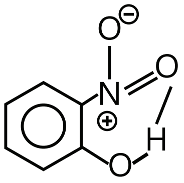
In (I), there is H-bonding in (II) (aldehyde), dipole-dipole interaction, in (III) (ether), slightly polar due to EN of O, and in (IV) (alkane), van der waals interaction (non-polar).

c. Boiling point order: II > III > I

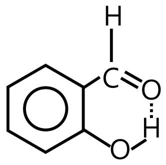
Solubility order: II > III > I

In (II), three (-OH) groups, more H-bonding; in (II), one (-OH) group, less H-bonding; in (I) (alkane), van der Waals interaction.

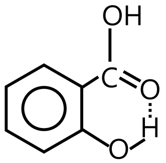
Sol 6: In ortho-isomers of (I), (II), and III, intramolecular H-bonding (chelation) occurs which inhibits the intermolecular attraction between these molecules and thus lowers the boiling point and also reduces H-bonding of these molecules with H_2O, thereby, decreases water solubility. Intramolecular chelation does not occur on p-and m-isomers.



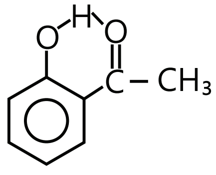
o-Nitophenol



o-Hydroxybenzaldehyde
(Salicyaldehyde)



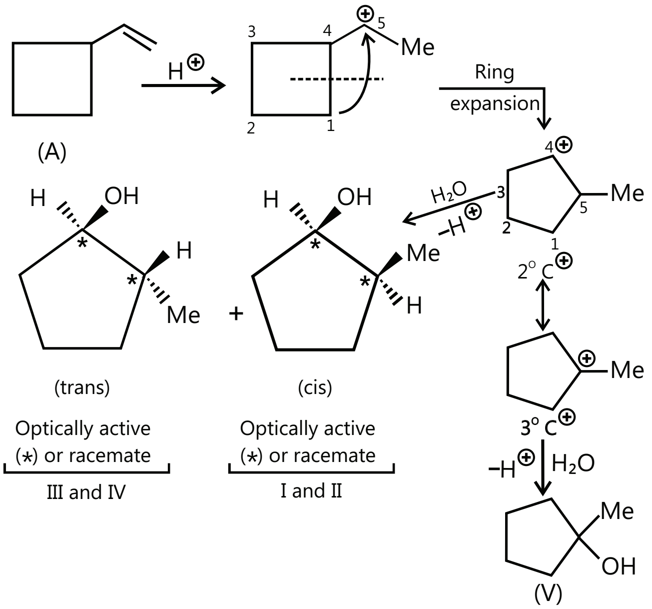
o-Hydroxybenzoic acid
(Salicylic acid)



o-Hydroxy acetophenone

Sol 7: Chelated o-isomers have a minimum attraction with H_2O, and they are steam volatile or steam distills. Steam volatile or steam distills are the compounds which are mixed with boiling H_2O but not dissolved. On passing steam to such boiling mixture, steam carries the compound with it.

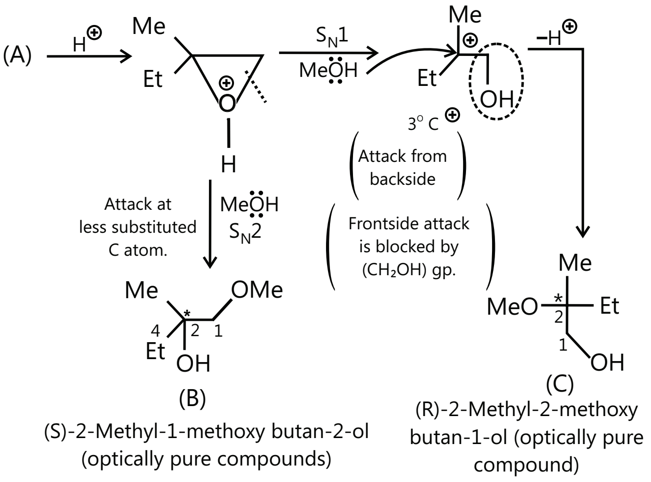
Sol 8:



The total number of isomeric products including stereoisomers is 5.

Sol 9: Greater the steric hindrance in the ether molecule encountered in the formation of the coordinate bond, weaker is the Lewis basicity. In (i), R groups (the side of the ring) are 'tied back' leaving a very exposed O atom free to serve as basic site. In other words, more compact the molecule (due to ring), more easily O atom can donate its LP $\bar{e}$'s to the Lewis acid, and therefore, stronger the Lewis base.

Sol 10:

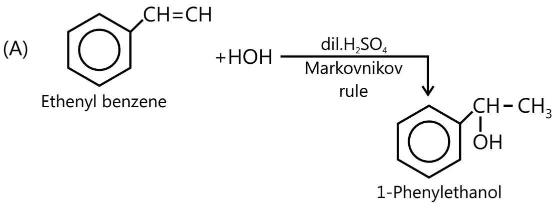


(B) is obtained by S_N2 by the attack of nucleophile $\left(\mathrm{Me}\underset{..}{\overset{..}{\mathrm{O}}}\mathrm{H}\right)$ at less substituted C, without changing the configuration or groups priorities and the product is S-stereoisomer.

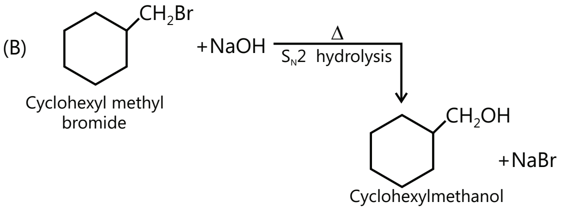
(C) is obtained by S_N1 ring opening to give stable 3° $C^{\oplus}$. The nucleophile $\left(\mathrm{Me\ddot{O}H}\right)$ attacks from the backside because front side attack is blocked by the ($-CH_2OH$) group.

Sol 11:

(A)



(B)

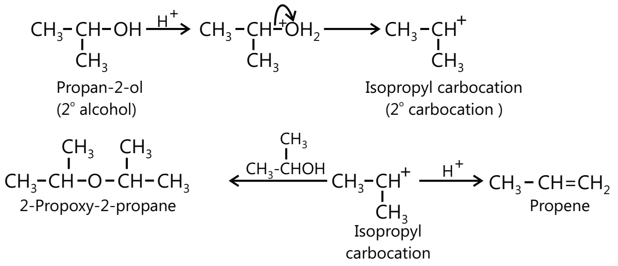


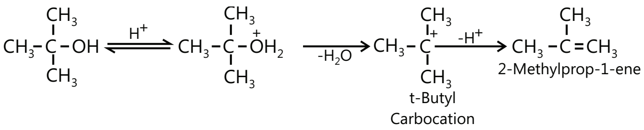
(C)

$$\underset{\text{1-Bromopentane}}{CH_3CH_2CH_2CH_2CH_2Br} + NaOH \xrightarrow[S_N2\ \text{hydrolysis}]{\Delta} \underset{\text{Pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH} + NaBr$$

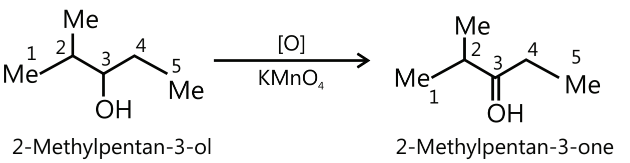
Sol 12: Acid –catalyzed dehydration of 1° alcohols to ethers takes place by S_N2 reaction Involving nucleophilic attack by the alcohol molecule on the protonated alcohol molecule as.

However, under these conditions, 2° alcohols give alkenes rather than ethers. This is because of the stearic hindrance, nucleophilic attack by the alcohol on the protonated alcohol molecule does not take place. Instead of this, the protonated 2° and 3° alcohols lose a molecule of water to form stable 2° and 3° carbocations. These carbocations then prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.

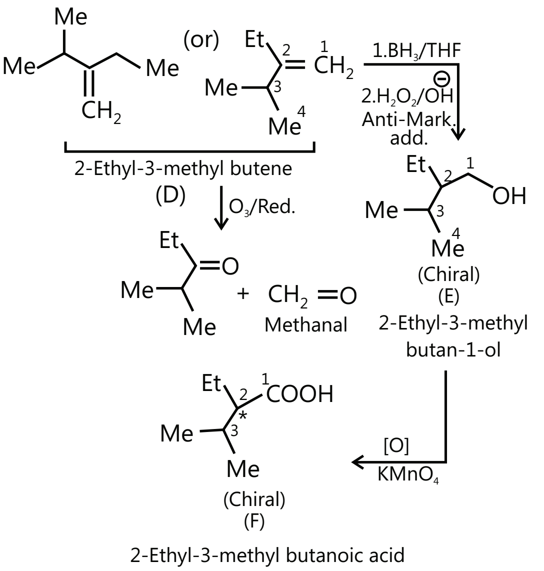




Sol 13: Proceed reserve from the oxidation of 2-methylpentan-3-ol.



