Chapter 25

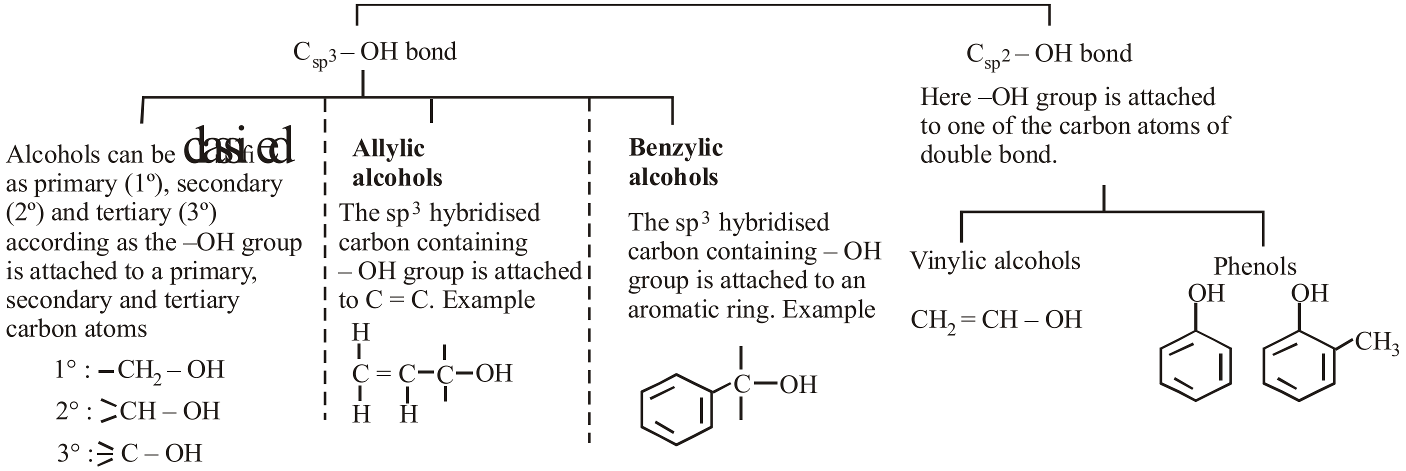
Alcohols, Phenols And Ethers

A. ALCOHOLS AND PHENOLS

CLASSIFICATION

Alcohols and phenols are classified as mono–, di–, tri– or polyhydric depending upon whether they contain one, two, three or many hydroxyl groups in their structures.

Monohydric alcohols are further classified according to hybridisation of C-atom to which –OH is attached.



C_{sp^3} – OH bond

Alcohols can be classified as primary (1º), secondary (2º) and tertiary (3º) according as the –OH group is attached to a primary, secondary and tertiary carbon atoms

1° : –CH$_2$ – OH

2° : >CH – OH

3° : ⋗C – OH

Allylic alcohols

The sp^3 hybridised carbon containing – OH group is attached to C = C. Example

Benzylic alcohols

The sp^3 hybridised carbon containing – OH group is attached to an aromatic ring. Example

C_{sp^2} – OH bond

Here –OH group is attached to one of the carbon atoms of double bond.

Vinylic alcohols

CH$_2$ = CH – OH

Phenols

Ethers are classified as

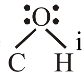
(i) simple or symmetrical, if alkyl or aryl groups attached to O-atom are same. Example: CH_3OCH_3.

(ii) mixed or unsymmetrical if the two groups attached to O–atom are different. Example : $CH_3OC_2H_5$.

Ethers can be further classified into aliphatic and aromatic ethers. Aromatic ethers can be further classified into phenolic or alkylarylethers (contain alkyl and aryl group) and aryl ethers (contain aryl group only).

STRUCTURES OF FUNCTIONAL GROUPS

In alcohols, O of –OH bond is attached to *sp*^{3} hybridised carbon.

The bond angle  is less than tetrahedral angle (109°28’) due to repulsion between unshared pair of e^{-1}s on O.

In phenols, –OH group is attached to sp^2 hybridised C of aromatic ring. The C–O bond length in phenols is less than methanol.

This is because of

(i) partial double bond character of C–O bond

(ii) sp^2 – hybridised state of C to which O is attached.

In alcohols and phenols due to high electronegativity O–atom aquires partial negative charge and results in formation of dipole.

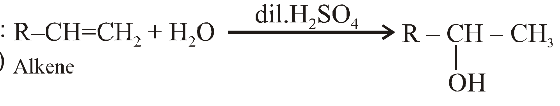
$$\overset{\delta+}{R}—\overset{\delta-}{O}—\overset{\delta+}{H}$$

Dipole moment of alcohols are higher than phenols. It is because C–O bond in phenol is less polar due to electron-withdrawing effect of the benzene ring whereas in alcohols C–O bond is more polar due to electron donating effect of – R group.

In ethers, 2 bond pairs and 2 lone pairs on O are arranged approximately tetrahedrally. The bond angle is slightly greater than tetrahedral angle due to repulsive interaction between bulky –R groups.The C–O bond length is almost same as that in alcohols.

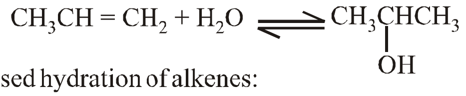
(i) From Alkenes:

(a) Acid catalysed hydration:
(Markovnikov's addition)



$$\underset{\text{Alkene}}{R\text{–}CH\text{=}CH_2} + H_2O \xrightarrow{\text{dil.}H_2SO_4} R - \underset{\underset{OH}{|}}{C}H - CH_3$$

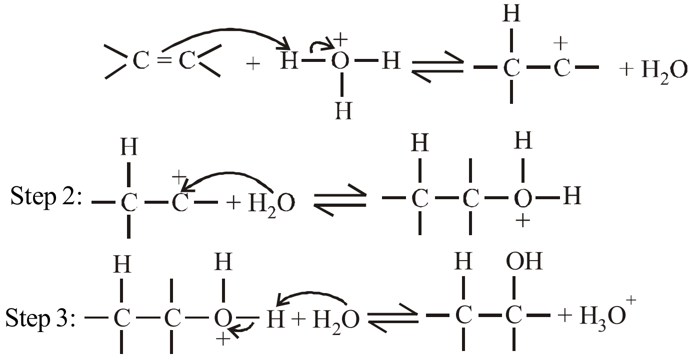
2° Alchol



$$CH_3CH = CH_2 + H_2O \rightleftharpoons CH_3\underset{\underset{OH}{|}}{C}HCH_3$$

Mechanism of acid catalysed hydration of alkenes:

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

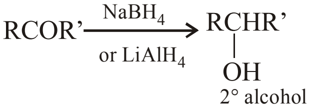


(b) Hydroboration - oxidation: $3R - CH\text{=}CH_2 + B_2H_6 \xrightarrow{\text{THF}} 3RCH_2CH_2OH + H_3BO_3$
(Anti-Markovnikov's addition)

$$3CH_3CH = CH_2 + B_2H_6 \longrightarrow (CH_3CH_2CH_2)_3B \xrightarrow[H_2O_2,\ OH^-]{H_2O} 3CH_3CH_2CH_2OH$$

(ii) Carbonyl Compounds

(a) Reduction of aldehydes: $RCHO \xrightarrow[\text{or } LiAlH_4 \text{ or } NaBH_4]{H_2/Pd} \underset{1° \text{ alcohol}}{RCH_2OH}$
and ketones



$$RCOR' \xrightarrow[\text{or } LiAlH_4]{NaBH_4} R\underset{\underset{OH}{|}}{C}HR'$$

2° alcohol

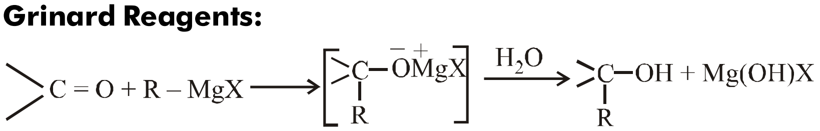
Note: 3°alcohol cannot be obtained by this method.

(b) Reduction of acids and : $RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$
esters

$$RCOOR' \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH + R'OH$$

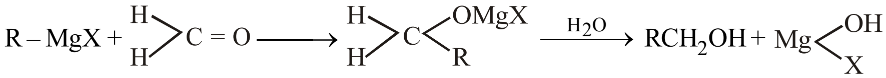
Commercially, acids are reduced to alcohols by first converting them into esters.

(iii) Grinard Reagents:



$$>C = O + R - MgX \longrightarrow \left[>\underset{\underset{R}{|}}{C}-\overset{-}{O}\overset{+}{Mg}X \right] \xrightarrow{H_2O} >\underset{\underset{R}{|}}{C}-OH + Mg(OH)X$$

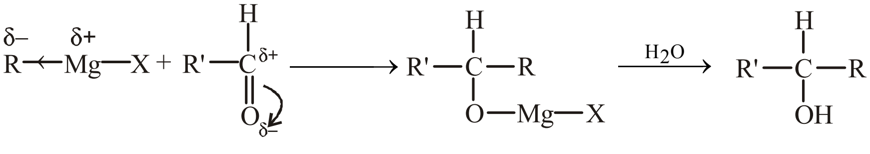
When formaldehyde is used primary alchols are formed.



$$R - MgX + \frac{H}{H}\!>C = O \longrightarrow \frac{H}{H}\!>C<\!\frac{OMgX}{R} \xrightarrow{H_2O} RCH_2OH + Mg<\!\frac{OH}{X}$$

Alcohol

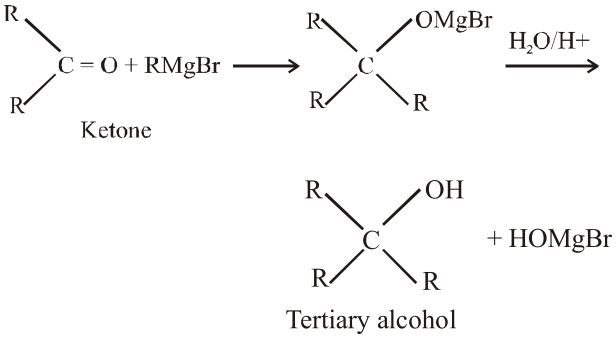
with aldehydes other than HCHO secondary alcohols are obtained. Secondary alchol can also be prepared by addition of esters.



Aldehyde

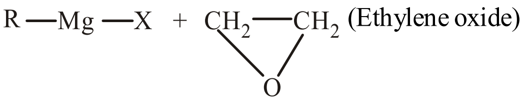
(Secondary alcohol)

If carbonyl compound is ketone, product will be tertiary alcohol.



(iv) With Ethylene Oxide :

The alcohol obtained has two carbon atoms more than alkyl group of the Grignard reagent.



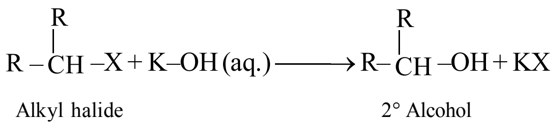
$$\longrightarrow R–CH_2–CH_2–O–Mg–X$$

$$\xrightarrow{H_2O} \underset{\text{Alcohol}}{R–CH_2CH_2OH} + Mg(X)OH$$

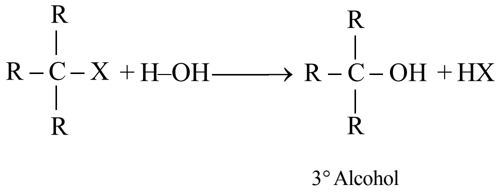
(v) From Alkyl Halides (Hydrolysis) :

The hydrolysis occurs by nucleophilic substitution reaction.

$$R–CH_2–X + AgOH(aq.) \longrightarrow \underset{1° \text{ Alcohol}}{R–CH_2–OH} + AgX$$



$$\underset{\text{Alkyl halide}}{R-\overset{R}{\overset{|}{C}H}-X} + K–OH\,(aq.) \longrightarrow \underset{2° \text{ Alcohol}}{R–\overset{R}{\overset{|}{C}H}–OH} + KX$$



$$R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-X + H–OH \longrightarrow \underset{3° \text{ Alcohol}}{R-\underset{R}{\underset{|}{\overset{R}{\overset{|}{C}}}}-OH} + HX$$

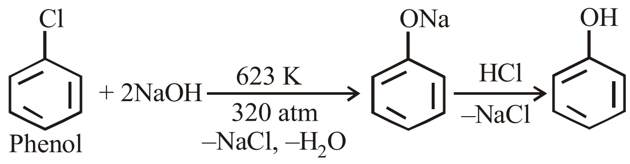
(vi) From Primary Amines :

Primary alcohols are formed when primary amines are treated with nitrous acid (HNO_2)

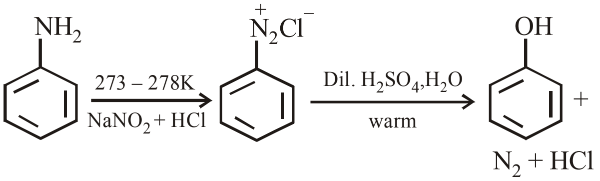
$$R-NH_2 + HNO_2 \xrightarrow{HCl} R–OH + N_2 + H_2O$$

PREPARATION OF PHENOLS

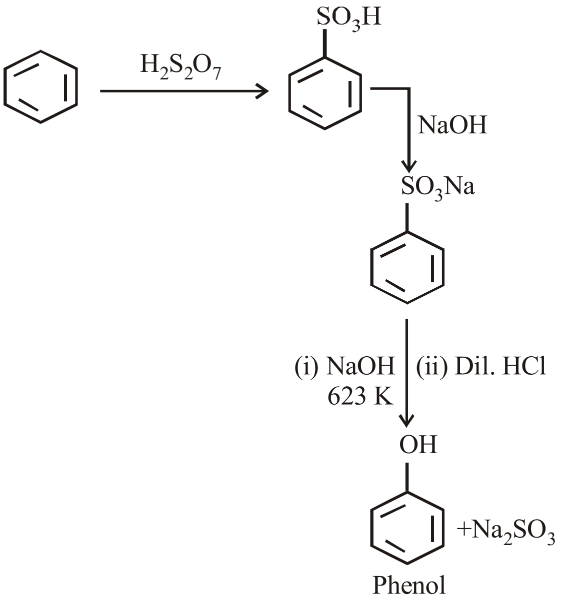
(i) From Haloarenes



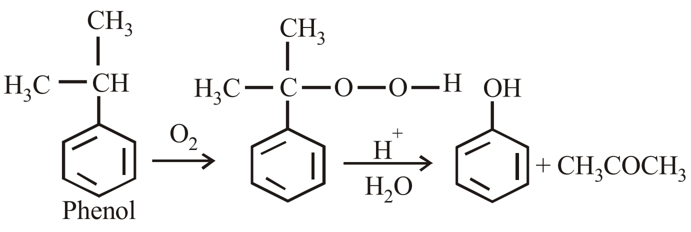
(ii) From Diazonium Salts



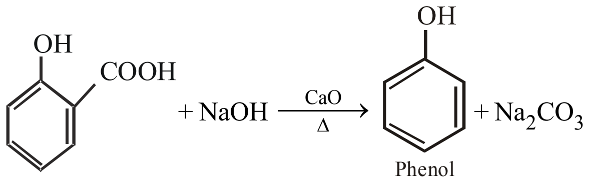
(iii) From Benzene Sulphonic Acid



(iv) From Cumene



(v) By Distilling a Phenolic Acid with Soda Lime (Decarboxylation).



PHYSICAL PROPERTIES OF ALCOHOLS AND PHENOLS

(i) Boiling points:

Boiling point increases with increase in number of C-atoms due to increase in van der Walls force.