The possible structure of (D) is:



Sol 14:

i. DU in $\left(A\right)=\dfrac{\left(2n_C+2\right)-n_H}{2}=\dfrac{\left(8\times2+2\right)-8}{2}=5°$

ii. Five DU and $\left(C:H\approx1:1\right)$ suggest benzene ring (4 DU) and 1 DU has to be accounted.

iii. It does not contain (-COOH) group, since it is not soluble in $NaHCO_3$.

iv. It is soluble in NaOH, which suggests phenolic (OH) group.

v. (A) contains three O atoms, which suggests an ester group (-COOR) and one phenolic (OH) group.

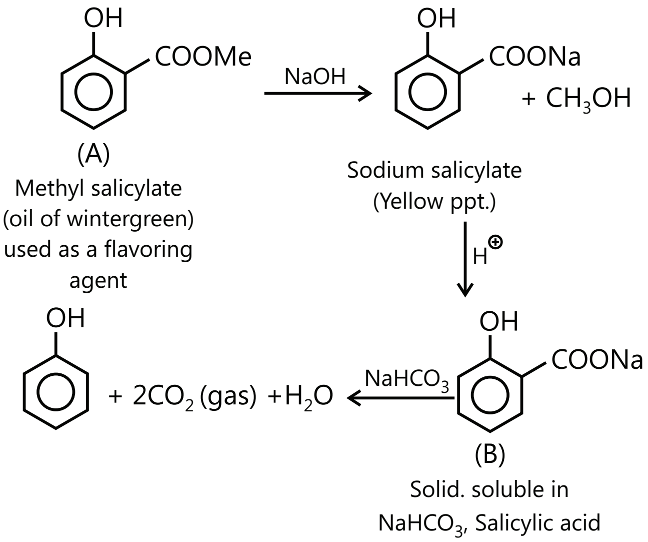
The presence of an ester group is also indicated by the reaction of (B) with $NaHCO_3$.

$$\underset{(-COOR)}{(A)} \xrightarrow[\text{Boiled}]{NaOH} \text{Residue} \xrightarrow[\text{distilled}\ \left(\text{suggests ortho compound}\right)]{\text{Steam}}$$

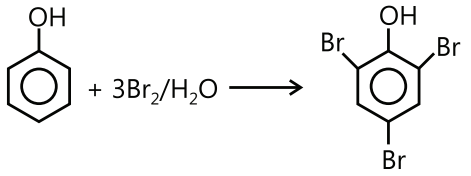
Distillate $\xrightarrow{NaOH}$ Yellow ppt. $\xrightarrow{H^{\oplus}}$

$(B)(-COOH\ group)\begin{pmatrix}\text{Dissolves}\\ \text{in } NaHCO_3\end{pmatrix}$

vi. Yellow precipitate with NaOH is a characteristic test for methyl salicylate.



Sol 15:



Mw = C_6H_6O Mw = $C_6H_3OBr_3$

= 94 gm   = 331 gm

(A)   (B)

331 gm of (B) is obtained from 94 gm of (A).

33.1 gm (B) is obtained from = $\frac{94}{331}\times 33.1$

= 9.4 gm of phenol

Weight of phenol = 9.4 gm

$$=\frac{9.4}{94}=0.1\text{ mol}$$

ii. NaOH will react with both CH_3COOH and phenol.

Total molar equivalent of NaOH = 100×2

= 200 mEq

$= \frac{200}{1000} = 0.2$ Eq. of NaOH

= 0.2 mol of NaOH

Acid + Phenol = 0.2 mol

Acid + 0.1 mol = 0.2 mol

$\therefore$ Acid = 0.2 – 0.1 = 0.1 mol

= 0.1 Eq.

1 Eq. of CH_3COOH= 60 gm

0.1 Eq. of CH_3COOH= 6 gm

Weight of acid = 6 gm

Weight of phenol = 9.4 gm

Mass percentage of acid = $\frac{6}{30}\times 100 = 20\ \%$

Mass percentage of phenol $=\frac{9.4}{30}\times 100 = 31.3\ \%$

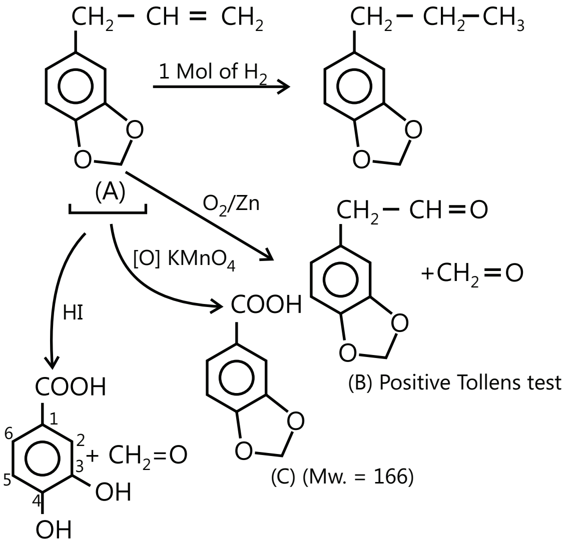
Sol 16: i. Six DU in (A) and $(C:H\approx 1:1)$ suggest benzene ring (4 DU).

ii. (A) does not contain phenolic group since it does not dissolve in NaOH and does not colour with $FeCl_3$.

iii. (A) reacts with 1 Eq. of H_2, which suggests one (C = C) bond. Ozonolysis also suggests one (C = C) bond. It also counts one more DU.

iv. Remaining two oxygen atoms must be present in fused ring (which is conformed by the formation of 3, 4-dihydroxybenzoic acid with HI) (Acetal ring).

Reactions:



Exercise 2

Single Correct Choice Type

Sol 1: (C) Four DU in A and (C: H $\approx$ 1: 1) suggest benzene ring with one extra C atom. Reactivity with NaOH and $FeCl_3$ suggest (A) to be a phenol. The formation of a tribromo product suggests that o-positions are vacant. Hence. (A) is m-cresol.

Sol 2: (D) The ether preparation follows the following steps-

1. Protonation
2. Nucleophilic substitution(S_N2)
3. Deprotonation by the base and release of HCl by shifting of bonds due to the presence of a good leaving group to give stability.

Sol 3: (D) All of the given statements regarding glycerol are correct.

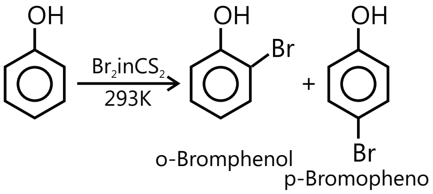
Sol.4: (B)

$$CH_3-CHBr-CH_3 \xrightarrow{\text{alc. KOH}} CH_3CH=CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}}$$

$$CH_3CH_2-CH_2Br \xrightarrow{CH_3ONa} \underset{\text{1–Methoxypropane}}{CH_3CH_2CH_2OCH_3}$$

Sol 5: (B) Ethers on exposure to sunlight slowly react with oxygen from air to form peroxide. These peroxide are unstable and decompose on distillation resulting violent reaction.

Sol 6: (B)



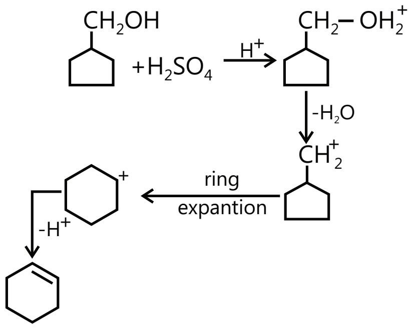
Sol 7: (D) Phenol is more acidic than cresol but less acidic than nitrophenol. P-nitrophenol is more acidic than m-nitrophenol. Thus, the correct order is p-nitrophenol > m-nitrophenol > phenol > cresol.

Sol 8: (B) The addition of a proton at β-carbon gives a carbocation (I) which is resonance stabilized because of electron donating effect of –OH group. The addition of Br^- ion to the carbocation gives the main product.

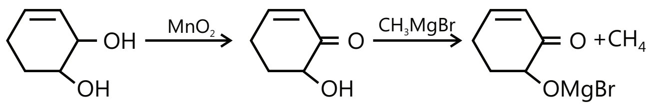
Sol 9: (C) Oxymercuration demercuration is anti Markovnikov addition of water molecule to alkenes.

Sol.10: (A) Ethers on hydrolysis gives alcohol.

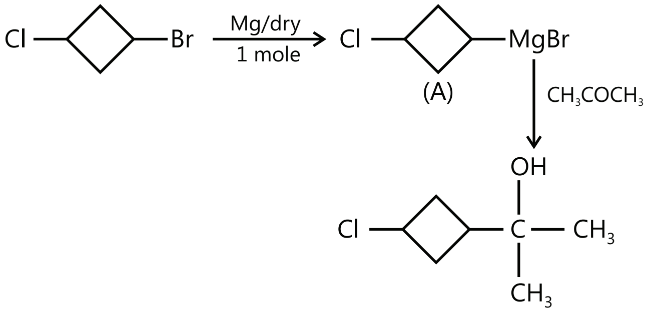
Sol 11: (C)



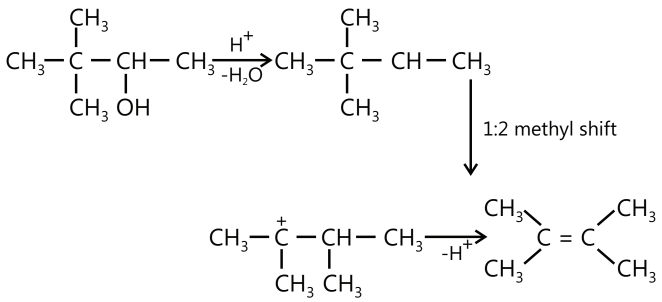
Sol 12: (B)



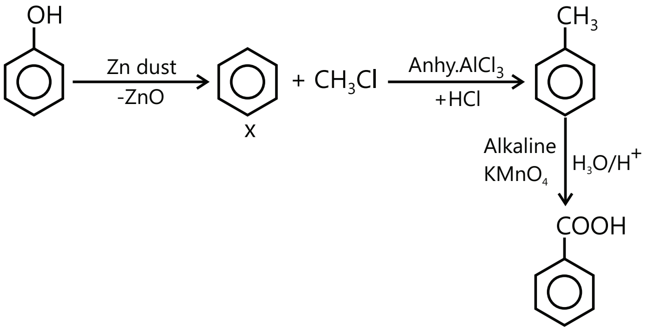
Sol 13: (A)



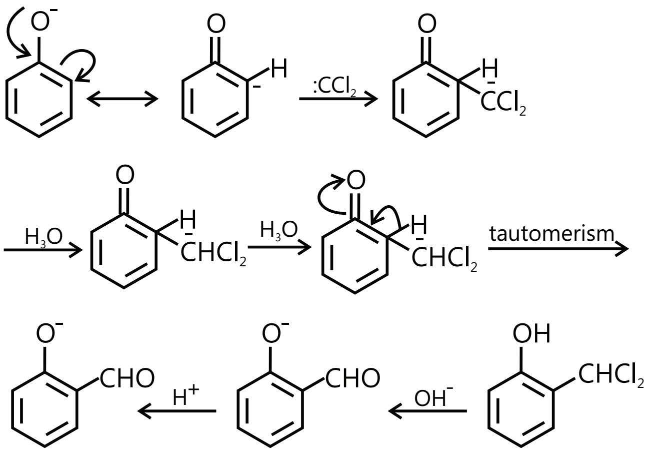
Sol 14: (A)



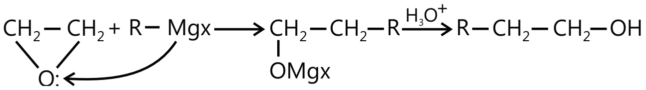
Sol 15: (D)



Sol 16: (D)



Sol 17: (A)

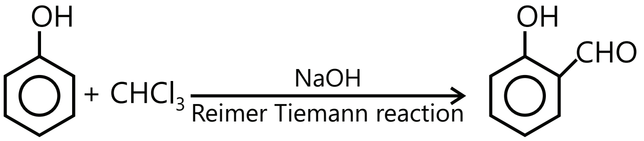


$CH_2-CH_2 + R-MgX \longrightarrow CH_2-CH_2-R \xrightarrow{H_3O^+} R-CH_2-CH_2-OH$

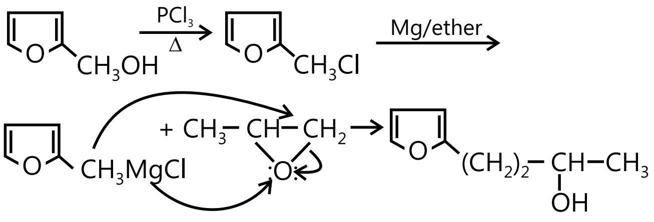
Sol 18: (D) Heating of alkyl halide with sodium or potassium alkoxide gives ether. This is a good method for preparation of simple as well as mixed either known as Williamson's synthesis.

RX + NaOR' → R-O-R' + NaX

Sol 19: (B)

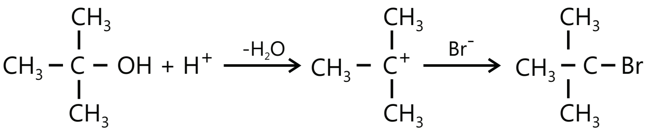


Sol 20: (C)



Previous Years' Questions

Sol 1: (A)

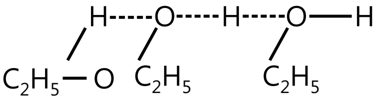


$CH_3-C(CH_3)_2-OH + H^+ \xrightarrow{-H_2O} CH_3-C^+(CH_3)_2 \xrightarrow{Br^-} CH_3-C(CH_3)_2-Br$

2-methylpropan-2-ol

3° carbocation

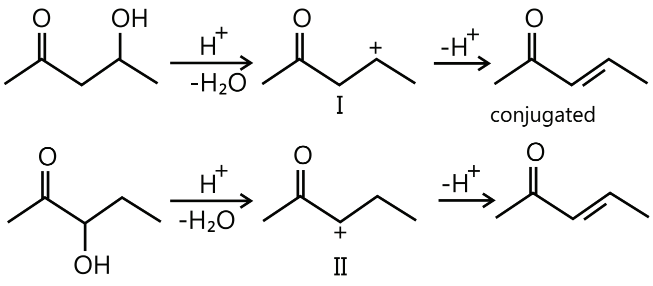
Sol 2: (A) Ethanol is capable in forming intermolecular H-bonds :



Sol 3: (D) $OH \rightarrow O^- + H^+$ (has maximum electronegativity difference)

Sol 4: (B) Thiol, RSH, on combustion produces $CO_2(g)$, $SO_2(g)$ and H_2O. At 298 K, H_2O will be liquid phase.

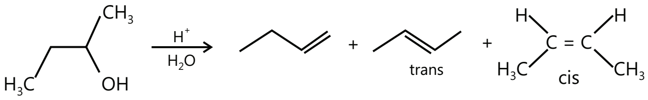
Sol 5: (A)



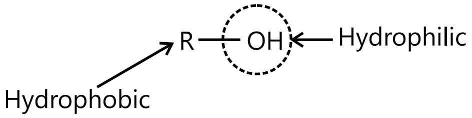
Although both reactions are giving the same product, carbocation I is more stable than II.

Sol 6: (A) A is an alcohol and its oxidation product gives Tollen's test i.e., B must be a aldehyde (CH_3CH_2CHO)

Sol 7: (D)



Sol 8: (C)



Increasing molecular weight increases hydrocarbon (R) proportion that lowers the solubility in water.

Sol 9: (F) 2° - alcohol on oxidation yields ketone while 1° alcohol on oxidation produces aldehyde which can further be oxidized to acid.

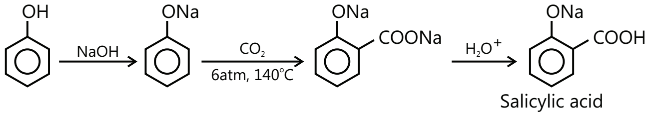
Sol 10: (F) Ethanol is weaker acid than water, not neutralized with NaOH.

Sol 11: (D) Esterification reaction is involved

$$CH_3COOH(\ell)+C_2H_5OH(\ell)\xrightarrow{H^+}CH_3COOC_2H_5(\ell)+H_2O(\ell)$$

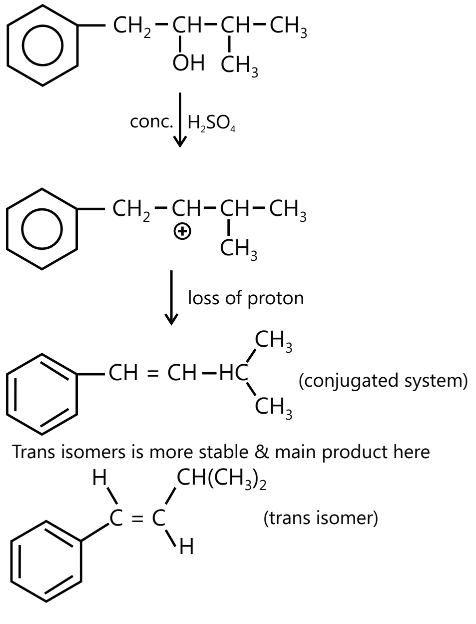
Sol 12: (D)

Kolbe – Schmidt reaction is



Salicylic acid

Sol 13 : (A)



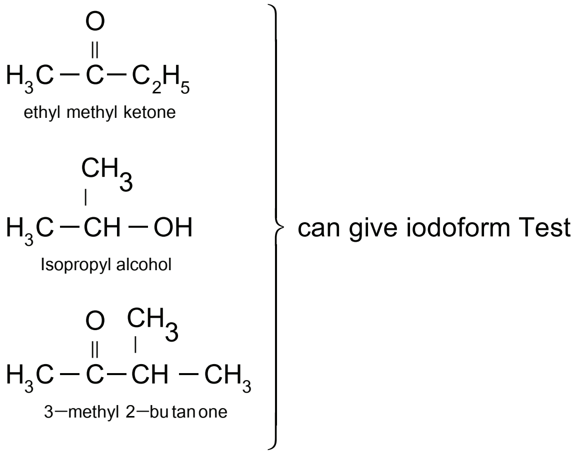
Sol 14: (B) Ortho–Nitrophenol is less soluble in water than p– and m– Nitrophenols because o–Nitrophenol shows Intramolecular H–bonding.