Among isomeric alcohols, the boiling points decreases with branching as surface area decreases. Thus b. pts. decrease in the order.

Primary > Secondary > Tertiary

B Pts. of alcohols and phenols are higher than hydrocarbons, alkyl halides and ethers. This is due to intermolecular H-bonding in them as a result of which they exist as associated molecules. This intermolecular H-bonding is missing in hydrocarbons and ethers.

(ii) Solubility:

Their solubility in water is due to formation of H-bonds with water. Thus more will be the capability to form H-bonds more will be solubility of given alcohol and phenol.

Solubility decreases with increase in size of alkyl / aryl groups (i.e., hydrophobic group).

The solubility of phenols in water is much lower than that of alcohols because of the larger hydrocarbon part.

(iii) Formation of Alcoholate

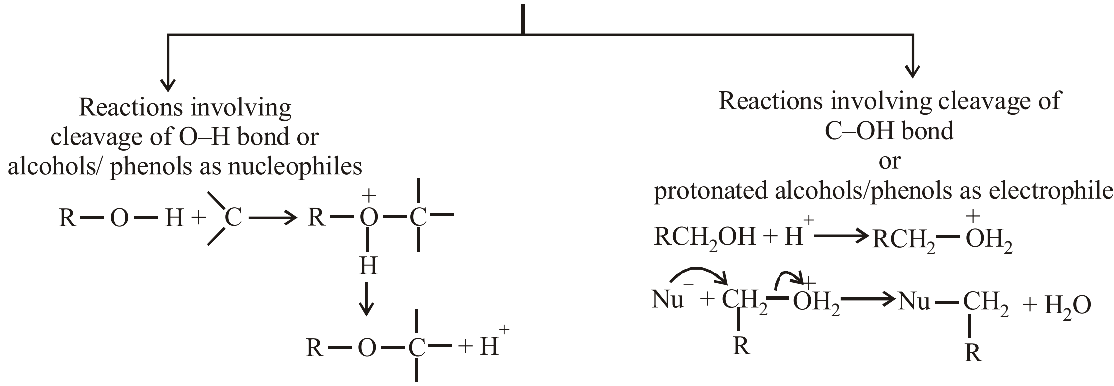
Lower alcohols such as CH_3OH and C_2H_5OH react with anhydrous $CaCl_2$ or $MgCl_2$ to form solid derivatives called alcoholates.

$CaCl_2 + 4\,CH_3OH \rightarrow CaCl_2.4\,CH_3OH$

$CaCl_2 + 3\,C_2H_5OH \rightarrow CaCl_2.3\,C_2H_5OH$

$MgCl_2 + 6\,C_2H_5OH \rightarrow MgCl_2.6C_2H_5OH.$

CHEMICAL PROPERTIES OF ALCOHOLS AND PHENOLS



Reactions involving cleavage of O–H bond or alcohols/ phenols as nucleophiles

$$R-O-H + \rangle C \longrightarrow R-\overset{+}{\underset{H}{O}}-\overset{|}{\underset{|}{C}}- \downarrow R-O-\overset{|}{\underset{|}{C}}- + H^+$$

Reactions involving cleavage of C–OH bond or protonated alcohols/phenols as electrophiles

$$RCH_2OH + H^+ \longrightarrow RCH_2-\overset{+}{O}H_2$$

$$\overset{-}{Nu} + \underset{R}{CH_2}-\overset{+}{O}H_2 \longrightarrow Nu-\underset{R}{CH_2} + H_2O$$

I. Cleavage of O–H Bond

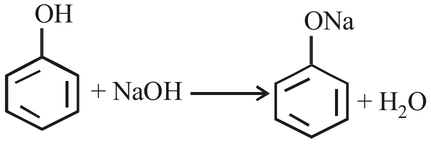
The general order of reactivity of alcohols in this type of reaction is :–

Primary > Secondary > Tertiary

(i) Acidity of Alcohols and Phenols:

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

$$6\left(CH_3\right)_3COH + 2Al \longrightarrow 2\left(\left(CH_3\right)_3CO\right)_3Al + 3H_2$$



The acidic order of alcohols is

MeOH > 1° > 2° > 3°

Acidity of alcohols: They are acidic due to polar O–H bond. Alkyl groups increases the e^- density on O atom of the O–H bond. As a result, the electrons of the O–H bond are not sufficiently attracted towards the oxygen atom thereby decreasing the polarity of O–H bond. Thus tending to decrease the acid strength. Acid strength order of alcohols will be 1° > 2 ° > 3°. Due to same reason, alcohols are weaker acids than water.

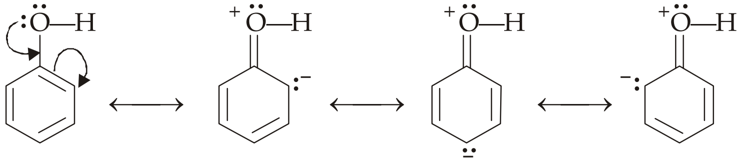
Basic strength order of alkoxides.

$$R_3CO^- > R_2CHO^- > RCH_2O^-$$

Acidity of phenols: Phenols are stronger acids than alcohols and water. This is explained as follows:

(a) In phenols, –OH is directly attached to sp^2 – hybridised carbon. As a result, e^- density on O decreases. This increases polarity of O–H bond resulting in increased ionisation of phenols than alcohols.

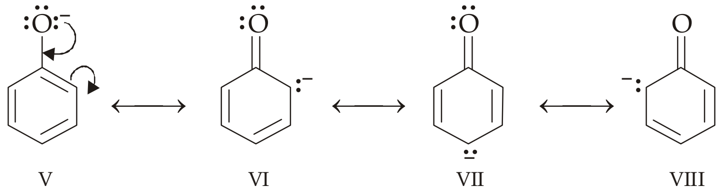
Further, greater acidity of a phenol than an alcohol is due to possibility of resonance in phenol which leads to electron-deficient oxygen atom. Presence of electron-deficient oxygen atom (see structures II, III and IV) in turn weakens the $-\overset{+}{O}\longrightarrow\!\!\!\leftarrow H$ bond, and thus facilitates release of proton.



I II III IV

Such structures are not possible in alcohols.

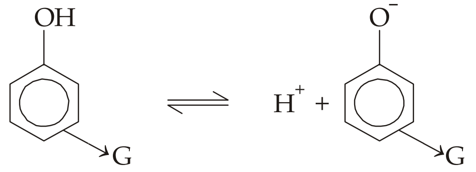
(b) Once hydrogen atom is removed from phenol, the ion (phenoxide) is very much stabilized due to delocalization of its negative charge.



Resonance in phenoxide ion (note that structures VI to VIII are equivalent)

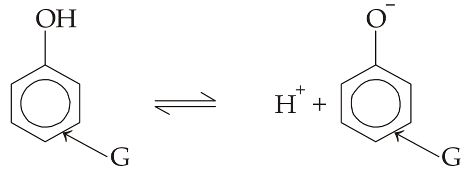
Remember that phenoxide ion is very much more stable than the parent compound phenol because phenoxide ion does not involve charge separation, while in phenol three equivalent resonanting structures (II to IV) involve charge separation.

(c) Electron-withdrawing substituents increase the acidity of phenols ; while electron-releasing substituents decrease acidity.



G withdraws electrons, thus disperses the –ve charge of the ion, stabilises it and hence increases ionization of the parent phenol.

(where G = —NO_2, —CN, —CHO, —COOH, —$\overset{+}{N}R_3$, —X)



G releases electrons, thus intensifies the -ve charge of the ion, destabilises it and hence decreases ionization of the parent phenol.

(ii) Esterification:

$$Ar/R-OH+R'-COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR'+H_2O$$

$$Ar/R-H+(R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR'+R'COOH$$

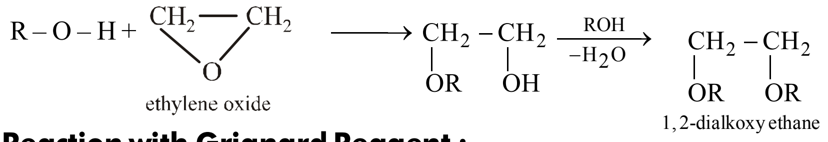
$$R/Ar-OH+R'COCl \xrightarrow{Py} R/ArOCOR'+HCl$$

The order of ease of formation of ester

Primary alcohol > Secondary alcohol > Tertiary alcohol

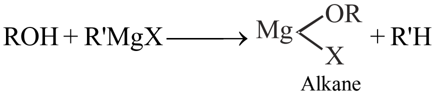
$HCOOH > CH_3COOH > (CH_3)_2CH.COOH > (CH_3)_3C.COOH$

(iii) Reaction with Ethylene Oxide :



$$R-O-H+\underset{\text{ethylene oxide}}{CH_2-CH_2 \text{ (O)}} \longrightarrow \underset{OR\quad\ OH}{CH_2-CH_2} \xrightarrow[-H_2O]{ROH} \underset{\text{1,2-dialkoxy ethane}}{\underset{OR\quad\ OR}{CH_2-CH_2}}$$

(iv) Reaction with Grignard Reagent :

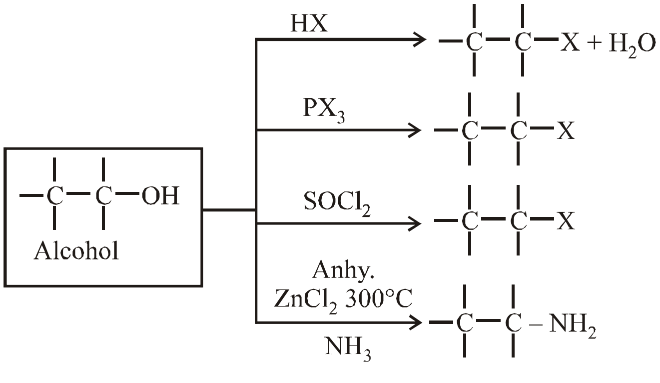


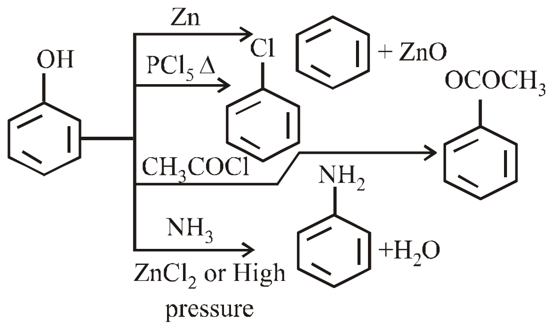
$$ROH+R'MgX \longrightarrow Mg\langle{}^{OR}_{X} + \underset{\text{Alkane}}{R'H}$$

II. Cleavage of C–OH Bond

The order of reactivity in this type of reaction is –

3° alcohol > 2° alcohol > 1° alcohol





Reactions Involving the Alcohol Molecule as a Whole.

(i) Dehydration:

$$>C-C<-OH \xrightarrow[\text{or anhy } ZnCl_2 \text{ or } Al_2O_3]{\text{Conc. } H_2SO_4 \text{ or } H_3PO_4} >C=C< + H_2O$$

(ii) Reaction with H_2SO_4 :

(a) $C_2H_5OH + H_2SO_4 \xrightarrow{110^oC} CH_3CH_2OSO_3H$

Ethyl hydrogen sulphate

(b) $\underset{\text{(excess)}}{CH_3–CH_2–OH} + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{140°C}$

$$CH_3–CH_2–\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}–CH_2–CH_3$$

Diethyl ether

(c) $CH_3 - CH_2 - OH + \underset{\text{(excess)}}{H_2SO_4} \xrightarrow{160°} CH_2 = CH_2$

(iii) Oxidation :

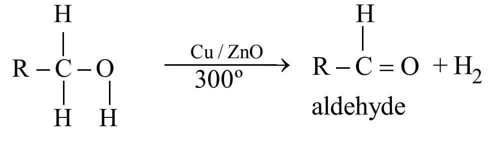
(a) $RCH_2OH \xrightarrow[\text{PCC}]{CrO_3 \text{ or}} RCHO$

(b) $R_2CHOH \xrightarrow[\text{PCC}]{CrO_3 \text{ or}} R_2CO$

(iv) Reduction :

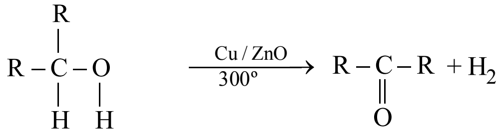
$R–O–H + 2HI \xrightarrow[150° C]{Red P} R–H + H_2O + I_2$

(v) Dehydrogenation :



$$R-\overset{H}{\underset{H}{C}}-\underset{H}{O} \xrightarrow[300°]{Cu/ZnO} \underset{\text{aldehyde}}{R-\overset{H}{C}=O} + H_2$$

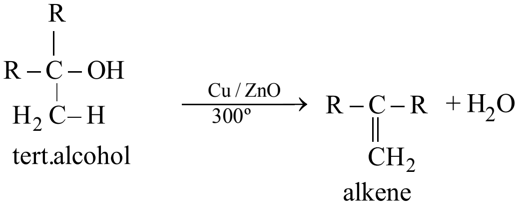
primary alcohol



$$R-\overset{R}{\underset{H}{C}}-\underset{H}{O} \xrightarrow[300°]{Cu/ZnO} R-\underset{O}{\overset{}{\underset{\|}{C}}}-R + H_2$$

secondary alcohol

Ketone



$$R-\overset{R}{\underset{H_2C-H}{C}}-OH \xrightarrow[300°]{Cu/ZnO} R-\underset{CH_2}{\underset{\|}{C}}-R + H_2O$$

tert.alcohol

alkene

Note:

(a) Reaction of R–OH with HX is used to distinguish between 1°, 2°, 3° alcohols (Lucas test) is discussed later. Reactivity order of halogen acid is HI > HBr > HCl

(b) 1° alcohols on oxidation give aldehydes while 2° alcohols give ketones. 3° alcohols do not undergo oxidation reactions. Under strong conditions like strong oxidising agent ($KMnO_4$) and elevated temperatures, cleavage of various C–C bonds takes place and a mixture of acids with lesser no. of C–atoms is formed.

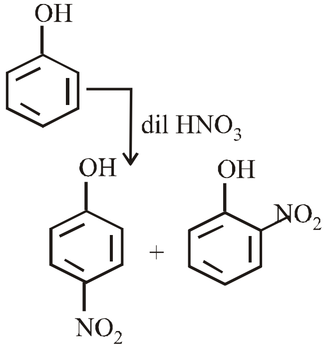
(c) With Cu, 3° alcohols undergo dehydration to form alkenes.

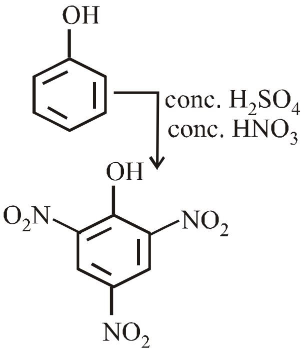
(where G = —R, —OR, —NR_2)

Reactions of Phenols

(i) Electrophilic aromatic substitution

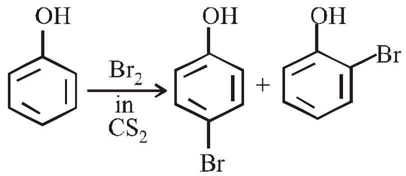
(a) Nitration

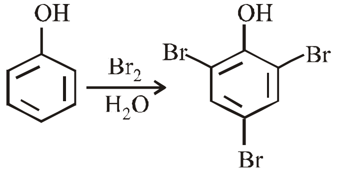




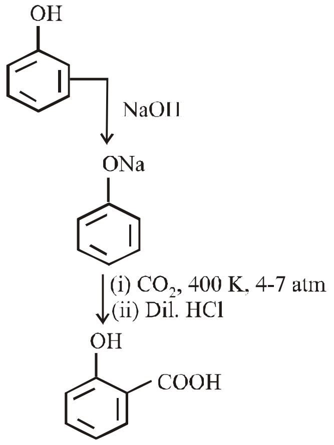
(Picric acid)

(b) Halogenation



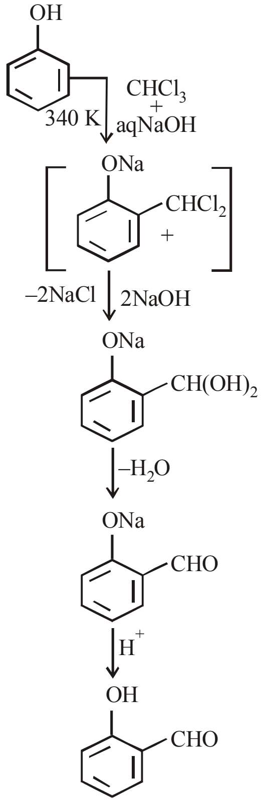


(ii) Kolbe's Reaction



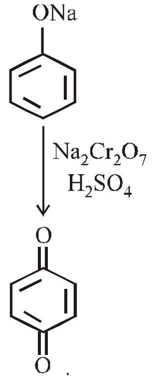
Salicylic acid

(iii) Riemer-Tiemann Reaction



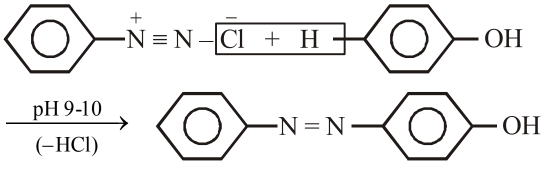
Salicylaldehyde

(iv) Oxidation



benzoquinone

(v) Coupling Reaction



p-hydroxyazobenzene

Note: o – and p– nitrophenols can be separated by steam distillation. o – isomer is steam volatile due to intramolecular H-bonding while p-isomer is less volatile due to intermolecular H-bonding which causes association of molecules.

SOME IMPORTANT ALCOHOLS

(i) Methanol (CH_3OH)

It is also known as wood spirit

$$CO + 2H_2 \xrightarrow[\substack{200-300\text{atm} \\ 573-673\text{K}}]{ZnO-Cr_2O_3} CH_3OH$$

It is a colourless liquid and boils at 337 K. It is highly poisonous, even small quantities can cause blindness and large amounts can cause death. It is used as a solvent in paints, varnishes and for making formaldehyde

(ii) Ethanol (C_2H_5OH)

It is obtained by fermentation

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} \underset{\text{Glu cos e}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$$

It is a colourless liquid and boils at 351 K. It is used as a solvent in paint industry and in preparation of a number of carbon compounds.

(iii) Denatured Alcolol

The commercial alcohol is made unfit for drinking by mixing in it some $CuSO_4$ (to give it a colour) and pyridine (a foul smelling liquid) It is known as **denaturation** of alcohol.

(iv) Power Alcohol

Alcohol used for generating power is called power alcohol. It consists of a mixture of absolute alcohol and petrol roughly in the ratio 20:80.

DISTINCTION BETWEEN 1°, 2° AND 3° - ALCOHOLS

(i) Oxidation

$$1° \text{ alcohols} \xrightarrow[\text{PCC}]{CrO_3 \text{ or}} \text{aldehyde}$$

$$2° \text{ alcohol} \xrightarrow[\text{PCC}]{CrO_3 \text{ or}} \text{ketone}$$

$$3° \text{ alcohol} \xrightarrow[\text{High temperature}]{KMnO_4}$$

Mixture of acids with lesser no. of C-atoms.

(ii) Action of hot copper

$$1^\circ \text{ alcohols} \xrightarrow[573K]{Cu} \text{aldehyde} + H_2$$

$$2^\circ \text{ alcohol} \xrightarrow[573K]{Cu} \text{ketone} + H_2$$

$$3^\circ \text{ alcohol} \xrightarrow[573K]{Cu} \text{alkene} + H_2O$$

(iii) Lucas Test

Lucas reagent is an equimolar mixture of conc. HCl and anhydrous $ZnCl_2$.

$$1^\circ \text{ alcohols} \xrightarrow[\text{reagent}]{\text{Lucas}}$$

No reaction occurs no turbidity appears

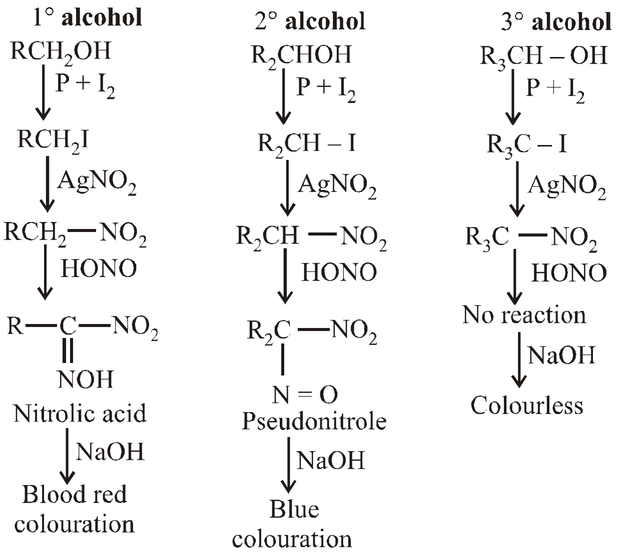
$$2^\circ \text{ alcohol} \xrightarrow{\text{Lucas reagent}}$$

Alkyl chloride (R_2CHCl) is formed turbidity appears in about 5 minutes

$$3^\circ \text{ alcohol} \xrightarrow{\text{Lucas reagent}}$$

Alkyl chloride (R_3CCl) is formed turbidity appears immediately.

(iv) Victor Meyer's Test



DISTINGUISH BETWEEN ALCOHOLS AND PHENOLS:

(i) Phenols react with $FeCl_3$ to give violet colouration whereas alcohols do not react.

(ii) Phenols on shaking with bromine water gives a white ppt. of 2, 4, 6-tribromophenol but alcohols do not.

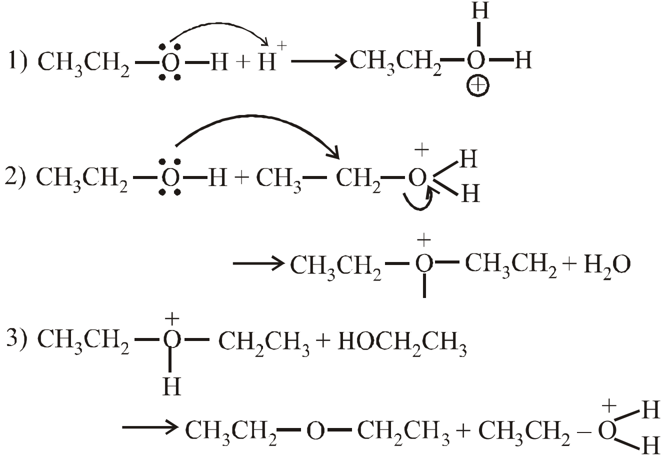
(B) ETHERS

PREPARATION OF ETHERS

(i) By Dehydration of Alcohols

$$CH_3CH_2OH \xrightarrow[413\text{ K}]{\text{Conc.}H_2SO_4} C_2H_5OC_2H_5$$

Mechanism:



(iii) Williamson's Synthesis

$$R - X + R' - O - Na \longrightarrow R - O - R' + NaX$$

Williamson synthesis can be applied for the synthesis of symmetrical as well as unsymmetrical ethers. It follows $S_N{}^2$ path, hence it is most successful when the alkyl halide, sulphonate, or sulphate is primary (or methyl). For preparation of 3° ethers, better results are obtained if alkyl halide is 1°. If 3° alkyl halide is used, alkene is formed instead of ether. For phenol ether, phenol is used as phenoxide moiety

$$C_6H_5\bar{O}Na^+ + CH_3Br \xrightarrow{\Delta} C_6H_5OCH_3 + NaBr$$

This method cannot be used for preparing diaryl ethers since aryl halides do not undergo nucleophilic substitution reactions easily.

(ii) By reaction of ethyl halide with dry Ag_2O :

$$CH_2—CH_2—\boxed{I + Ag}—O—\boxed{Ag + I}—CH_2—CH_3 \longrightarrow CH_3–CH_2–O–CH_2–CH_3 + 2AgI$$

$$CH_3 – \boxed{I + Ag} – O – \boxed{Ag + I} – CH_2 – CH_3 \longrightarrow CH_3 – O – CH_2 – CH_3 + 2AgI$$

PHYSICAL PROPERTIES OF ETHERS

Ethers are polar but very weakly. Their B.Pts. are comparable to those of alkanes and are much less than alcohols due to absence of H-bonding.

Ethers are only slightly soluble in water. Solubility of lower ethers in water is due to formation of H-bonds. As the molecular mass increases, the solubility of ethers in water decreases due to increase in hydrocarbon part.

CHEMICAL PROPERTIES OF ETHERS

(i) Reaction with HX

$R-O-R+HX\text{ (cold)}\longrightarrow RX+R-OH$

$R-OH+HX\longrightarrow RX+H_2O$

with unsymm ethrical ethers,

$R-O-R'+HX\longrightarrow R-X+R'-OH$

The smaller alkyl group forms the alkyl halide.

If one alkyl group is 3°, then 3° alkyl halide is formed

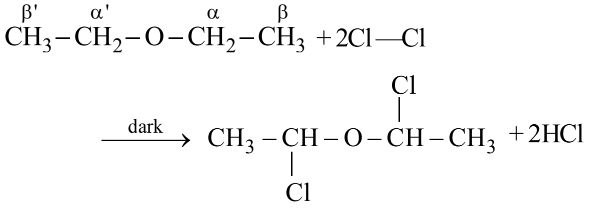
In anisole, CH_3I is the product formed

If HX is hot :

$$CH_3-CH_2-O-CH_2-CH_3+2\,H-X\xrightarrow{\Delta}2CH_3-CH_2-X+H_2O$$

(ii) Halogenation :

(a) In dark :



$$\overset{\beta'}{CH_3}-\overset{\alpha'}{CH_2}-O-\overset{\alpha}{CH_2}-\overset{\beta}{CH_3}+2Cl—Cl$$

$$\xrightarrow{\text{dark}}CH_3-\underset{\underset{Cl}{|}}{CH}-O-\overset{\overset{Cl}{|}}{CH}-CH_3+2HCl$$

α, α'-Dichlorodiethyl ether

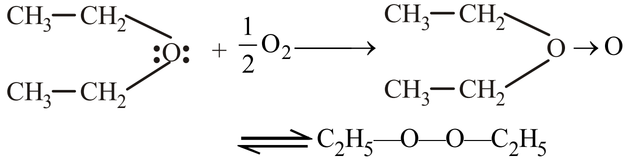
(b) In light

$$CH_3-CH_2-O-CH_2-CH_3+10Cl_2$$

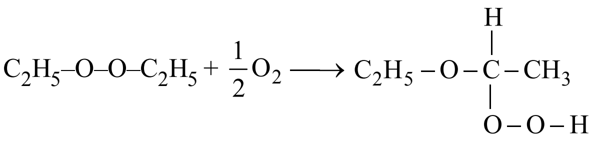
$$\xrightarrow{h\nu}CCl_3-CCl_2-O-CCl_2-CCl_3+10HCl$$

Perchlorodiethyl ether

(iii) Oxidation :



ether peroxide



$$C_2H_5-O-O-C_2H_5+\frac{1}{2}O_2\longrightarrow C_2H_5-O-\overset{\overset{H}{|}}{\underset{\underset{O-O-H}{|}}{C}}-CH_3$$

Ethoxyethyl hydroperoxide

(iv) Reaction with H_2SO_4 :

(a) With conc. H_2SO_4

$$C_2H_5—O—C_2H_5+H_2SO_4\xrightarrow{\Delta}C_2H_5OSO_2OH+C_2H_5OH$$

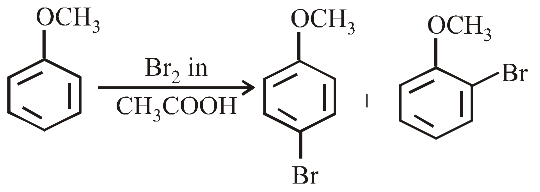
Ethyl hydrogen sulphate

(b) With dil. H_2SO_4 :

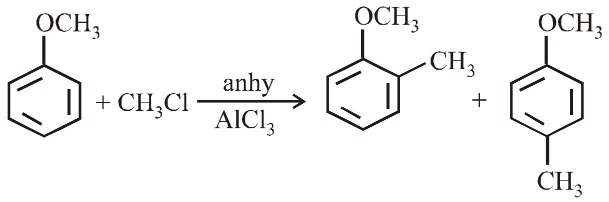
$$C_2H_5-O-C_2H_5+H-OH\xrightarrow{\text{dil.}H_2SO_4}2C_2H_5OH$$

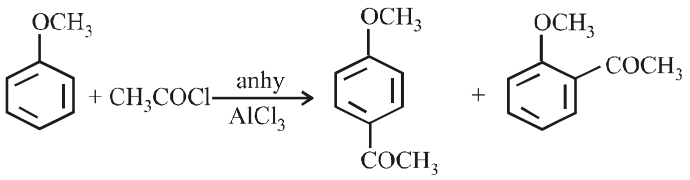
(v) Electrophilic Substitution

(a) Halogenation:

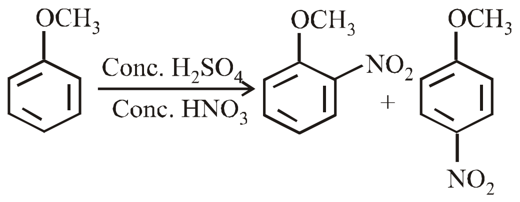


(b) Friedel-Crafts reaction:





(c) Nitration:



CONCEPT MAP

ALCOHOLS, PHENOLS AND ETHERS

Alcohols

Preparation

(a) **By acid catalysed hydration** Alkenes reacts with H_2O in presence of H_3O^+

(b) **By Hydroboration-Oxidation**
Diborane with alkene gives trialkyl boride which gives alcohol wih H_2O_2/OH^-

(c) **Reduction of Aldehydes and Ketones**

$$\text{Aldehyde} \xrightarrow{H_2/Pd} 1^\circ \text{ Alcohol}$$

$$\text{Ketone} \xrightarrow{NaBH_4} 2^\circ \text{ Alcohol}$$

(d) **Reduction of carboxylic acids**

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$$

Properties

(a) $2ROH + 2M \rightarrow 2R-\bar{O}\overset{+}{M} + H_2$

(b) $RCOOH + H-OR' \rightarrow RCOOR' + H_2O$

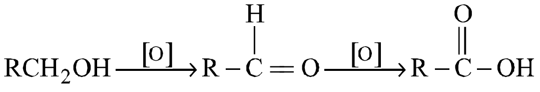
(c) $RCOCl + H-OR' \rightarrow RCOOR' + HCl$

(d) $ROH + R'MgX \rightarrow R'-H + ROMgX$

(e) $ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$

(f) $R-OH + HCl \xrightarrow{Anh.ZnCl_2} CH_3CH_2-Cl + H_2O$

(g) $CH_3CH_2OH \xrightarrow{Conc.H_2SO_4} CH_2=CH_2 + H_2O$

(h) 

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

Ethers

Preparation

(a) **Dehydration of alcohol**

$$2CH_3CH_2OH \xrightarrow{H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