Sol 15: (D) Iodoform is given by

1) methyl ketones $R-CO-CH_3$

2) alcohols of the type $R-CH(OH)CH_3$

Where R can be hydrogen also



$H_3C-\overset{\overset{O}{||}}{C}-C_2H_5$

ethyl methyl ketone

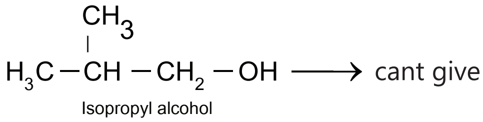
$H_3C-\overset{\overset{CH_3}{|}}{CH}-OH$

Isopropyl alcohol

$H_3C-\overset{\overset{O}{||}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

3—methyl 2—butanone

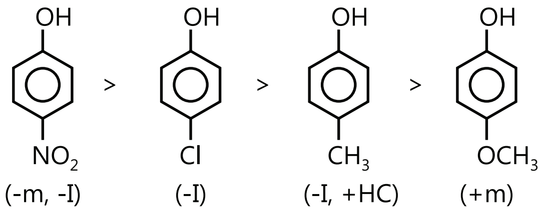
can give iodoform Test



$H_3C-\overset{\overset{CH_3}{|}}{CH}-CH_2-OH \longrightarrow$ cant give

Isopropyl alcohol

Sol 16 :(C)



Electron releasing group decreases and electron withdrawing group increases acidic strength.

Sol 17: (B) The reaction of alcohol with lucas reagent is mostly an S_N1 reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since 3° R – OH forms 3° carbocation hence it will react fastest.

JEE Advanced/Boards

Exercise 1

Sol 1: ROH reacts with cold conc. H_2SO_4 as follows:

1. $ROH + H_2SO_4 \longrightarrow R\overset{\oplus}{O}H_2 + HSO_4^{\ominus}$

$\longrightarrow ROSO_2\,OH + \cancel{H_2O}$

2. $H_2SO_4 + \cancel{H_2O} \longrightarrow H_3O^{\oplus} + HSO_4^{\ominus}$

$ROH + 2H_2SO_4 \longrightarrow ROSO_2OH + H_3O + HSO_4^{\ominus}$

Number of moles of particles formed per mole of solute (i) (van't Hoff factor) = 3 (The reaction does not produce $R^{\oplus}$, because $R^{\oplus}$ ion or even $R_3C^{\oplus}$ ion is not stable enough to persist)

$\therefore \Delta T_f = iK_f \times M$

$= 3x \times 0.1 = 0.3\text{ x K}$

Sol 2: Let the formula of alcohol is R(OH)n, and the formula of its acetyl derivative is $R(OCOCH_3)n$.

Molecular mass of $R(OCOCH_3)$ = (M + 42n)

M is the molecular mass of alcohol.

Molecular mass of $(CH_3 - CO\ -)$ group = 43

One H atom is replaced by (OH) group of CH_3COOH group

Therefore, molecular mass of $R(OCOCH_3)$

= [M + (43 - 1)n]

= (M + 42n)

$$R(OCOCH_3)_n \xrightarrow{nKOH} R(OH)_n + nCH_3COOH$$

Molecular mass of nKOH = 56n

0.218 gm of acetyl derivative requires 0.168 gm of KOH for hydrolysis.

$\therefore$ (M + 42n) gm of aceytyl derivative requires

$$= \frac{0.168(M+42n)}{0.218} = 56n$$

On solving, we get n = 3

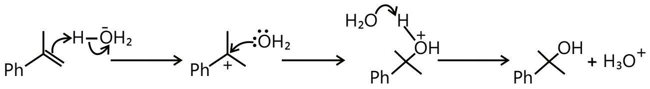
[Use the formula: $\frac{w(M+42n)}{W} = 56n$

w = Weight of KOH, W = weight of acetyl derivative,

M = Molecular mass of alcohol; n = Number of

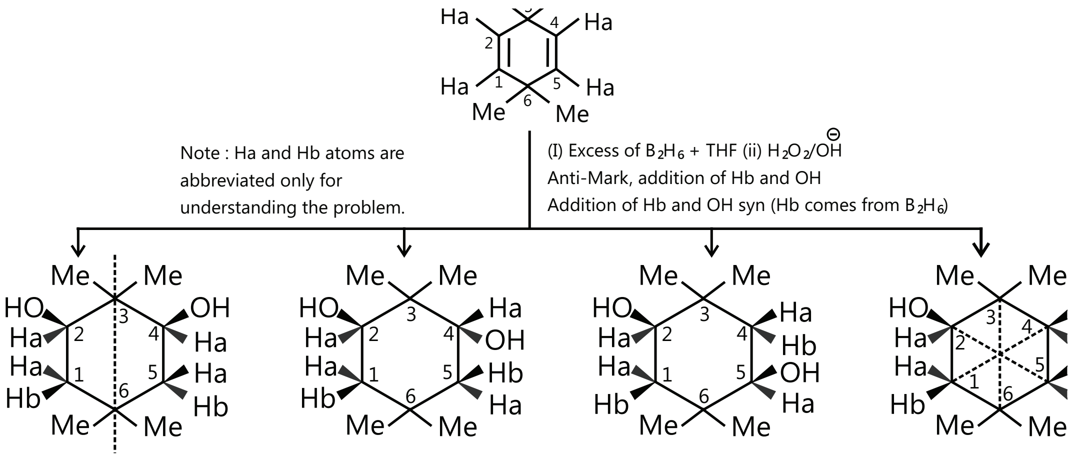
(-OH) groups]

Sol 3:



(b) Initial reaction of the alkene with H_3O^+ can form two carbocations. The more stable benzylic tertiary carbocation (shown in the above mechanism) is formed in preference to the less stable primary carbocation. This is the rate determining step, and thus controls the product distribution. Formation of the more stable carbocation is the mechanistic basis for Markovnikov's rule.

Sol 4:



(C₁) (OH at 2 and 4)

[Both -OH in cis but both -OH and Hb are in anti position]

(Optically inactive plane of sysmm.)

(C₂) (OH at 2 and 4)

[Both -OH in trans and both -OH and Hb are in anti position]

(Optically active)

(C₃) (OH at 2 and 5)

[Both -OH in cis bt both -OH and Hb are in anti position]

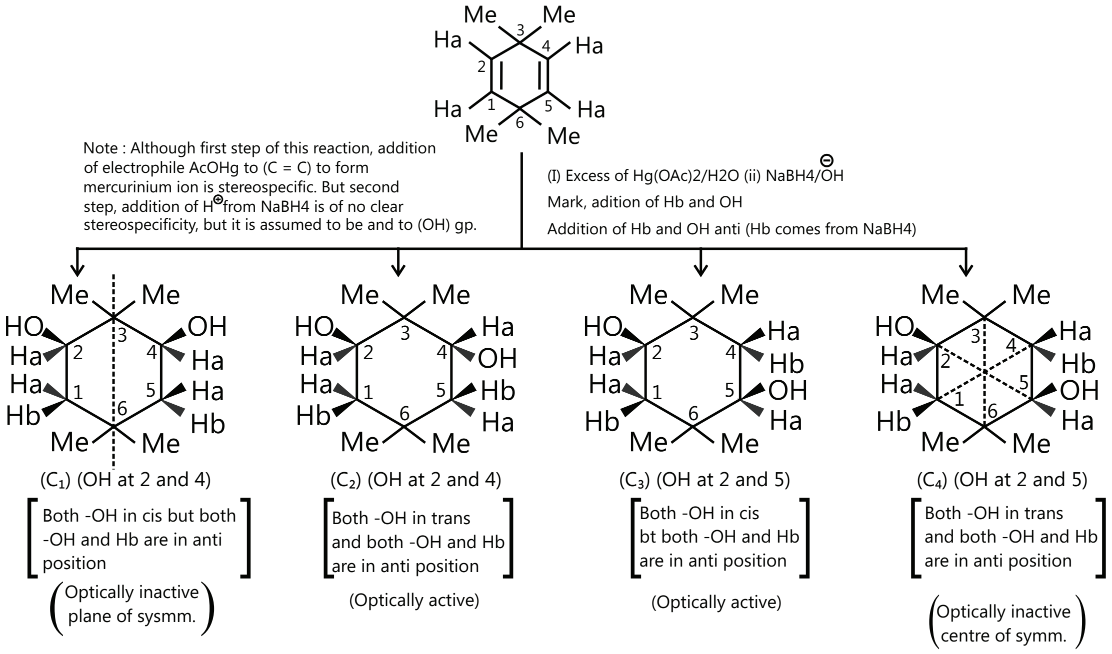
(Optically active)

(C₄) (OH at 2 ar

Both -OH in trar and both -OH a are in anti positi

(Optically inacti centre of symı

Thus, the number of isomers excluding enantiomers is 4.