(b) **Williamson's synthesis**

$$R-X + R'-ONa \rightarrow ROR' + NaX$$

Properties

(a) $R-O-R' + HX \rightarrow RX + R'OH$

(b) Methoxy benzene

$$\xrightarrow[\text{Ethanoic acid}]{Br_2} o\text{- and, } p\text{-bromo Methoxy benzene}$$

$$\xrightarrow[CH_3Cl]{Anhy.AlCl_3} o\text{- and } p\text{-methyl methoxy benzene}$$

$$\xrightarrow{H_2SO_4 + HNO_3} o\text{- and } p\text{-nitro methoxy benzene}$$

Phenols

Preparation

(a) $\text{Chlorobenzene} + NaOH \xrightarrow[\text{(ii) HCl}]{\text{(i) 623K, 300 atm}} \text{Phenol}$

(b) $\text{Benzene} \xrightarrow[\text{(ii) NaOH, } H^+]{\text{(i) Oleum}} \text{Phenol}$

(c) $\text{Aniline} \xrightarrow[273-278K]{NaNO_2 + HCl} \text{Diazonium salt} \xrightarrow{H_2O} \text{Phenol}$

(d) $\text{Cumene} \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) } O_2} \text{Phenol}$

Properties

(a) Nitration give o- and p-nitrophenol

(b) With Br_2 / H_2O it gives 2, 4, 6- tribromophenol

(c) In presence of low polarity solvents like $CHCl_3$ and CS_2 on bromination it gives o, and p-bromophenol

(d) $\text{Phenol} + CO_2 \xrightarrow{400K,\ 4-7atm} \text{Salicylic acid}$

(e) $\text{Phenol} + CHCl_3 \xrightarrow{NaOH} \text{Salicylaldehyde}$

EXERCISE - 1

Conceptual Questions

1. Lucas reagent is
(a) conc. HCl and anhydrous $ZnCl_2$
(b) conc. HNO_3 and hydrous $ZnCl_2$
(c) conc. HCl and hydrous $ZnCl_2$
(d) conc. HNO_3 and anhydrous $ZnCl_2$

2. Glycerol on oxidation with bismuth nitrate produces
(a) oxalic acid (b) glyceric acid
(c) glyoxalic acid (d) meso oxalic acid

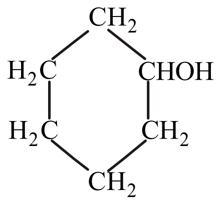
3. The alcohol manufactured from water gas is
(a) ethanol (b) methanol
(c) isobutanol (d) butanol

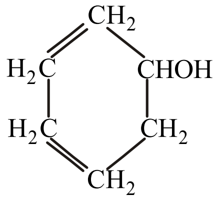
4. Which of the following are isomers ?
(a) Methyl alcohol and dimethyl ether
(b) Ethyl alcohol and dimethyl ether
(c) Acetone and acetaldehyde
(d) Propionic acid and propanone

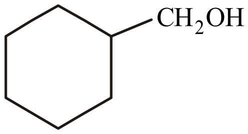
5. Dehydration of alcohol is an example of
(a) Redox reaction (b) Elimination reaction
(c) Substitution reaction (d) Addition reaction

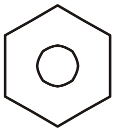
6. Methylated spirit is
(a) methanol (b) methanol + ethanol
(c) methanoic acid (d) methanamide

7. The structural formula of cyclohexanol is

(a) 

(b) 

(c) 

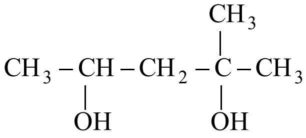
(d) 

8. Molecular formula of amyl alcohol is
(a) $C_7H_{14}O$ (b) $C_6H_{13}O$ (c) $C_5H_{12}O$ (d) $C_5H_{10}O$

9. Phenol is more readily soluble in
(a) NaOH solution
(b) dil. HCl
(c) both NaOH and HCl
(d) $NaHCO_3$

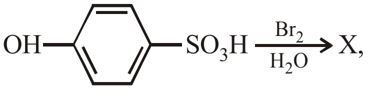
10. Absolute alcohol is
(a) 100% pure ethanol
(b) 95% alcohol + 5% H_2O
(c) ethanol + water + phenol
(d) 95% ethanol + 5% methanol

11. Which of the following is dihydric alcohol ?
(a) Glycerol (b) Ethylene glycol
(c) Catechol (d) Resorcinol

12. The IUPAC name of  is :

$CH_3-\underset{OH}{CH}-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_3$

(a) 1, 1-dimethyl-1, 3-butanediol
(b) 2-methyl-2, 4-pentanediol
(c) 4-methyl-2, 4-pentanediol
(d) 1, 3, 3-trimethyl-1, 3-propanediol

13. 

X is identified as
(a) 2, 4, 6-tribromophenol
(b) 2-bromo-4-hydroxylbenzene sulphonic acid
(c) 3, 5-dibromo-4-hydroxybenzene sulphonic acid
(d) 2-bromophenol

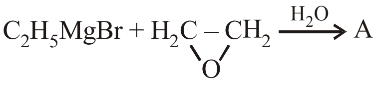
14. The C–O–H bond angle in ethanol is nearly
(a) 90° (b) 104°
(c) 120° (d) 180°

15. Methanol is industrially prepared by
(a) oxidation of CH_4 by steam at 900°C
(b) reduction of HCHO using $LiAlH_4$
(c) reaction HCHO with a solution of NaOH
(d) reduction of CO using H_2 and $ZnO - Cr_2O_3$.

16. When alcohol reacts with concentrated H_2SO_4, intermediate compound formed is :
(a) carbonium ion
(b) alkoxy ion
(c) alkyl hydrogen sulphate
(d) none of the above

17. HBr reacts fastest with
(a) 2-Methylpropan-1-ol (b) 2-Methylpropan-2-ol
(c) propan-2-ol (d) propan-1-ol.

18. In the following reaction 'A ' is



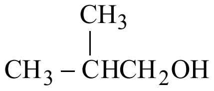
$C_2H_5MgBr + \underset{O}{H_2C-CH_2} \xrightarrow{H_2O} A$

(a) $C_2H_5CH_2CHO$ (b) $C_2H_5CH_2CH_2OH$
(c) $C_2H_5CH_2OH$ (d) C_2H_5CHO

19. *n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?
(a) PCl_5
(b) Reduction
(c) Oxidation with potassium dichromate
(d) Ozonolysis

20. Ethylene oxide when treated with Grignard reagent yields
(a) tertiary alcohol (b) cyclopropyl alcohol
(c) primary alcohol (d) secondary alcohol

21. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is

(a) 
$CH_3-\overset{\overset{\large CH_3}{|}}{C}HCH_2OH$
(b) $PhCHOHCH_3$
(c) $CH_3CH_2CH(OH)CH_2CH_3$
(d) $C_6H_5CH_2CH_2OH$

22. The best method to prepare cyclohexene from cyclohexanol is by using
(a) Conc. HCl + $ZnCl_2$ (b) Conc. H_3PO_4
(c) HBr (d) Conc. HCl

23. $C_6H_5-CH=CHCHO \xrightarrow{X} C_6H_5CH=CHCH_2OH$. In the above sequence X can be
(a) H_2/Ni (b) $NaBH_4$
(c) $K_2Cr_2O_7/H^+$ (d) Both (a) and (b)

24. Which of the following reactions will not result in the formation of anisole?
(a) Phenol + dimethyl sulphate in presence of a base
(b) Sodium phenoxide is treated with methyl iodide
(c) Reaction of diazomethane with phenol
(d) Reaction of methylmagnesium iodide with phenol

25. Acid catalyzed hydration of alkenes except ethene leads to the formation of
(a) primary alcohol
(b) secondary or tertiary alcohol
(c) mixture of primary and secondary alcohols
(d) mixture of secondary and tertiary alcohols

26. Isopropyl alcohol is obtained by reacting which of the following alkenes with concentrated H_2SO_4 followed by boiling with H_2O?
(a) Ethylene (b) Propylene
(c) 2-Methylpropene (d) Isoprene

27. Which one of the following is not formed when glycerol reacts with HI ?
(a) $CH_3—CHI—CH_3$
(b) $CH_3—CH=CH_2$
(c) $CH_2OH—CHI—CH_2OH$
(d) $CH_2=CH—CH_2I$

28. Dehydration of 2-butanol yields
(a) 1-butene (b) 2-butene
(c) 2-butyne (d) both (a) and (b)

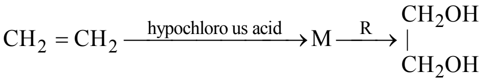
29. Which of the following reagent is best to change glycerol to acrolein ?
(a) P_2O_5 (b) Conc. H_2SO_4
(c) Anhydrous $CaCl_2$ (d) $KHSO_4$

30. The reaction of Lucas reagent is fastest with:
(a) $(CH_3)_2CHOH$ (b) $CH_3(CH_2)_2OH$
(c) CH_3CH_2OH (d) $(CH_3)_3COH$

31. Which one of the following statements is correct?
(a) Phenol is more acidic than carbonic acid
(b) Phenol is less acidic than ethyl alcohol
(c) Phenol is more acidic than ethanol
(d) Phenol is more acidic than acetic acid

32. Which one of the following alcohols is least soluble in water?
(a) CH_3OH (b) C_3H_7OH
(c) C_4H_9OH (d) $C_{10}H_{21}OH$

33. In a reaction :


$CH_2=CH_2 \xrightarrow{\text{hypochloro us acid}} M \xrightarrow{R} \begin{array}{l}CH_2OH\\|\\CH_2OH\end{array}$

Here M = molecule and R = reagent. The M and R are :
(a) $CH_2–CH_2$ and KOH
(b) CH_3CH_2Cl and NaOH
(c) $CH_2OH–CH_2Cl$ and aq. $NaHCO_3$
(d) CH_3CH_2OH and KOH

34. The dehydration of 2-methylbutanol with conc. H_2SO_4 gives :
(a) 2-Methylbutene as major product
(b) Pentene
(c) 2-Methylbut-2-ene as major product
(d) 2-Methylpent-2-ene

35. The product formed by the reduction of glycolic acid with HI, is :
(a) formic acid (b) ethane
(c) iodoacetic acid (d) glycol

36. Ethyl alcohol can be prepared from Grignard reagent by the reaction of :
(a) HCHO (b) R_2CO
(c) RCN (d) RCOCl

37. Which one can differentiate between C_2H_5OH and CH_3OH
(a) H_2O (b) $Na_2CO_3 + I_2$
(c) NH_3 (d) HCl

38. In the reaction :

$$A \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \text{acetone} \xrightarrow{\text{oxidation}} \text{acetic acid}$$

A is
(a) 1- propanol (b) 2-butanol
(c) 2-propanol (d) ethanol

39. In the reaction :

$CH_3OH \xrightarrow{\text{oxidation}} A \xrightarrow{NH_3} B$; A and B respectively are
(a) HCHO, $HCOONH_4$ (b) HCOOH, $HCOONH_4$
(c) HCOOH, $HCONH_2$ (d) HCHO, $HCONH_2$

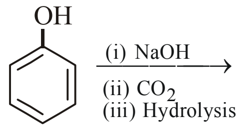
40. The end product of the reaction

$C_2H_5OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow{H_3O^+} C$ is
(a) propanol (b) propanoic acid
(c) propanamide (d) none of these

41. Glycerol is more viscous than ethanol due to

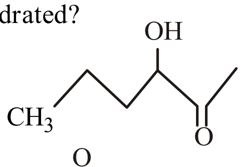
(a) high molecular weight
(b) high boiling point
(c) many hydrogen bonds per molecule
(d) Fajan's rule

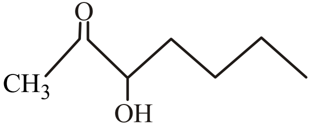
42. The product obtained from the reaction is:

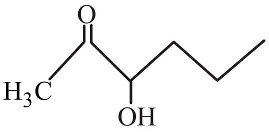


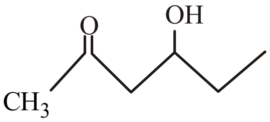
(a) Benzene (b) Toluene
(c) Salicylic acid (d) Benzoic acid

43. Which one of the following compounds will be most readily dehydrated?

(a)


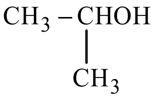
(b)


(c)


(d)


44. Following compounds are given:

(i) CH_3CH_2OH (ii) CH_3COCH_3

(iii)

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CHOH}$
(iv) CH_3OH

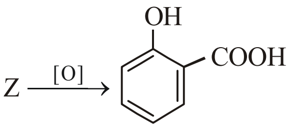
Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform?

(a) (i) and (ii) (b) (i), (iii) and (iv)
(c) only (i) (d) (i), (ii) and (iii)

45. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of

(a) H-bonding in ethanol
(b) H-bonding in dimethyl ether
(c) CH_3 group in ethanol
(d) CH_3 group in dimethyl ether

46. $X \xrightarrow[\text{Heat}]{\text{NaOH}} Y \xrightarrow{CHCl_3 + KOH}$



in the above reaction, Z is :

(a) phenol (b) benzoic acid
(c) salicylaldehyde (d) carbolic acid

47. When phenol is heated with $CHCl_3$ and NaOH then salicylaldehyde is produced. This reaction is known as

(a) Rosenmund's reaction (b) Reimer-Tiemann reaction
(c) Friedel-Crafts reaction (d) Sommelet reaction

48. The intermediate formed in aldol condensation is

(a) aldol (b) carbanion
(c) alcohol (d) α-hydrogen ester

49. When phenol is treated with excess bromine water. It gives

(a) *m*-Bromophenol (b) *o*-and *p*-Bromophenols
(c) 2,4-Dibromophenol (d) 2,4, 6-Tribromophenol.

50. Which is formed when benzalamine react with nitrous acid

(a) C_6H_5OH (b) C_6H_5ON
(c) $C_6H_5N_2OH$ (d) $C_6H_5CH_2OH$

51. The reaction :

$$C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$$

is known as

(a) Kharasch effect (b) Williamson's synthesis
(c) Darzen's procedure (d) Hunsdiecker reaction

52. Benzyl alcohol is obtained from benzaldehyde by:

(a) Perkin's reaction (b) Wurtz reaction
(c) Cannizzaro's reaction (d) Claisen's reaction

53. On distillation with Zn dust, phenol gives :

(a) acetophenone (b) benzoic acid
(c) benzene (d) benzophenone

54. The most suitable reagent for the conversion of

$RCH_2OH \longrightarrow RCHO$ is :

(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) CrO_3
(d) PCC (pyridine chlorochromate)

55. Phenol is more acidic than alcohol because.

(a) phenol is more stable than water
(b) phenol is aromatic and alcohol is aliphatic
(c) phenoxide ion is resonance stabilised
(d) None of these

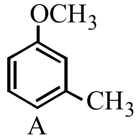
56. To distinguish between salicylic acid and phenol, one can use :

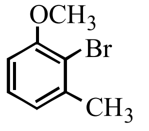
(a) $NaHCO_3$ solution
(b) 5% NaOH solution
(c) neutral $FeCl_3$
(d) bromine water

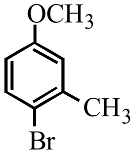
57. Which of the following has lowest boiling point ?

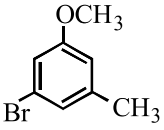
(a) *p*-Nitrophenol (b) *m*-Nitrophenol
(c) *o*-Nitrophenol (d) Phenol

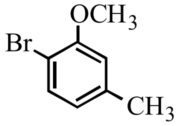
58. The major product obtained on the monobromination (with $Br_2/FeBr_3$) of the following compound A is :


A

(a) 

(b) 

(c) 

(d) 

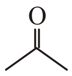
59. Which one is formed when sodium phenoxide is heated with ethyl iodide ?
(a) Phenetole (b) Ethyl phenyl alcohol
(c) Phenol (d) None of these

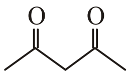
60. $CH_3OC_2H_5$ and $(CH_3)_3C-OCH_3$ are treated with hydriodic acid. The fragments obtained after reactions are
(a) $CH_3I + HOC_2H_5; (CH_3)_3CI + HOCH_3$
(b) $CH_3OH + C_2H_5I; (CH_3)_3CI + HOCH_3$
(c) $CH_3OH + C_2H_5I; (CH_3)_3COH + CH_3I$
(d) $CH_3I + HOC_2H_5; CH_3I + (CH_3)_3COH.$

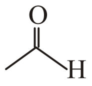
61. In the reaction $Ar-OH + RX \xrightarrow{\text{alkali}} A$, A is
(a) an aldehyde (b) an aryl chloride
(c) an ether (d) a ketone

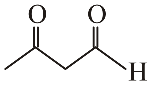
62. In Williamson's synthesis, ethoxyethane is prepared by
(a) passing ethanol over heated alumina
(b) sodium ethoxide with ethyl bromide
(c) ethyl alcohol with sulphuric acid
(d) ethyl iodide and dry silver oxide

63. Maximum enol content is in

(a) 

(b) 

(c) 

(d) 

64. Formation of diethyl ether from ethanol is based on a
(a) dehydration reaction
(b) dehydrogenation reaction
(c) hydrogenation reaction
(d) heterolytic fission reaction

65. A fruity smell is produced by the reaction of C_2H_5OH with
(a) CH_3COCH_3 (b) CH_3COOH
(c) PCl_5 (d) CH_3CHO

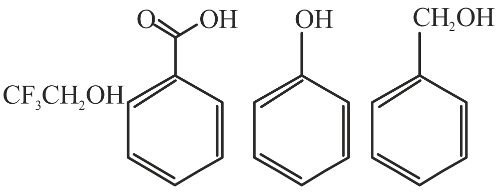
66. The reaction of sodium ethoxide with ethyl iodide to form diethyl ether is termed
(a) electrophilic substitution
(b) nucleophilic substitution
(c) electrophilic addition
(d) radical substitution

67. The major product of the reaction between tert-butyl chloride and sodium ethoxide is
(a) 2-methylprop-1-ene
(b) 1-butene
(c) 2-butene
(d) ethene

68. Which of the following product is formed, when ether is exposed to air ?
(a) Oxide (b) Alkanes
(c) Alkenes (d) Peroxide of diethyl ether

69. Ether which is liquid at room temperature is
(a) $C_2H_5OCH_3$ (b) CH_3OCH_3
(c) $C_2H_5OC_2H_5$ (d) None of these

70. What is the correct order of acidity from weakest to strongest acid for these compounds?



I II III IV

(a) I < IV < III < II
(b) III < IV < I < II
(c) IV < I < III < II
(d) II < III < I < IV

71. In the following reaction

$$C_2H_5OC_2H_5 + 4[H] \xrightarrow{\text{Red P + HI}} 2X + H_2O, \text{ X is}$$

(a) ethane (b) ethylene
(c) butane (d) propane

72. The ether that undergoes electrophilic substitution reactions is
(a) $CH_3OC_2H_5$ (b) $C_6H_5OCH_3$
(c) CH_3OCH_3 (d) $C_2H_5OC_2H_5$

73. Etherates are
(a) ethers
(b) solution in ether
(c) complexes of ethers with Lewis acid
(d) complexes of ethers with Lewis base

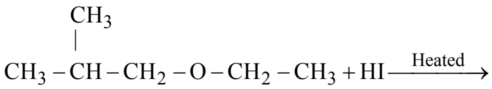
74. The compound that undergoes dehydration very easily is
(a) 2-methylpropan-2-ol
(b) ethyl alcohol
(c) 3-methyl-2-butanol
(d) propyl alcohol

75. Diethyl ether on heating with conc. HI gives two moles of
(a) ethanol (b) iodoform
(c) ethyl iodide (d) methyl iodide

76. Methylphenyl ether can be obtained by reacting
(a) phenolate ions and methyl iodide
(b) methoxide ions and bromobenzene
(c) methanol and phenol
(d) bromo benzene and methyl bromide

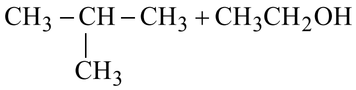
77. Which of the following alcohols gives the best yield of dialkyl ether on being heated with a trace of sulphuric acid?
(a) 2-Pentanol
(b) Cyclopentanol
(c) 2-Methyl-2-butanol
(d) 1-Pentanol

78. In the reaction:

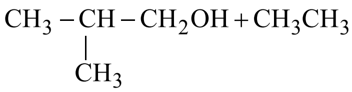


$CH_3-\underset{|}{\overset{CH_3}{CH}}-CH_2-O-CH_2-CH_3+HI\xrightarrow{\text{Heated}}$

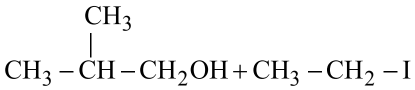
Which of the following compounds will be formed?

(a)


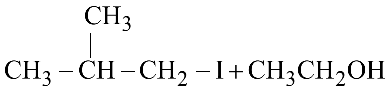
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_3+CH_3CH_2OH$

(b)


$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2OH+CH_3CH_3$

(c)


$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2OH+CH_3-CH_2-I$

(d)


$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-I+CH_3CH_2OH$

79. Consider the following reaction,

ethanol $\xrightarrow{PBr_3} X \xrightarrow{\text{alc.KOH}} Y$

$\xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4 \text{ room temperature}} Z;$

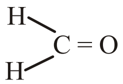
the product Z is:
(a) $CH_3CH_2-O-CH_2-CH_3$
(b) $CH_3-CH_2-O-SO_3H$
(c) CH_3CH_2OH
(d) $CH_2=CH_2$

80. $H_2COH\cdot CH_2OH$ on heating with periodic acid gives:

(a) 2 HCOOH

(b)


$\underset{CHO}{\overset{CHO}{|}}$

(c) 2


$H_2C=O$

(d) $2\,CO_2$

81. Consider the following reaction:

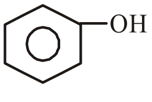
Phenol $\xrightarrow{\text{Zn dust}} X \xrightarrow[\text{Anhydrous } AlCl_3]{CH_3Cl} Y$

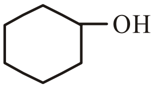
$\xrightarrow{\text{Alkaline } KMnO_4} Z$

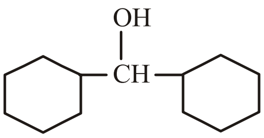
The product Z is:
(a) benzaldehyde (b) benzoic acid
(c) benzene (d) toluene

82. Which one of the following compounds has the most acidic nature?

(a)


(b)


(c)


(d)


83. Among the following four compounds
(i) phenol (ii) methylphenol
(iii) meta-nitrophenol (iv) para-nitrophenol
the acidity order is :
(a) ii > i > iii > iv (b) iv > iii > i > ii
(c) iii > iv > i > ii (d) i > iv > iii > ii

84. When glycerol is treated with excess of HI, it produces:
(a) glycerol triiodide (b) 2–iodopropane
(c) allyl iodide (d) propene

85. Which of the following compounds can be used as antifreeze in automobile radiators ?
(a) Methyl alcohol (b) Glycol
(c) Nitrophenol (d) Ethyl alcohol

86. In the following sequence of reactions,

$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[\text{ether}]{Mg} B \xrightarrow{HCHO}$

$C \xrightarrow{H_2O} D$

the compound D is
(a) propanal (b) butanal
(c) *n*-butyl alcohol (d) *n*-propyl alcohol.

87. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives
(a) 2, 4, 6-trinitrobenzene (b) *o*-nitrophenol
(c) *p*-nitrophenol (d) nitrobenzene

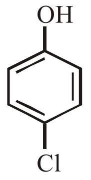
88. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is
(a) salicylaldehyde (b) salicylic acid
(c) phthalic acid (d) benzoic acid

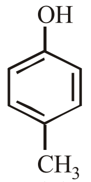
89. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is
(a) 2-Butanol (b) 2- Methylpropan-2-ol
(c) 2-Methylpropanol (d) 1- Butanol

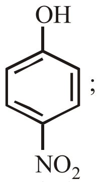
90. The correct order of acid strength of the following compounds :
(A) Phenol (B) *p*–Cresol
(C) *m*–Nitrophenol (D) *p*–Nitrophenol
(a) D > C > A > B (b) B > D > A > C
(c) A > B > D > C (d) C > B > A > D

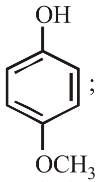
91. Consider the following reaction :
$C_2H_5OH+H_2SO_4 \longrightarrow$ Product
Among the following, which one cannot be formed as a product under any conditions ?
(a) Ethylene (b) Acetylene
(c) Diethyl ether (d) Ethyl-hydrogen sulphate

92. Arrange the following compounds in order of decreasing acidity :


(I);


(II);


(III);


(IV);

(a) II > IV > I > III (b) I > II > III > IV
(c) III > I > II > IV (d) IV > III > I > II

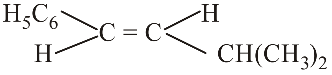
93. Isopropylbenzene is oxidized in the presence of air to compound 'A'. When compound 'A' is treated with dilute mineral acid, the aromatic product formed is

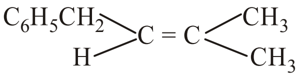
(a) phenol (b) benzene

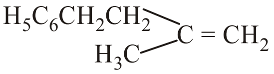
(c) benzaldehyde (d) acetophenone

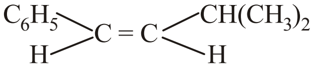
94. The main product of the following reaction is

$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{conc.H_2SO_4} ?$

(a)


(b)


(c)


(d)


95. Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is :

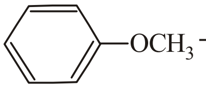
(a) 2-Bromophenol (b) 3-Bromophenol

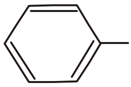
(c) 4-Bromophenol (d) 2, 4, 6-Tribromophenol

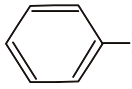
96. Which of the following reagents may be used to distinguish between phenol and benzoic acid?

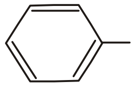
(a) Aqueous NaOH (b) Tollen's reagent

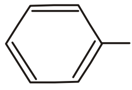
(c) Molisch reagent (d) Neutral $FeCl_3$

97. In the reaction

$—OCH_3 \xrightarrow{HBr}$ the products are

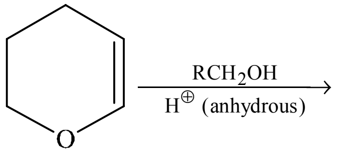
(a)

$—OCH_3$ and H_2

(b)

—Br and CH_3Br

(c)

—Br and CH_3OH

(d)

—OH and CH_3Br

98. The major product of the following reaction is



(a) a hemiacetal (b) an acetal

(c) an ether (d) an ester

99. Which one of the following compounds will be most readily attacked by an electrophile ?

(a) Chlorobenzene (b) Benzene

(c) Phenol (d) Toluene

100. Propene, $CH_3CH = CH_2$ can be converted into 1-propanol by oxidation. Indicate which set of reagents amongst the following is ideal to effect the above conversion ?

(a) $KMnO_4$ (alkaline)

(b) Osmium tetraoxide (OsO_4/CH_2Cl_2)

(c) B_2H_6 and alk. H_2O_2

(d) O_3/Zn

EXERCISE - 2

Applied Questions

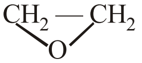
1. Which one of the following reagents is used to reduce an aldehyde to primary school?

(a) N_2H_4/KOH

(b) Zn/Hg and conc. HCl

(c) $LiAlH_4$

(d) Alkaline $CuSO_4$ containing Rochelle salt

2. Reaction of

with RMgX leads to formation of

(a) RCHOHR (b) $RCHOHCH_3$

(c) RCH_2CH_2OH (d)


3. The ionization constant of phenol is higher than that of ethanol because :

(a) phenoxide ion is bulkier than ethoxide

(b) phenoxide ion is stronger base than ethoxide

(c) phenoxide ion is stabilized through delocalization

(d) phenoxide ion is less stable than ethoxide

4. Which one of the following reaction provides a primary alcohol?

(a) Hydration of alkyne

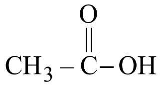
(b) Oxymercuration of alkene

(c) Oxidation hydroboration of alkene

(d) Reaction of Grignard reagent with acetaldehyde

5. Propan-1-ol may be prepared by the reaction of propene with

(a) H_3BO_3 (b) H_2SO_4/H_2O

(c) B_2H_6,$NaOH–H_2O_2$ (d)

$CH_3-\overset{\overset{O}{||}}{C}-OH$

6. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is

(a) formation of carbocation

(b) elimination of water

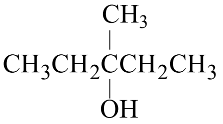
(c) formation of an ester

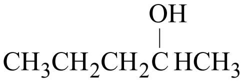
(d) protonation of alcohol molecule

7. When 2-methoxypropane is heated with HI, in the mole ratio 1 : 1, the major products formed are

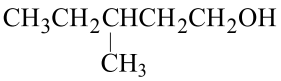
(a) methanol and 2-iodopropane
(b) methyl iodide and 2-propanol
(c) methyl iodide and 2-iodopropane
(d) methanol and 2-propanol

8. Among the following compounds which can be dehydrated very easily is

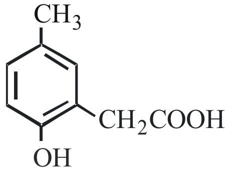
(a) 
$CH_3CH_2\overset{CH_3}{\underset{OH}{C}}CH_2CH_3$

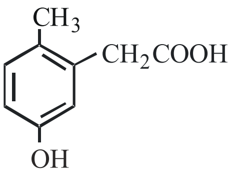
(b) 
$CH_3CH_2CH_2\overset{OH}{C}HCH_3$

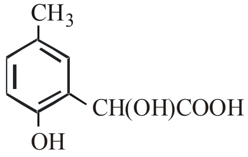
(c) $CH_3CH_2CH_2CH_2CH_2OH$

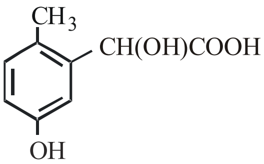
(d) 
$CH_3CH_2\underset{CH_3}{C}HCH_2CH_2OH$

9. *p*-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

(a) 

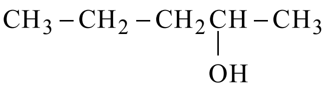
(b) 

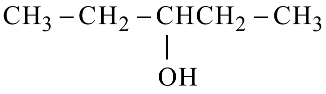
(c) 

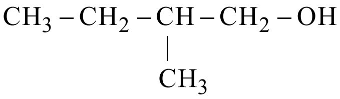
(d) 

10. A compound 'A' having the molecular formula $C_5H_{12}O$, on oxidation gives a compound 'B' with molecular formula $C_5H_{10}O$. Compound 'B' gave a 2,4-dinitrophenylhydrazine derivative but did not answer haloform test or silver mirror test. The structure of compound 'A' is

(a) $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH$

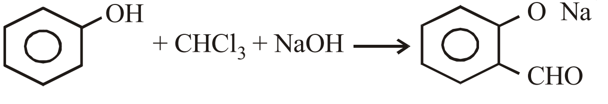
(b) 
$CH_3 - CH_2 - CH_2\underset{OH}{C}H - CH_3$

(c) 
$CH_3 - CH_2 - \underset{OH}{C}HCH_2 - CH_3$

(d) 
$CH_3 - CH_2 - \underset{CH_3}{CH} - CH_2 - OH$

11. HBr reacts with $CH_2= CH - OCH_3$ under anhydrous conditions at room temperature to give

(a) $BrCH_2 - CH_2 - OCH_3$ (b) $H_3C - CHBr - OCH_3$
(c) CH_3CHO and CH_3Br (d) $BrCH_2CHO$ and CH_3OH

12. 