Note : Although first step of this reaction, addition of electrophile AcOHg to (C = C) to form mercurinium ion is stereospecific. But second step, addition of $H^{\oplus}$ from NaBH4 is of no clear stereospecificity, but it is assumed to be and to (OH) gp.

(I) Excess of Hg(OAc)2/H2O (ii) NaBH4/$\overset{\ominus}{OH}$

Mark, adition of Hb and OH

Addition of Hb and OH anti (Hb comes from NaBH4)

(C_1) (OH at 2 and 4)

[Both -OH in cis but both -OH and Hb are in anti position]

(Optically inactive plane of sysmm.)

(C_2) (OH at 2 and 4)

[Both -OH in trans and both -OH and Hb are in anti position]

(Optically active)

(C_3) (OH at 2 and 5)

[Both -OH in cis bt both -OH and Hb are in anti position]

(Optically active)

(C_4) (OH at 2 and 5)

[Both -OH in trans and both -OH and Hb are in anti position]

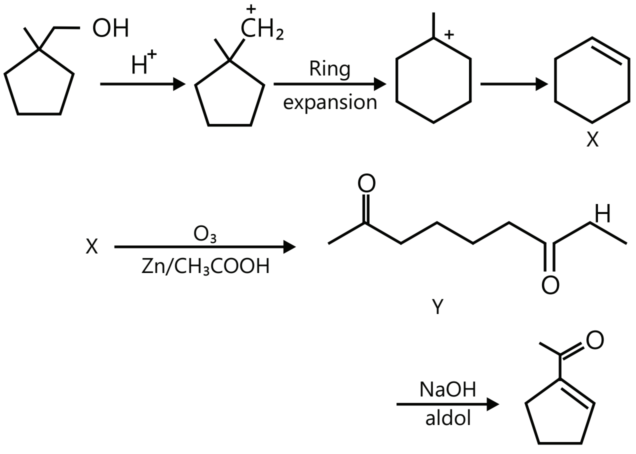
(Optically inactive centre of symm.)

Thus, the number of isomers excluding enantiomers is 4.

Note: The products B_1 and C_1, B_2 and C_2, B_3 and C_3, B_4 and C_4 are same.

If the reaction (a) is carried out with excess of B_2D_6 + THF + $H_2O_2/\overset{\ominus}{OH}$ and (b) is carried out with excess of $Hg(OAc)_2$ + H_2O + $NaBD_4$, then in place of H_b, D will come in all product, and the product, and the products B_1 and C_1, B_2 and C_2, B_3 and C_3, and B_4 and C_4 would be different.

Sol 5:



Sol 6: Compound 'X' $\xrightarrow{\text{Lucas reagent}}$ No reaction at room temperature.

$$C_5H_8O \xrightarrow[\text{AgNO}_3]{\text{Ammoniacal}} \text{ppt}$$

$$X \xrightarrow[\text{CH}_3\text{MgBr}]{\text{Excess of}} CH_4\ ;\ X \xrightarrow[\text{HI excess}]{H_2/Pt} n-\text{pentane}$$

Above information suggest that X has a terminal triple bond and it contain primary –OH group.

$$\Rightarrow\ H-C\equiv C-CH_2-CH_2-CH_2OH \xrightarrow{Ag(NH_3)_2^+} Ag-C\equiv C-CH_2CH_2CH_2OH$$

Sol 7:

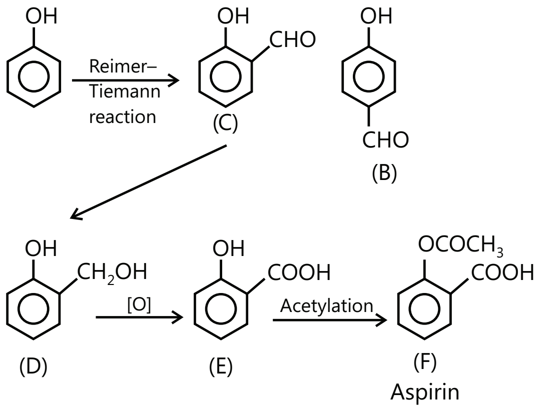
(A) ⟶ Positive Liebermann's test (test for phenol)

$\xrightarrow{CHCl_3+KOH}$ B + C (Stem volatile⇒ortho)

↓

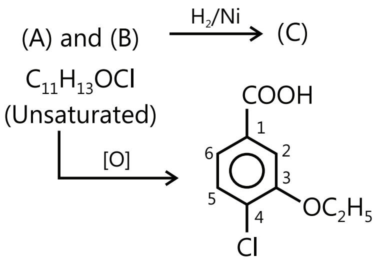
Positive Schiff's test (test for (-CHO)group)

$$(C) \xrightarrow{LialH_4} (D)(C_7H_8O_2) \xrightarrow{[O]} (E) \xrightarrow{\text{Acetylation}} \text{Aspirin (pain killer)}$$

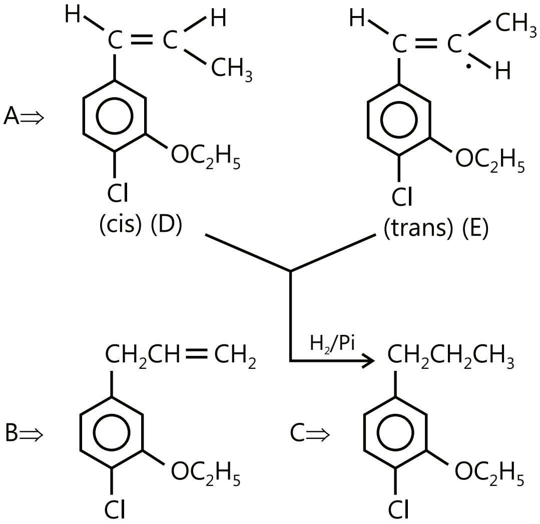


Aspirin

Sol 8:



(Nice C atom)
(So two C atoms in the side chain with double bond)



Sol 9: The rations of atoms in the minor products are:

$$C:H:N:O \;::\; \frac{42.86}{12}:\frac{2.40}{1}:\frac{16.67}{14}:\frac{38.07}{16}$$
$$::\; 3.57 : 2.40 : 1.19 : 2.38$$
$$::\; 3 : 2 : 1 : 2$$

Empirical formula of the minor product: $C_3H_2NO_2$

Molar empirical formula mass of the minor product is

$\left(3\times12+2\times1+1\times14+2\times16\right)$ gm mol^{-1} = 84 gm mol^{-1}

Let M be the molar mass of the minor product. For 5.5 gm of the minor product dissolved in 45 gm benzene, the molality of solution is given by

$$m=\frac{55\ \text{gm}/M}{0.045\ \text{kg}}$$

Substituting this in the expression of elevation of boiling point, we get

$$\Delta T_a = K_b m$$

$$1.84\ K=\left(2.53\ K\ \text{kg}\ \text{mol}^{-1}\right)\left(\frac{55\ \text{gm}/M}{0.045\ \text{kg}}\right)$$

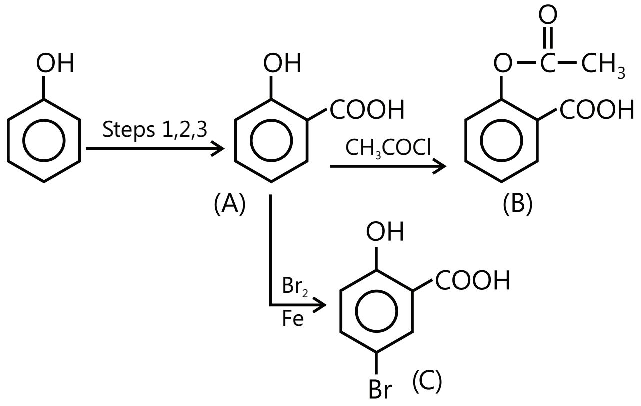
$$M=\left(\frac{2.53\times55}{1.84\times0.045}\right)\text{gm mol}^{-1} = 168\ \text{gm mol}^{-1}$$

Number of unit of empirical formula in the molecular formula

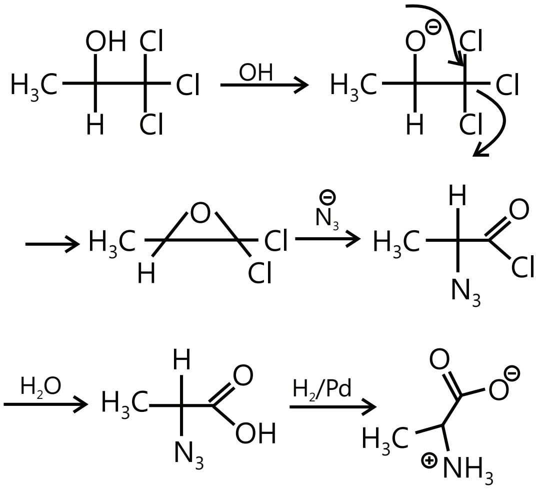
$$=\frac{168\ \text{gm mol}^{-1}}{84\ \text{gm mol}^{-1}}=2$$

Hence, the molecular formula of the minor product is $2\left(C_3H_2NO_2\right)$, i.e., $C_6H_4\left(NO_2\right)_2$. The product is m-dinitrobenzene.