The electrophile involved in the above reaction is

(a) trichloromethyl anion ($\overset{\ominus}{C}Cl_3$)
(b) formyl cation ($\overset{\oplus}{C}HO$)
(c) dichloromethyl cation ($\overset{\oplus}{C}HCl_2$)
(d) dichlorocarbene (**:** CCl_2)

13. $\text{Phenol} \xrightarrow{NaNO_2\,/\,H_2SO_4} B \xrightarrow{H_2O} C \xrightarrow{NaOH} D$

Name of the above reaction is

(a) Liebermann's reaction
(b) Phthalein fusion test
(c) Reimer-Tiemann reaction
(d) Schotten-Baumann reaction

14. Phenol can be converted to o-hydroxy-benzaldehyde by

(a) Kolbe's reaction (b) Reimer-Tiemann reaction
(c) Wurtz reaction (d) Cannizaro reaction

15. $Y\ (\text{mix}) \xleftarrow[2]{\text{conc. HI}} (CH_3)_3C - O - CH_3 \xrightarrow[1]{\text{Anhydrous HI}} X\ (\text{mix})$

(a) X and Y are identical mixture of CH_3I and $(CH_3)_3C - OH$
(b) X and Y are identical mixture of CH_3OH & $(CH_3)_3C–I$
(c) X is mixture of CH_3I and $(CH_3)_3C - OH$
(d) Y is mixture of CH_3OH & $(CH_3)_3C–I$

16. What are the starting materials to get 2-methylpropene as the major product ?

(a) Sodium methoxide and *sec*-butyl bromide.
(b) Sodium ethoxide and *sec*-butyl bromide.
(c) Sodium *tert*-butoxide and ethyl bromide.
(d) Sodium methoxide and *tert*-butyl bromide.

17. $ClCH_2CH_2OH$ is stronger acid than CH_3CH_2OH because of:

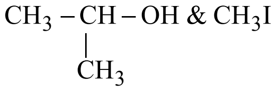
(a) – I effect of Cl increases negative charge on O atom of alcohol
(b) – I effect of Cl disperses negative charge on O atom to produce more stable cation
(c) – I effect of Cl disperses negative charge on O atom to produce more stable anion
(d) None of these

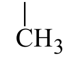
18. $CH_3 - CH = CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2/H_2O} X + Na$

$\longrightarrow Y + CH_3Cl \longrightarrow Z + HI \xrightarrow{0°C} A + B$

What are A and B ?

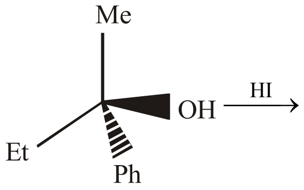
(a) $CH_3 - CH_2 - CH_2 - OH$ & CH_3I

(b) 
$CH_3 - \underset{CH_3}{CH} - OH$ & CH_3I

(c) 
$CH_3 - \underset{CH_3}{CH} - I$ & CH_3OH

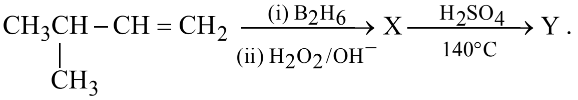
(d) $CH_3 - CH_2CH_2I$ & CH_3OH

19. How many iodides are produced in more than 5% yield?



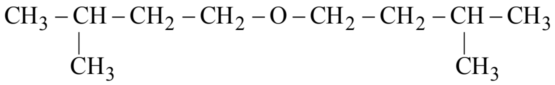
(a) 5 (b) 2

(c) 3 (d) 1

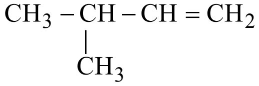
20.


$$\underset{\underset{CH_3}{|}}{CH_3CH}-CH=CH_2 \xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ B_2H_6} X \xrightarrow[140°C]{H_2SO_4} Y.$$

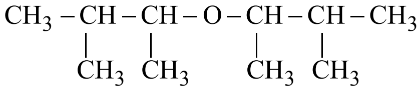
What is Y ?

(a)


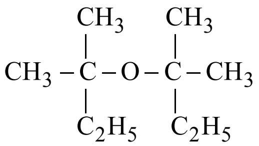
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-O-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

(b)


$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2$$

(c)


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

(d)


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-O-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-CH_3$$

21. Compound 'A' of molecular formula $C_4H_{10}O$ on treatment with Lucas reagent at room temperature gives compound 'B'. When compound 'B' is heated with alcoholic KOH, it gives isobutene. Compound 'A' and 'B' are respectively

(a) 2-methyl-2-propanol and 2-methyl-2-chloropropane

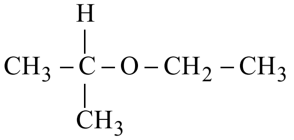
(b) 2-methyl-1 -propanol and 1-chloro-2-methylpropane

(c) 2-methyl-1 -propanol and 2-methyl-2-chloropropane

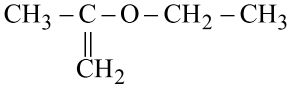
(d) butan-2-ol and 2-chlorobutane

22. $\underset{(C_5H_{10}O)}{(X)} \xrightarrow{H_3O^+} Y + Z$ (Y and Z both give the Iodoform test). The compound X is –

(a) $CH_3-CH=CH-O-CH_2-CH_3$

(b)


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

(c)


$$CH_3-\underset{\underset{CH_2}{||}}{C}-O-CH_2-CH_3$$

(d) Both (a) and (c)

DIRECTIONS for Qs. 23 to 25 : These are Assertion-Reason type questions. Each of these questions contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

(a) Statement-1 is true, Statement-2 is true, Statement-2 is a correct explanation for Statement -1

(b) Statement-1 is true, Statement-2 is true ; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is true, Statement-2 is false

(d) Statement-1 is false, Statement-2 is true

23. **Statement-1 :** A triester of glycerol and palmitic acid on boiling with aqueous NaOH gives a solid cake having soapy touch

Statement-2 : Free glycerol is liberated which is a greasy solid

24. **Statement-1 :** Phenol undergo Kolbe reaction, ethanol does not.

Statement-2 : Phenoxide ion is more basic than ethoxide ion.

25. **Statement-1 :** Lucas reagent is a mixture of anhydrous $ZnCl_2$ and concentrate HCl

Statement-2 : Primary alcohol produce ppt. with Lucas reagents.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

Exemplar Questions

1. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields

(a) *o* – cresol (b) *m* – cresol

(c) 2, 4 – dihydroxytoluene (d) benzyl alcohol

2. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?

(a) 1 (b) 2

(c) 3 (d) 4

3. What is the correct order of reactivity of alcohols in the following reaction?

$$R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$$

(a) $1° > 2° > 3°$ (b) $1° < 2° < 3°$

(c) $3° > 2° > 1°$ (d) $3° > 1° > 2°$

4. CH_3CH_2OH can be converted into CH_3CHO by ....

(a) catalytic hydrogenation

(b) treatment with $LiAlH_4$

(c) treatment with pyridinium chlorochromate

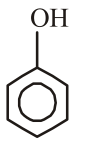
(d) treatment with $KMnO_4$

5. The process of converting alkyl halides into alcohols involves ....

(a) addition reaction (b) substitution reaction

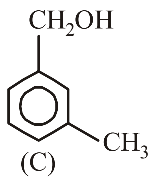
(c) dehydrohalogenation (d) rearrangement reaction

6. Which of the following compounds is aromatic alcohol?

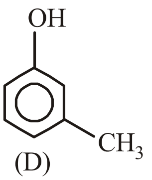


(A)

(B)



(C)

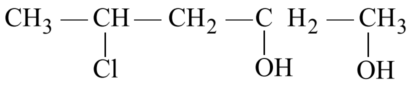


(D)

(a) A, B, C, D (b) A, D

(c) B, C (d) A

7. Give IUPAC name of the compound given below.

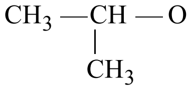


$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{C}\;H_2-\underset{\underset{OH}{|}}{CH_3}$$

(a) 2-chloro-5-hydroxyhexane
(b) 2-hydroxy-5-chlorohexane
(c) 5-chlorohexan-2-ol
(d) 2-chlorohexan-5-ol

8. IUPAC name of m-cresol is ....
(a) 3-methylphenol (b) 3-chlorophenol
(c) 3-methoxyphenol (d) benzene-1,3-diol

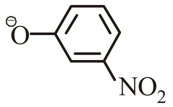
9. IUPAC name of the compound



$CH_3-\underset{\underset{CH_3}{|}}{CH}-OCH_3$ is

....
(a) 1-methoxy-1methylethane
(b) 2-methoxy-2-methylethane
(c) 2-methoxypropane
(d) isopropylmethyl ether

10. Which of the following species can act as the strongest base?
(a) $^{\ominus}OH$ (b) $^{\ominus}OR$
(c) $^{\ominus}OC_6H_5$ (d)

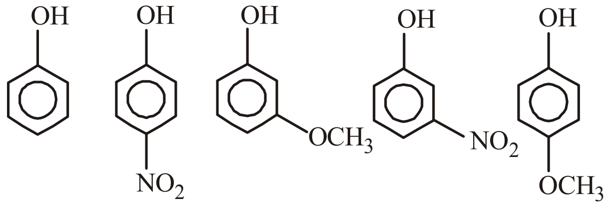


11. Which of the following compounds will react with sodium hydroxide solution in water?
(a) C_6H_5OH (b) $C_6H_5CH_2OH$
(c) $(CH_3)_3COH$ (d) C_2H_5OH

12. Phenol is less acidic than ....
(a) ethanol (b) *o* - nitrophenol
(c) *o*-methylphenol (d) *o*-methoxyphenol

13. Which of the following is most acidic?
(a) Benzyl alcohol (b) Cyclohexanol
(c) Phenol (d) *m*-chlorophenol

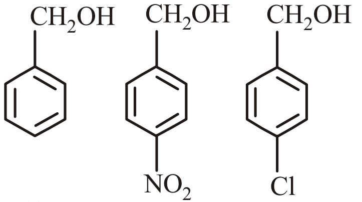
14. Mark the correct order of decreasing acid strength of the following compounds.



(i) (ii) (iii) (iv) (v)

(a) V > IV > II > I > III (b) II > IV > I > III > V
(c) IV > V > III > II > I (d) V > IV > III > II > I

15. Mark the correct increasing order of reactivity of the following compounds with HBr/HCl.



(I) (II) (III)

(a) I < II < III (b) II < I < III
(c) II < III < I (d) III < II < I

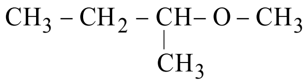
16. Arrange the following compounds in increasing order of boiling point.
Propan - 1- ol, butan - 1 - ol, butan - 2 - ol, pentan - 1 - ol
(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
(d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

NEET/AIPMT (2013-2017) Questions

17. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?

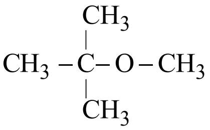
[2013]

(a)



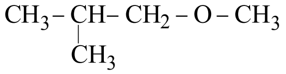
$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-O-CH_3$

(b)



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_3$

(c)



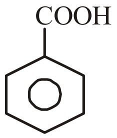
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_3$

(d) $CH_3-CH_2-CH_2-CH_2-O-CH_3$

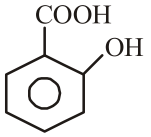
18. Phenol is distilled with Zn dust followed by Friedel Crafts alkylation with propyl chloride in the presence of $AlCl_3$ to give a compound (B). (B) is oxidised in the presence of air to form the compound (C). The structural formula of (C) is

[NEET Kar. 2013]

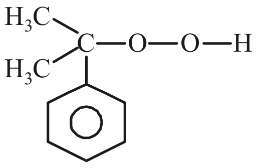
(a)



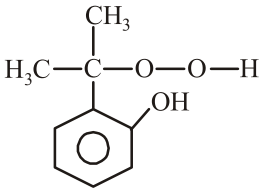
(b)



(c)



(d)



19. Number of isomeric alcohols of molecular formula $C_6H_{14}O$ which give positive iodoform test is ***[NEET Kar. 2013]***
(a) two (b) three
(c) four (d) five

20. Among the following sets of reactants which one produces anisole? ***[2014]***

(a) $CH_3CHO; RMgX$

(b) $C_6H_5OH; NaOH ; CH_3I$

(c) C_6H_5OH; neutral $FeCl_3$

(d) $C_6H_5–CH_3; CH_3COCl; AlCl_3$

21. Which of the following will not be soluble in sodium hydrogen carbonate? ***[2014]***

(a) 2, 4, 6-trinitrophenol

(b) Benzoic acid

(c) *o*-Nitrophenol

(d) Benzenesulphonic acid

22. Identify Z in the sequence of reactions: ***[2014]***

$$CH_3CH_2CH{=}CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$$

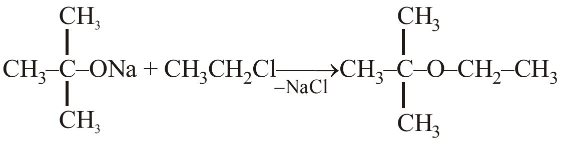
(a) $CH_3—(CH_2)_3—O—CH_2CH_3$

(b) $(CH_3)_2\,CH_2—O—CH_2CH_3$

(c) $CH_3(CH_2)_4—O—CH_3$

(d) $CH_3CH_2—CH(CH_3)—O—CH_2CH_3$

23. The reaction



$$CH_3–\overset{CH_3}{\underset{CH_3}{C}}–ONa + CH_3CH_2Cl \xrightarrow[-NaCl]{} CH_3–\overset{CH_3}{\underset{CH_3}{C}}–O–CH_2–CH_3$$

is called :- ***[2015]***

(a) Williamson continuous etherification process

(b) Etard reaction

(c) Gatterman - Koch reaction

(d) Williamson Synthesis

24. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group ? ***[2015 RS]***

(a) $–CH_2Cl$ (b) $–COOH$

(c) $–CHCl_2$ (d) $–CHO$

25. Which of the following reaction (s) can be used for the preparation of alkyl halides ? ***[2015 RS]***

(I) $CH_3CH_2OH + HCl \xrightarrow{anh.ZnCl_2}$

(II) $CH_3CH_2OH + HCl \longrightarrow$

(III) $(CH_3)_3COH + HCl \longrightarrow$

(IV) $(CH_3)_2CHOH + HCl \xrightarrow{anh.ZnCl_2}$

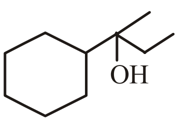
(a) (I), (III) and (IV) only

(b) (I) and (II) only

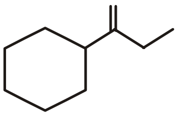
(c) (IV) only

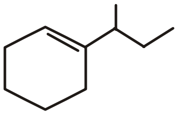
(d) (III) and (IV) only

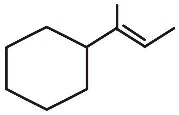
26. Which of the following is not the product of dehydration of

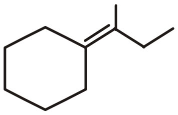


? ***[2015 RS]***

(a)


(b)


(c)


(d)


27. Which of the following reagents would distinguish cis-cyclopenta-1,2-diol from the trans-isomer? ***[2016]***

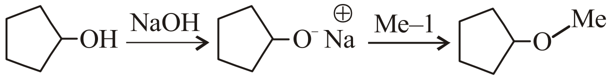
(a) Acetone

(b) Ozone

(c) MnO_2

(d) Aluminium isopropxide

28. The reaction



Can be classified as :- ***[2016]***

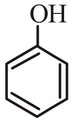
(a) Williamson ether synthesis reaction

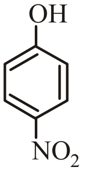
(b) Alcohol formation reaction

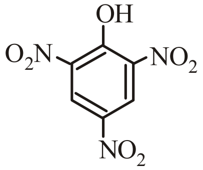
(c) Dehydration reaction

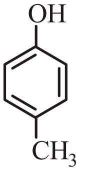
(d) Williamson alcohol synthesis reaction

29. Which one is the most acidic compound ? ***[2017]***

(a)


(b)


(c)


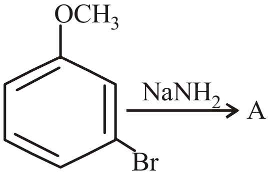
(d)


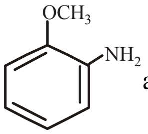
30. The heating of phenyl-methyl ethers with HI produces

(a) Iodobenzene (b) Phenol ***[2017]***

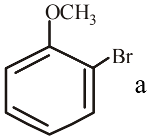
(c) Benzene (d) Ethyl chlorides

31. Identify A and predict the type of reaction ***[2017]***

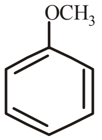


(a)


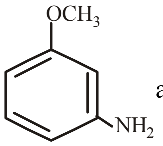
and elimination addition reaction

(b)


and cine substitution reaction

(c)


and cine substitution reaction

(d)


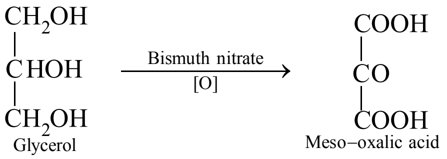
and substitution reaction

Hints & Solutions

EXERCISE - 1

1. (a) Lucas reagent is conc. HCl + anhyd. $ZnCl_2$.