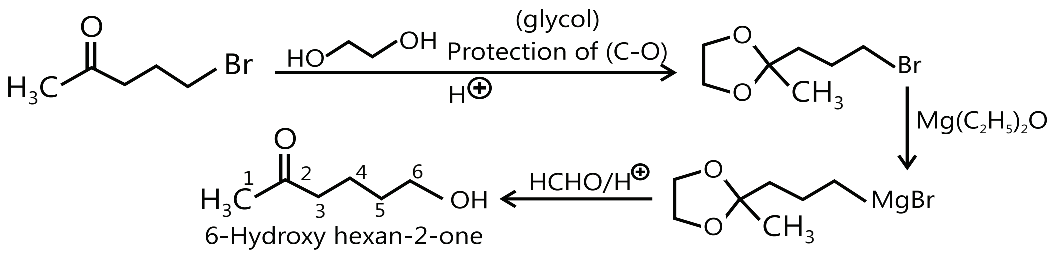
Sol 10:



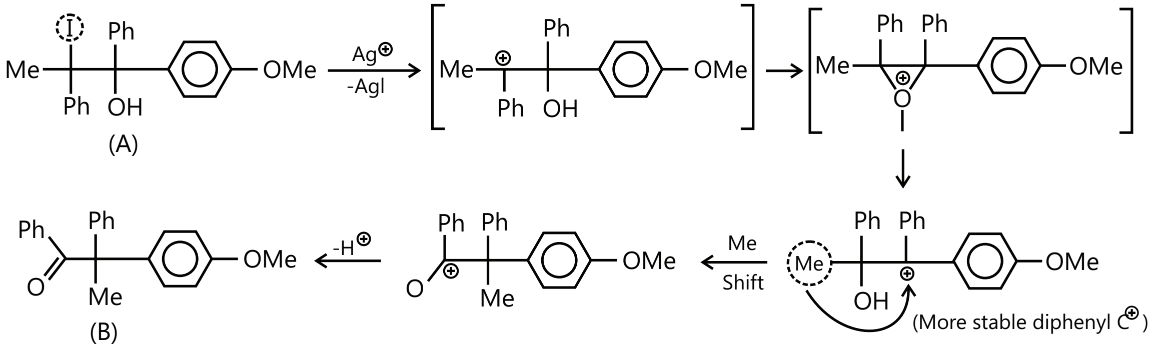
Sol 11:



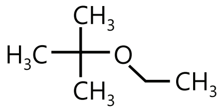
Sol 12:



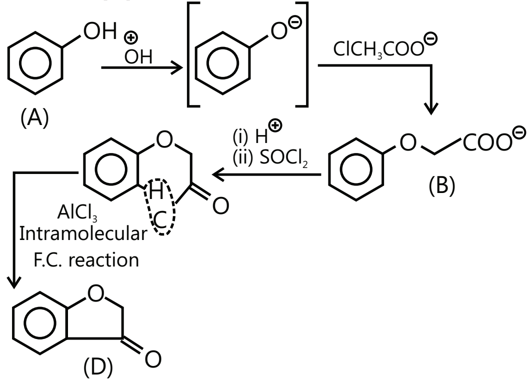
Sol 13: It is an intramolecular S_N2 -type reaction that proceeds through an intermediate epoxide.

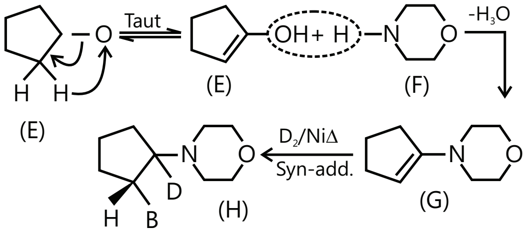


Sol 14: t-Butylalcohol on heating in the presence conc. H_2SO_4 forms a stable 3° carbocation which then reacts with C_2H_5OH (nucleophile) to give the product.

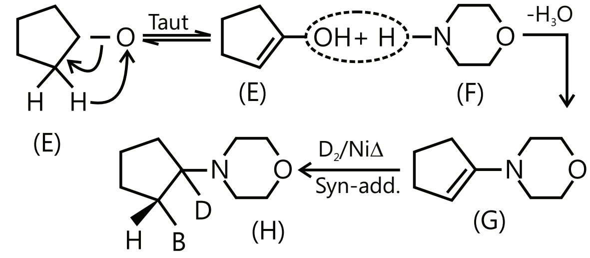


Sol 15: (A)

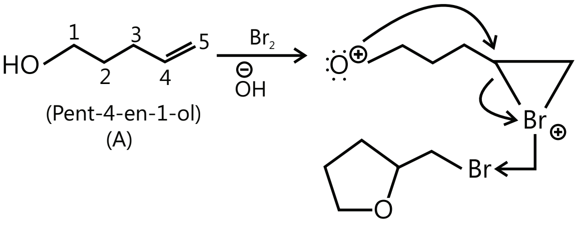




(b)



Sol 16:



Exercise 2

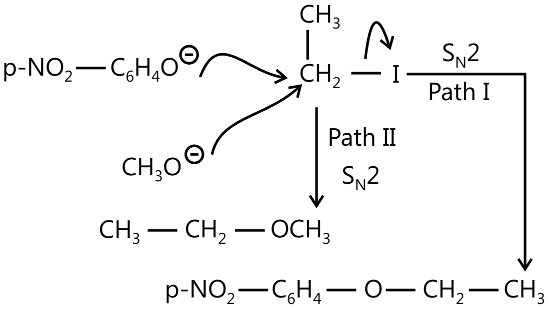
Single Correct Choice Type

Sol 1: (D) All of the above given statements are correct.

Sol 2: (B) vicinal diol sites are only two, thus only 2 equivalents of HIO_4 will be consumed

Sol 3: (D) Refer mechanism of esterification in the theory.

Sol 4: (A) iv. $C_2H_5O^-$ acts as a base. It abstracts $H^{\oplus}$ from phenol to form PhO^- ion. $C_2H_5O^-$ is a stronger nucleophile than PhO^-. Hence the product is obtained by path II.



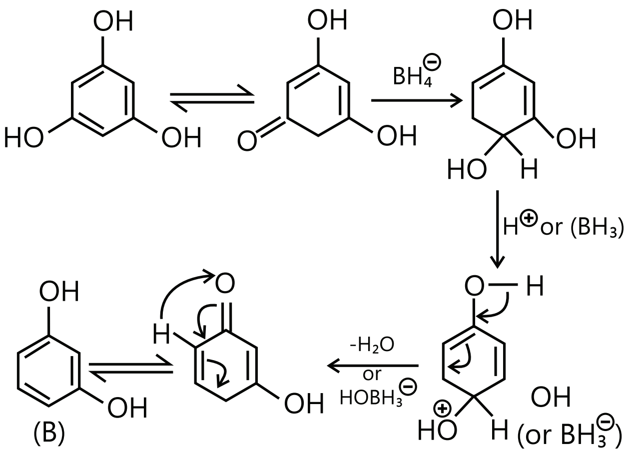
(Acidic character: $PhOH > C_2H_5OH$)

(Basic and nucleophilic character: $PhO^- < C_2H_5O^-$)

Sol 5: (A) 1. Presence of electron-donating or electron-withdrawing group on the respective rings.

2. S_N2 reaction mechanism is followed in which protonation is followed by attack of halo group.

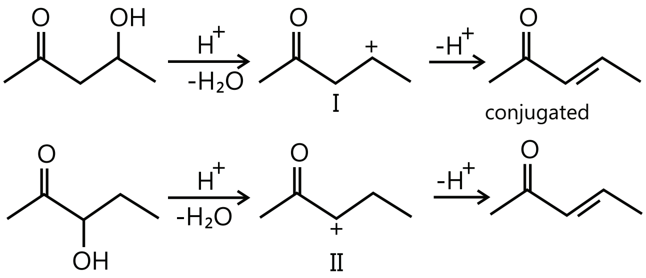
Sol 6: (C)



Sol 7: (C) $CH_3-CH_2-O-CH_2-CH_3+HI \rightarrow 2C_2H_5I$

Sol 8: (A) $CO+H_2 \xrightarrow[\text{heat}]{ZnO-Cr_2O_3} CH_3OH$

Sol 9: (A) Although both reactions are giving the same product, carbocation I is more stable than II.



Sol 10: (B) BF_3, being a good lewis acid accepts a pair of electrons to give us a good conjugate acid, and not a nucleophile.

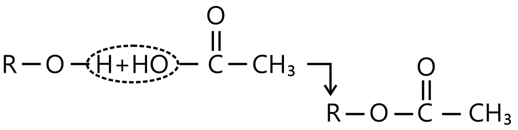
Sol 11: (B) Method (c) would give rearranged product also. It would give a mixture of 2-bromo and 3-bromo pentane. In methods (a) and (b), no rearrangement occurs and it gives (B) exclusively. The tosyl group a good leaving group, is then easily displaced by reaction with Br^- in an S_N2 reaction.