2. (d)



$$\underset{\text{Glycerol}}{\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}} \xrightarrow[\text{[O]}]{\text{Bismuth nitrate}} \underset{\text{Meso-oxalic acid}}{\begin{matrix} COOH \\ | \\ CO \\ | \\ COOH \end{matrix}}$$

3. (b) Methanol

$$\underset{\text{water gas}}{CO + 2H_2} \xrightarrow[\substack{673K \\ \text{High pressure}}]{Cr_2O_3-ZnO} \underset{\text{Methanol}}{CH_3OH}$$

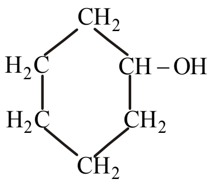
4. (b) C_2H_5OH and CH_3-O-CH_3 are isomers.

5. (b) Example

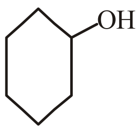
$$R-CH_2-CH_2-OH \xrightarrow[\Delta]{Al_2O_3} R-CH=CH_2 + H_2O$$

6. (b) 5-10 % methanol and remaing ethanol is called methylated spirit. It is also known as denatured alcohol because it is unfit for drinking.

7. (a)

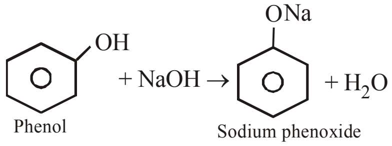


or



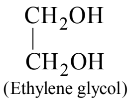
8. (c)

9. (a) Phenol is more soluble in NaOH and forms salts.



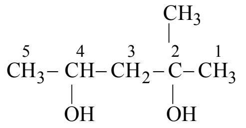
10. (a)

11. (b) Glycols are dihydric alcohols (having two hydroxyl groups). Ethylene glycol is the first member of this series.



$$\underset{\text{(Ethylene glycol)}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}}$$

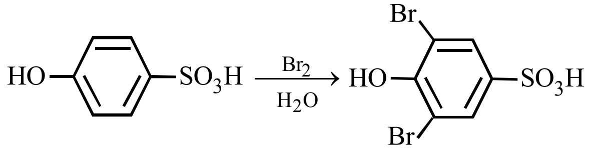
12. (b)



$$\overset{5}{CH_3}-\underset{\substack{| \\ OH}}{\overset{4}{CH}}-\overset{3}{CH_2}-\underset{\substack{| \\ OH}}{\overset{\substack{CH_3 \\ | \\ 2}}{C}}-\overset{1}{CH_3}$$

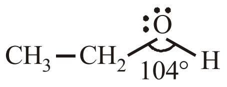
2-methyl- 2, 4-pentanediol.

13. (c)



– OH group is highly activating. This is a type of electrophillic substitution reaction at ortho and para position.

14. (b) In C_2H_5OH,



Due to presence of lone pair of electrons on oxygen, there occurs a small decrease in bond angle from the normal tetrahedral bond angle (109°28′)

15. (d) Water gas is mixed with half its volume of hydrogen.The mixture is compressed to approximately 200 – 300 atmospheres. It is then passed over a catalyst [ZnO + Cr_2O_3] at 300°C. Methyl alcohol vapours are formed which are condensed

$$\underset{\text{Water gas}}{CO + 2H_2} \xrightarrow[300°C]{ZnO+Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3OH}$$

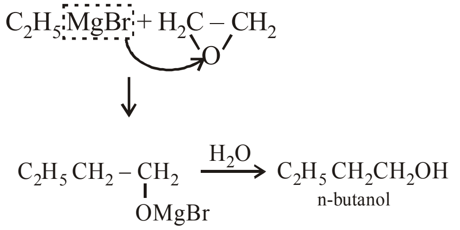
16. (a)

$$R-CH_2-OH \xrightarrow[\text{Protonation}]{H^+}$$

$$\underset{\text{carbonium ion}}{R-\overset{+}{C}H_2} + H_2O$$

17. (b) Greater the stability of the intermediate carbocation, more reactive is the alcohol. Since 2-methylpropan-2-ol generates 3° carbocation, therefore, it reacts fastest with HBr.

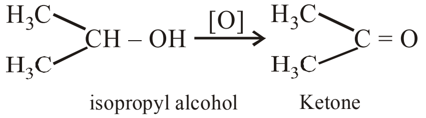
18. (b)



19. (c) Primary alcohol on oxidation give aldehyde which on further oxidation give carboxylic acid whereas secondary alcohols give ketone.

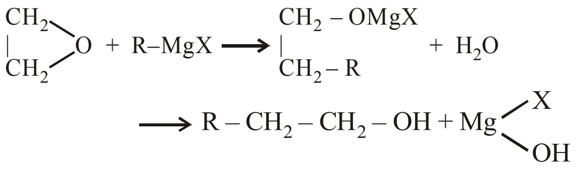
$$\underset{\text{n-propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{[O]}$$

$$CH_3CH_2CHO \xrightarrow{[O]} CH_3CH_2COOH$$



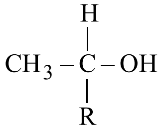
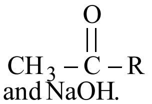
isopropyl alcohol Ketone

20. (c) Ethylene oxide when treated with Grignard Reagent gives primary alcohol.



$$\underset{CH_2}{\overset{CH_2}{|}}\!\!>O + R{-}MgX \longrightarrow \underset{CH_2-R}{\overset{CH_2-OMgX}{|}} + H_2O$$

$$\longrightarrow R-CH_2-CH_2-OH+Mg<^{X}_{OH}$$

21. (b) The compounds containing  $CH_3-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-OH$ or  $CH_3-\overset{\overset{O}{\|}}{C}-R$ (R = H, alkyl or aryl) give CHI_3 with I_2 and NaOH.

22. (b) Conc. HCl, HBr and conc. HCl + $ZnCl_2$ all are nucleophiles, thus convert alcohols to alkyl halides. However, conc. H_3PO_4 is a good dehydrating agent which converts an alcohol to an alkene.

23. (b) $NaBH_4$ and $LiAlH_4$ attacks only carbonyl group and reduce it into alcohol group.

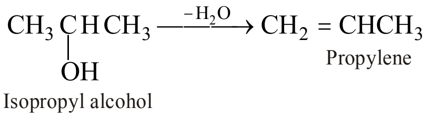
$$\underset{\text{cinnamic aldehyde}}{C_6H_5-CH=CHCHO}\xrightarrow{NaBH_4}\underset{\text{cinnamic alcohol}}{C_6H_5-CH=CH.CH_2OH}$$

24. (d) Phenol has active (acidic) hydrogen so it reacts with CH_3MgI to give CH_4, and not anisole

$$C_6H_5OH+CH_3MgI\longrightarrow CH_4+C_6H_5OMgI$$

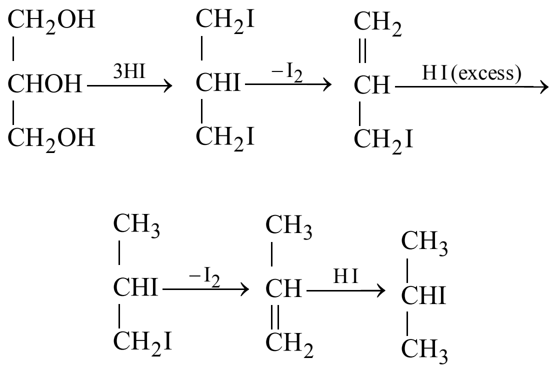
25. (b)

26. (b) Since the compound is formed by hydration of an alkene, to get the structure of alkene remove a molecule of water from the alcohol.



$$\underset{\text{Isopropyl alcohol}}{CH_3\underset{\underset{OH}{|}}{C}HCH_3}\xrightarrow{-H_2O}\underset{\text{Propylene}}{CH_2=CHCH_3}$$

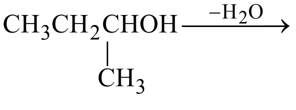
27. (c)



$$\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}\xrightarrow{3HI}\begin{matrix}CH_2I\\|\\CHI\\|\\CH_2I\end{matrix}\xrightarrow{-I_2}\begin{matrix}CH_2\\ \|\\CH\\|\\CH_2I\end{matrix}\xrightarrow{HI(excess)}\begin{matrix}CH_3\\|\\CHI\\|\\CH_2I\end{matrix}\xrightarrow{-I_2}\begin{matrix}CH_3\\|\\CH\\ \|\\CH_2\end{matrix}\xrightarrow{HI}\begin{matrix}CH_3\\|\\CHI\\|\\CH_3\end{matrix}$$

∴ All the compounds except (C), $CH_2OH-CHI-CH_2OH$ are formed during reaction of glycerol with excess HI.

28. (d)



$$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HOH\xrightarrow{-H_2O}$$

$$\underset{\text{(Major product)}}{CH_3CH=CHCH_3}+\underset{\text{(Minor product)}}{CH_3CH_2CH=CH_2}$$

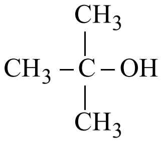
29. (d) Glycerol is dehydrated by using dehydrating agent like P_2O_5 or conc H_2SO_4 or $KHSO_4$ but $KHSO_4$ is best of them.

30. (d) Lucas reagent is anhydrous $ZnCl_2$ and conc. HCl. It is used to distinguish between 1°, 2° and 3° alcohols.

3° alcohols → immediate turbidity

2° alcohols → turbidity after 5 minutes

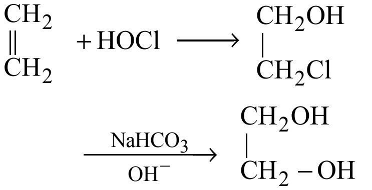
1° alcohols → No turbidity at room temp.

 $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$ is a tertiary alcohol hence it will give fastest reaction with Lucas reagent.

31. (b) Phenol is more acidic than ethanol. Phenols can turn blue litmus paper red but ethanol can not do so.

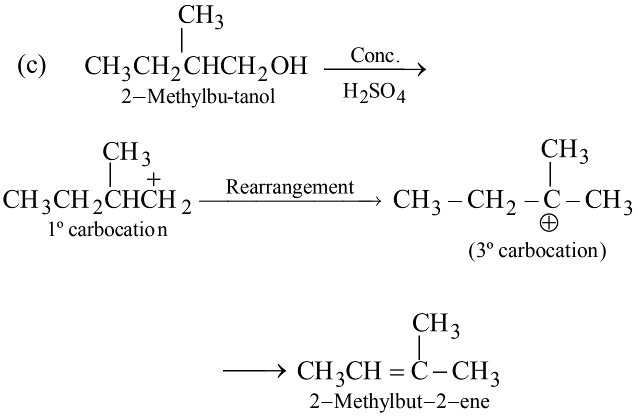
32. (d) Solubility of alcohol in water decreases with increase in molecular mass due to increase in water repelling alkyl part in alcohol.

33. (c)



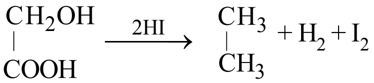
$$\underset{CH_2}{\overset{CH_2}{\|}}+HOCl\longrightarrow\underset{CH_2Cl}{\overset{CH_2OH}{|}}\xrightarrow[OH^-]{NaHCO_3}\underset{CH_2-OH}{\overset{CH_2OH}{|}}$$

34. (c)



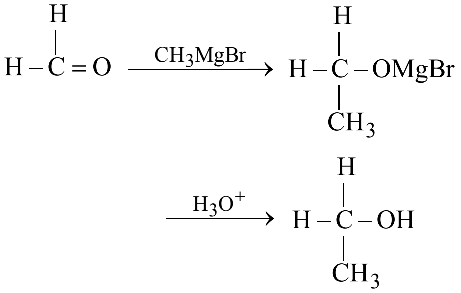
$$\underset{\text{2–Methylbu-tanol}}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2OH}\xrightarrow[H_2SO_4]{Conc.}\underset{\text{1° carbocation}}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}H\overset{+}{C}H_2}\xrightarrow{\text{Rearrangement}}\underset{\text{(3° carbocation)}}{CH_3-CH_2-\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}-CH_3}\longrightarrow\underset{\text{2–Methylbut–2–ene}}{CH_3CH=\overset{\overset{CH_3}{|}}{C}-CH_3}$$

35. (b)



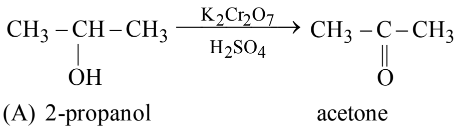
$$\underset{COOH}{\overset{CH_2OH}{|}}\xrightarrow{2HI}\underset{CH_3}{\overset{CH_3}{|}}+H_2+I_2$$

36. (a)



$$H-\overset{\overset{H}{|}}{C}=O\xrightarrow{CH_3MgBr}H-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-OMgBr\xrightarrow{H_3O^+}H-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-OH$$

37. (b) Iodoform test can differentiate between ethyl alcohol and methyl alcohol. Ethyl alcohol contains CH_3CO group so it gives Iodoform test whereas methyl alcohol does not give this test.