Sol 12: (C) c. 2.68 gm of (A) gives 14.08 gm of AgI

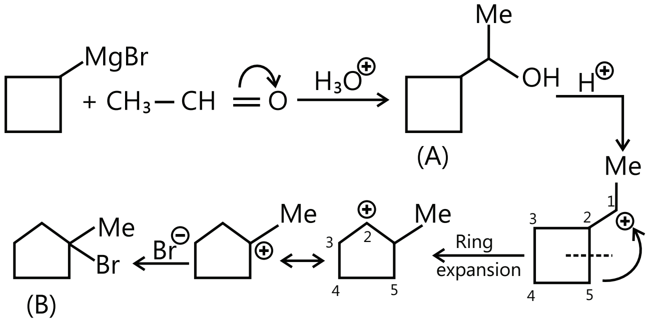
134 gm of (A) gives $\frac{14.08 \times 134}{2.68} = 704$ gm of AgI

$= \frac{704}{235}$ mol of AgI

= 3 (OMe) groups



Sol 13: (B)



Comprehension Type:

Sol 14 to 16: (C, C, B) Refer Reimer-Tiemann reaction from the theory part.

Assertion Reasoning Type

Sol 17: (D) Phenols can be chlorinated.Moreover, presence of –OH on the benzene ring, is an electron-donating group which makes the attachment of the Cl electrophile on the o- and p-position possible.

Sol 18: (A) self-explanatory. Remember, -NO_2 is an electron-withdrawing and –CH_3 is an electron-donating group.

Sol 19: (D) Electron-withdrawing nature of –NO_2 and electron-donating nature of –O-Ar makes the reaction possible.

Match the Columns

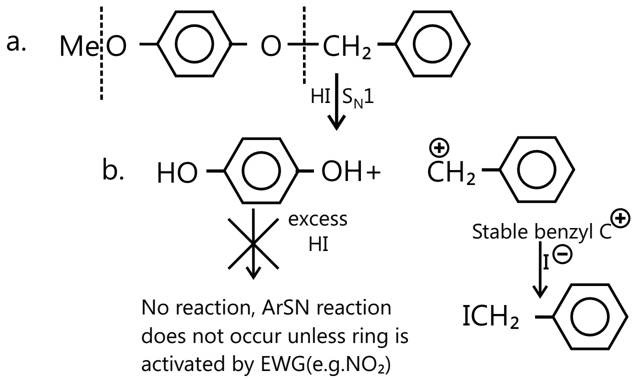
Sol 20: A → q, r; B → p, s; C → u; D → p, t; E → p, r, s; F → p, s

A. Reimer-Tiemann reaction proceeds by (CBrCl) (bromochlorocarbene), which acts as an electrophile. So, it is an SE reaction.

B. The reaction proceeds by the formation of carbocation with rearrangement.

C. No reaction proceeds by the formation of carbocation with rearrangement.

D.



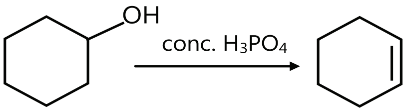
E. It is Friedel-Crafts alkylation which proceeds by the formation of a carbocation followed by rearrangement. So, it is an SE reaction.

F. It is hydration of alkene and proceeds by the formation of a carbocation with rearrangement.

Previous Years' Questions

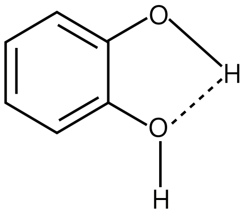
Sol 1: (B) $C_6H_5MeBr + (CH_3)_3\,COH \rightarrow C_6H_6 +$ $Mg[(CH_3)_3CO]Br$

Sol 2: (B)



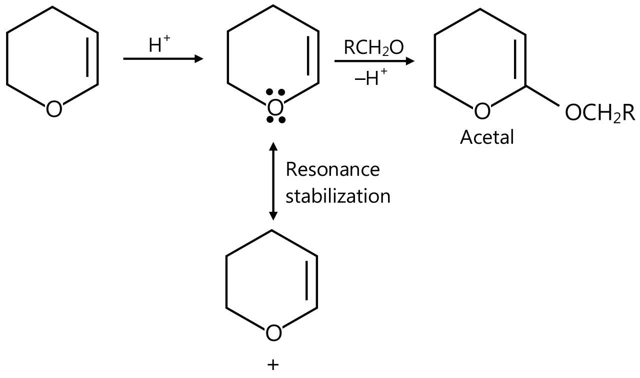
Concentrated H_3PO_4 solution does not involve any substitution product while with others, substitution products are also formed.

Sol 3: (C) All dihydroxy benzene will have higher boiling points, then monohydroxy benzene. Also among dihydroxy benzenes, 1,2-di-hydroxy benzene has lowest boiling point due to intra-molecular H-bonding.



Intramolecular H-bonding
in 1,2-dihydroxy benzene

Sol 4:

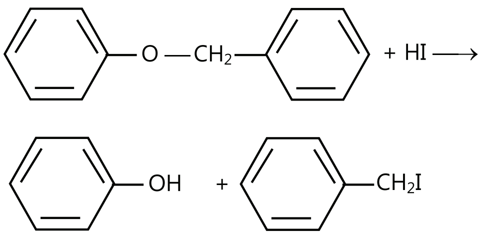


Sol 5: (C, E)

$$CH_3CH_2Br + O=\ddot{N}-O^- \longrightarrow \underset{\text{nitroethane}}{CH_3CH_2NO_2} + \underset{\text{ethyl nitrite}}{CH_3CH_2ONO}$$

ambident nucleophile

Sol 6: (A, D)

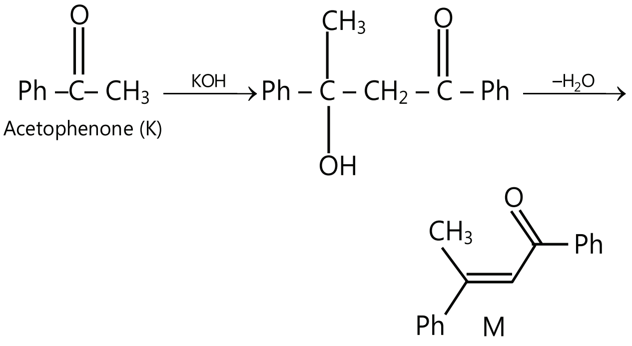


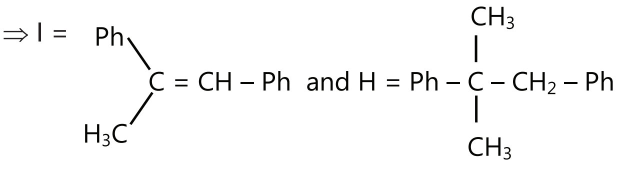
Phenol does not react further with HI.

Paragraph 1: Compound J must be benzaldehyde because it one treatment with KOH undergoing Cannizaro's reaction producing benzyl alcohol and potassium-benzoate (L).

$$\underset{J}{C_6H_5-CHO} \xrightarrow{KOH} \underset{\text{benzyl alcohol}}{C_6H_5-CH_2OH} + C_6H_5COOK(L)$$

Also M is aldol condensation product formed from acetophenone

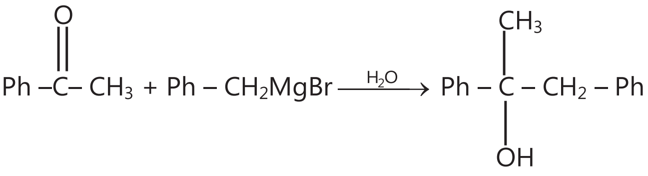




$$\Rightarrow I = (Ph)(H_3C)C = CH - Ph \text{ and } H = Ph - C(CH_3)_2 - CH_2 - Ph$$

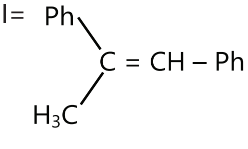
3° alcohol

Sol 7: (B)



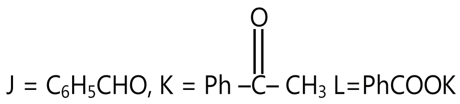
$$Ph-\overset{O}{\overset{\|}{C}}-CH_3 + Ph-CH_2MgBr \xrightarrow{H_2O} Ph-\underset{OH}{\overset{CH_3}{C}}-CH_2-Ph$$

Sol 8: (A)



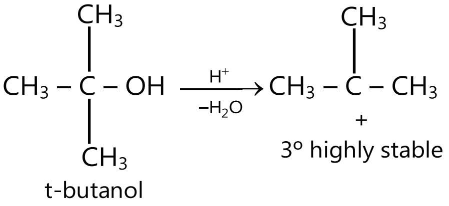
$$I = (Ph)(H_3C)C = CH - Ph$$

Sol 9: (D)



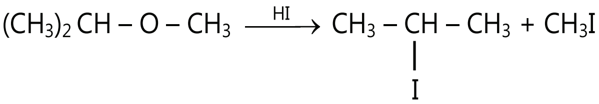
$$J = C_6H_5CHO,\ K = Ph-\overset{O}{\overset{\|}{C}}-CH_3\ L=PhCOOK$$

Sol 10: Acid catalysed dehydration proceeds via carbocation intermediate. Also, greater the stability of reactive intermediate, faster the reaction :



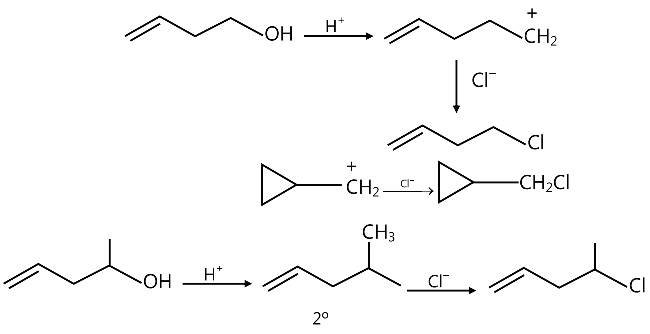
n-butanol forms less stable (1°) carbocation.

Sol 11:

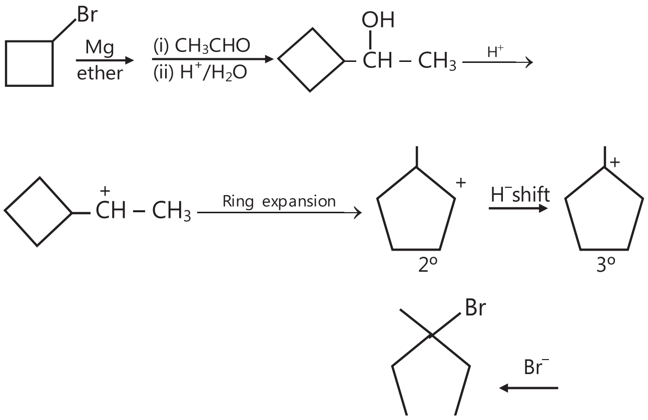


$$(CH_3)_2CH-O-CH_3 \xrightarrow{HI} CH_3-\underset{I}{CH}-CH_3 + CH_3I$$

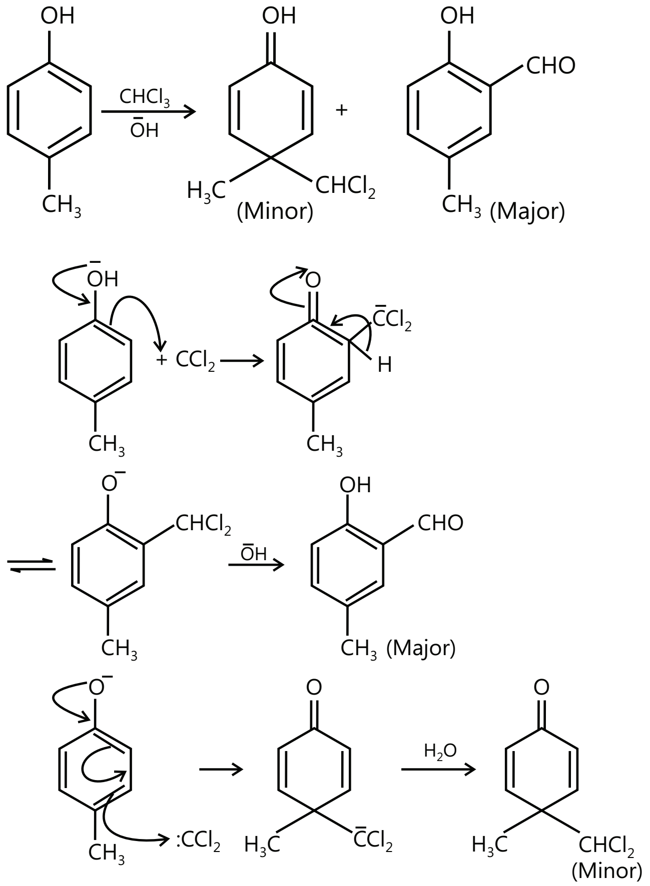
Sol 12:



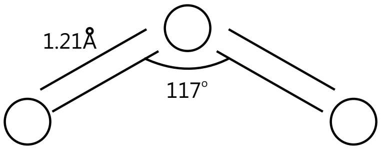
Sol 13:



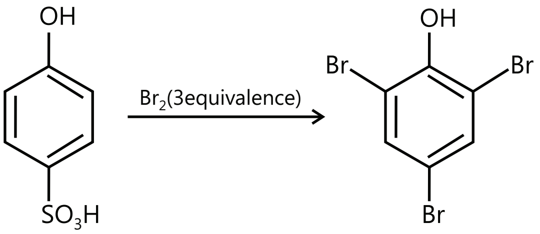
Sol:14 (B, D)



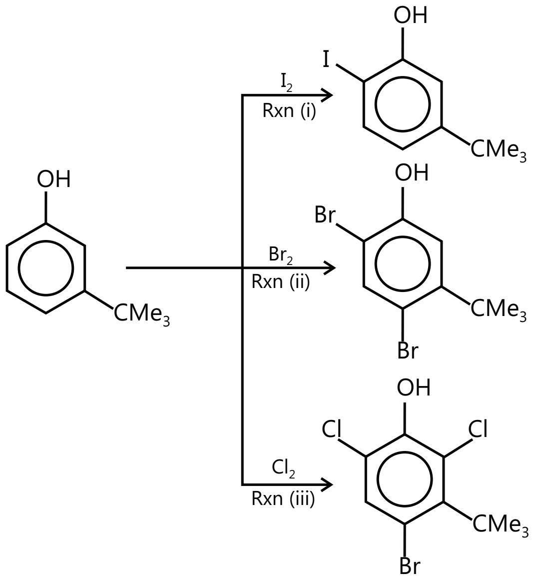
Sol 15: (A, C, D)



Sol16: (B)

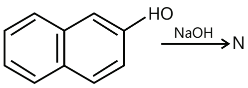


Sol 17: (A, B, C)

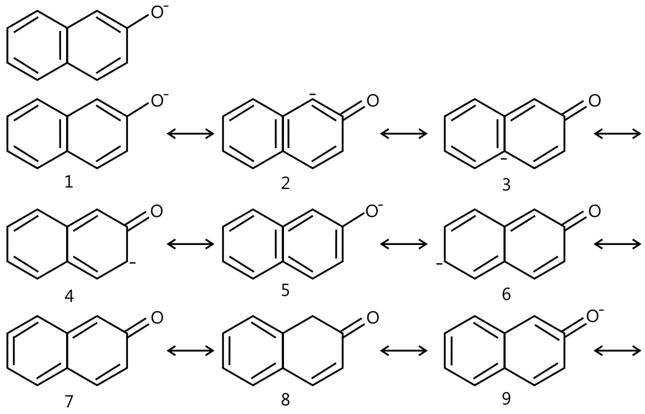


Sol 18: (C) When two phenyl groups are replaced by two para methoxy group, carbocation formed will be more stable.

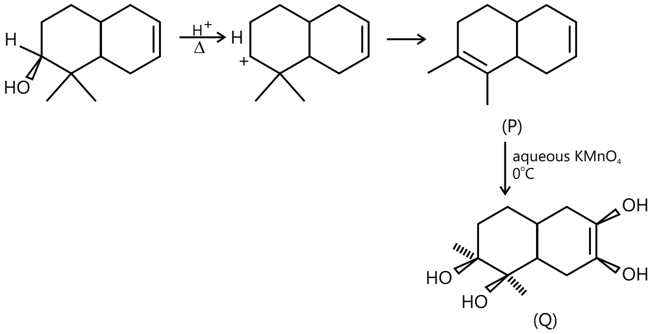
Sol 19: (9)



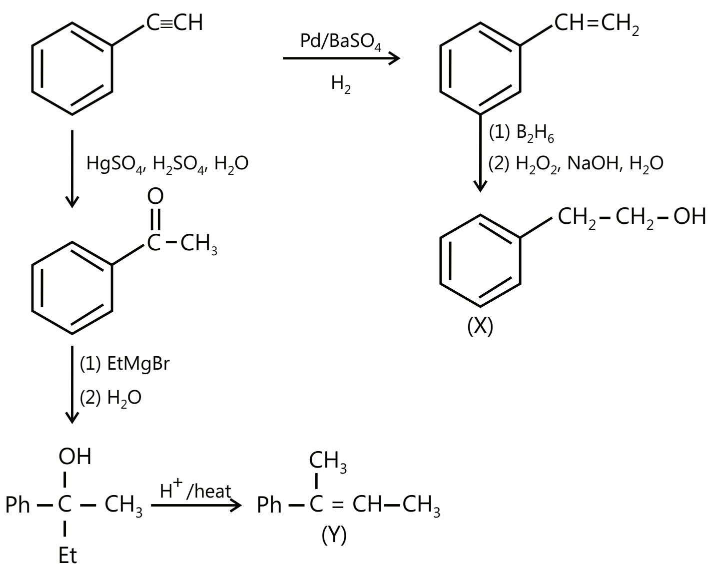
N is



Sol 20: (D)



Sol 21 (C) and 22 (D):



Sol 23: (B,C)