38. (c) 

$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\underset{\displaystyle O}{\underset{||}{C}}-CH_3$$

(A) 2-propanol acetone

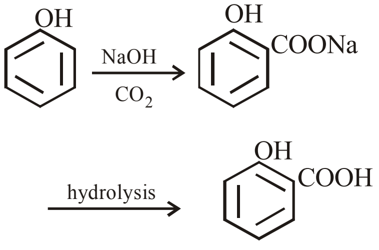
$$\xrightarrow{[O]} \underset{\text{acetic acid}}{CH_3COOH}$$

39. (b) $CH_3OH \xrightarrow{\text{Oxidation}} \underset{(A)}{HCOOH} \xrightarrow{NH_3} \underset{(B)}{HCOONH_4}$

40. (b) $C_2H_5OH \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow{KCN}$

$$CH_3CH_2CN \xrightarrow{H_3O^+} \underset{\text{propanoic acid}}{CH_3CH_2COOH}$$

41. (c) Because of larger (three per molecule) number of intermolecular hydrogen bonding in case of glycerol ($CH_2OH - CHOH - CH_2OH$) as compared to ethanol (CH_3CH_2OH), the attraction between molecules of glycerol is more than that of molecules of ethanol. Due to this glycerol is more viscous than ethanol.

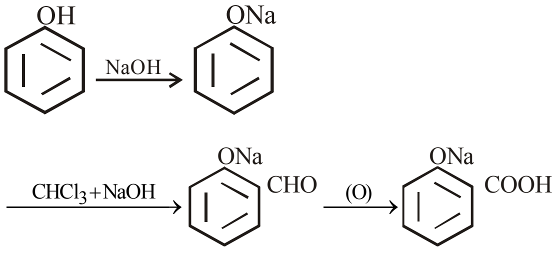
42. (c) 

Salicylic acid

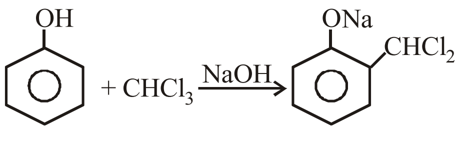
43. (d) The intermediate is carbocation which is destabilised by C = O group (present on α-carbon to the –OH group) in the first three cases. In (d), α–hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the C = O group.

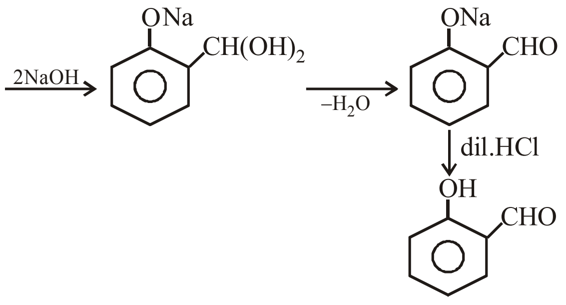
44. (d) Among the given compounds only CH_3OH does not give iodoform reaction.

45. (a) Due to H–bonding boiling point of C_2H_5OH is much higher than isomeric $(CH_3)_2O$.

46. (c) 

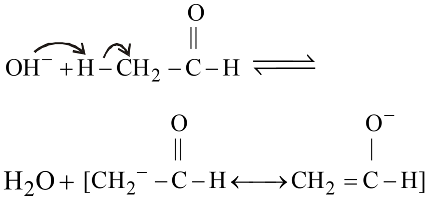
Salicylaldehyde

47. (b) 



Reimer-Tiemann reaction.

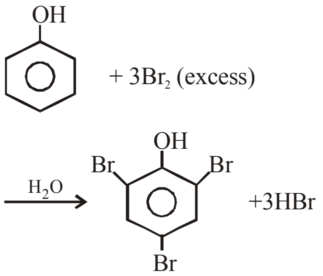
48. (b) Aldol condensation is carried out on aldehydes or ketones having α-hydrogen atom in presence of base which abstracts α- H atom from aldehyde/ketone to form corresponding carbanion which is stabilised by resonance.



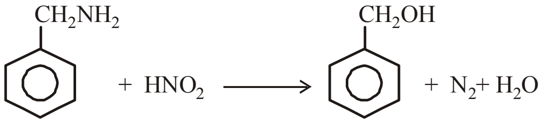
$$OH^- + H-CH_2-\overset{\displaystyle O}{\overset{||}{C}}-H \rightleftharpoons$$

$$H_2O + [CH_2^- -\overset{\displaystyle O}{\overset{||}{C}}-H \longleftrightarrow CH_2=\overset{\displaystyle O^-}{\overset{|}{C}}-H]$$

49. (d) With Br_2 water, phenol gives 2, 4, 6- tribromophenol.



2, 4, 6-Tribromophenol

50. (d) 

51. (c) Alkyl halides can be prepared by treating alcohol with $SOCl_2$.

$$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$$

This reaction is known as Darzen's procedure.

Note : $SOBr_2$ and SOI_2 are not used in this reaction because $SOBr_2$ is less stable and SOI_2 does not exist.

52. (c) Perkin reaction involves reaction of aromatic aldehyde with aliphatic acid anhydride in presence of sodium salt of the same acid as anhydride to form α, β-unsaturated acid.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH = CHCOOH + CH_3COOH$$

Wurtz reaction involves the reaction of an alkyl halide with metallic sodium in dry ether to form higher hydrocarbon.

$$RX + 2Na + XR \xrightarrow[\text{ether}]{\text{dry}} R-R + 2NaX$$

Cannizzaro reaction is given by aldehydes having no α-hydrogen atom to form a mixture of alcohol and sodium salt of the acid. It is a disproportionation reaction in which half of the aldehyde molecules are oxidised and other half reduced in presence of NaOH.

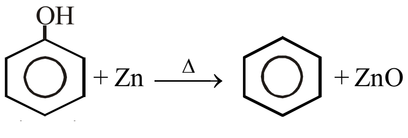
$$2C_6H_5CHO \xrightarrow{NaOH}$$

$$C_6H_5CH_2OH + C_6H_5COONa$$

Claisen reaction is the self condensation of esters having α-hydrogen atom in presence of strong base to form β-keto ester.

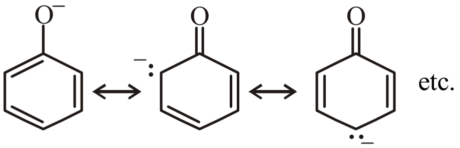
$$2CH_3COOC_2H_5 \xrightarrow[C_2H_5ONa]{C_2H_5OH}$$

$$CH_3\overset{O}{\overset{||}{C}}CH_2COOC_2H_5$$

53. (c) 

Phenol Benzene

54. (d) The most suitable reagent for converting alcohol to acetaldehyde is PCC. Other reagent will convert alcohol to acid.

55. (c) 

Resonance stabilisation of phenoxide ion
(conjugate base of phenol)

Conjugate base of ethyl alcohol, i.e., $C_2H_5O^-$ does not show resonance.

56. (a) 

Salicylic acid
(evolves CO_2 with $NaHCO_3$)

Phenol
(No reaction with $NaHCO_3$)

57. (c) *o*-Nitrophenol has intramolecular *H*-bonding.

58. (b) The reaction is an example of electrophilic aromatic substitution. Although both OCH_3 and CH_3 groups are *o*,*p*-directing, the OCH_3 group dominates. Product (b) is favoured because the new coming group (Br) experiences least hindrance.

59. (a) $C_6H_5ONa + C_2H_5I \xrightarrow{\Delta} \underset{\text{Phenetole}}{C_6H_5OC_2H_5} + NaI$

60. (a) In case of unsymmetrical ethers, the site of cleavage depends on the nature of alkyl group.

e.g. $CH_3-O-C_2H_5 + HI \xrightarrow{373K} CH_3I + C_2H_5OH$

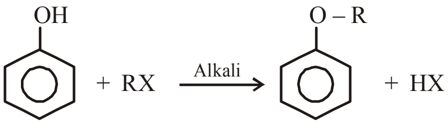
The alkyl halide is formed from the smaller alkyl group.

However, in case of tertiary alkyl ether following reaction occurs.

$$\underset{\textit{ter}\text{-butyl methyl ether}}{CH_3-OC(CH_3)_3} + HI \xrightarrow{373K}$$

$$(CH_3)_3C-I + CH_3OH$$

The alkyl halide is formed from the tertiary alkyl group and the cleavage of such ethers occurs by S_N1 mechanism as the product is controlled by the formation of more stable intermediate tertiary carbocation from protonated ether.

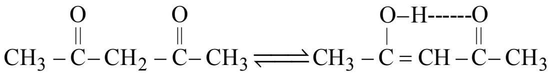
61. (c) 

62. (b) Williamson's synthesis -

$$CH_3-CH_2-ONa + Cl-CH_2-CH_3 \rightarrow$$

$$CH_3-CH_2-O-CH_2-CH_3$$

63. (b) Maximum enol content is in structure (b) because here the enol form is stabilised by H-bonding.



$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-CH_3 \rightleftharpoons CH_3-\overset{O-H\text{------}}{\overset{|}{C}}=CH-\overset{O}{\overset{||}{C}}-CH_3$$

keto form Acetylacetone enol form

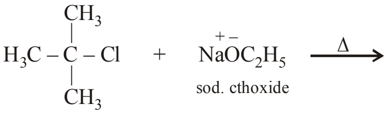
64. (a) Dehydration of alcohols gives ethers

65. (b) $C_2H_5OH + HOOCCH_3 \longrightarrow C_2H_5COOCH_3 + H_2O$

ethyl acetate (ester)
fruity smell

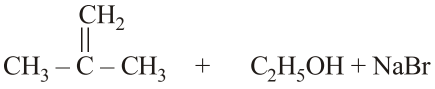
66. (b) Reaction of sodium ethoxide with ethyl iodide to produce diethyl ether is known as Williamson synthesis. It is a nucleophilic substitution reaction and proceeds via S_N2 mechanism.

67. (a) In Williamson's synthesis the reaction of alkyl halides with sodium alkoxides give ethers. However, if the alkyl halide is 3°, it undergoes elimination to give an alkene.



$$H_3C-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-Cl + \overset{+}{Na}\overset{-}{O}C_2H_5 \xrightarrow{\Delta}$$

tert-butyl chloride sod. cthoxide



$$CH_3-\overset{CH_2}{\overset{||}{C}}-CH_3 + C_2H_5OH + NaBr$$

2-Methyl-1-propene

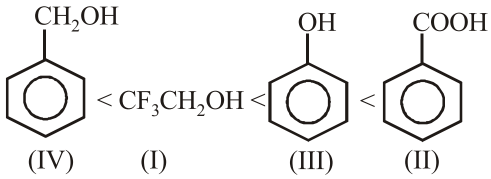
68. (d) $C_2H_5-O-C_2H_5 + O_2 \xrightarrow[25°C]{hv}$

$$CH_3-CH(OOH)-O-C_2H_5$$

69. (c) CH_3OCH_3 and $C_2H_5OCH_3$ are gases while $C_2H_5OC_2H_5$ (b. p. 308 K) is low boiling liquid.

70. (c) Carboxylic acids are stronger acids than phenols which in turn are stronger than alcohols. Out of benzyl alcohol and trifluoroethanol, the latter is more acidic due to the

presence of highly electronegative fluorine atoms. Thus, order of acidity is:



71. (a) $C_2H_5OC_2H_5 \xrightarrow[\text{Cleavage of ethers}]{\text{Red P / HI}} 2C_2H_5I$

$\xrightarrow[\text{Reduction}]{\text{Red P / HI}} \underset{\text{Ethane}}{2C_2H_6}$

72. (b) Only alkyl aryl ethers e.g., $C_6H_5OCH_3$ undergoes electrophilic substitution reactions.

73. (c) $R-O-R \xrightarrow{BF_3} \underset{\text{Etherate}}{\begin{matrix}R\\R\end{matrix}\!>\!\ddot{O} \rightarrow BF_3}$

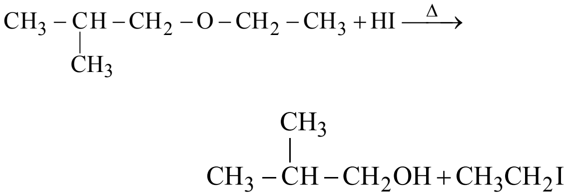
74. (a) The ease of dehydration of alcohols is 3° > 2° > 1°. Tertiary alcohols undergo dehydration more easily than primary and secondary alcohols.

75. (c) $C_2H_5OC_2H_5 + 2\,HI \xrightarrow{\Delta} 2\,C_2H_5I + H_2O$

76. (a) $C_6H_6O^- + CH_3I \rightarrow C_6H_5OCH_3 + I^-$

77. (d) 1-pentanol
Primary alcohols readily form ether when heated with conc. H_2SO_4.

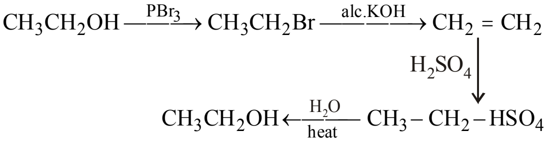
78. (c) In the cleavage of mixed ethers having two different alkyl groups, the alcohol and alkyl iodide that form depend on the nature of alkyl group. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide therefore



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3+HI\xrightarrow{\Delta}$$

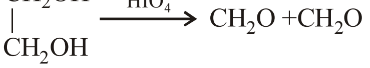
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH+CH_3CH_2I$$

79. (c)



$$\begin{array}{r}CH_3CH_2OH\xrightarrow{PBr_3}CH_3CH_2Br\xrightarrow{\text{alc.KOH}}CH_2=CH_2\\ \downarrow H_2SO_4\\ CH_3CH_2OH\xleftarrow[\text{heat}]{H_2O}CH_3-CH_2-HSO_4\end{array}$$

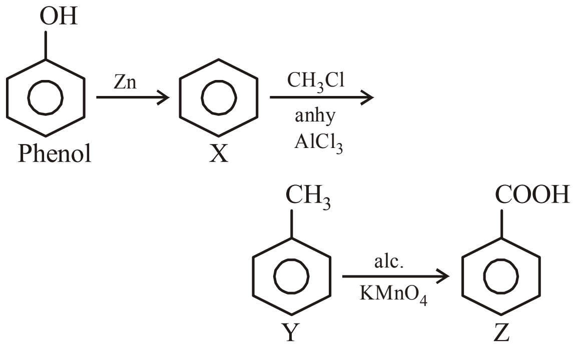
80. (c) 1, 2 – Diols, when treated with an aqueous solution of periodic acid give aldehyde



$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}\xrightarrow{HIO_4}CH_2O+CH_2O$$

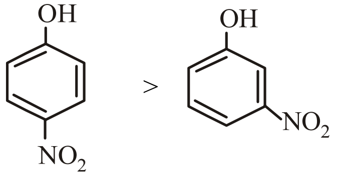
Note that a 1° alcohol gives CH_2O. Since in glycol both the OH groups, are primary hence give 2 molecules of CH_2O as by product.

81. (b)

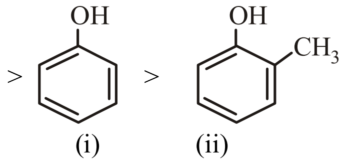


82. (b) Phenol is most acidic because its conjugate base is stabilised due to resonance, while the rest three compounds are alcohols, hence, their corrosponding conjugate bases do not exhibit resonance

83. (b)

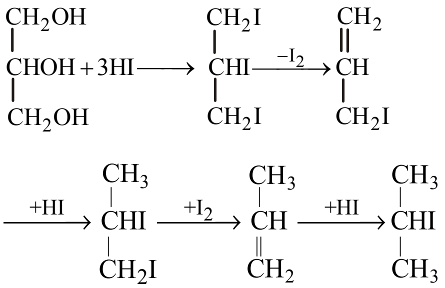


(– I and – M effects, (only – I effect)
both increase acidity)



(+ I effect of CH_3 group decreases acidity)

84. (b) Glycerol when treated with excess HI produces 2–iodopropane

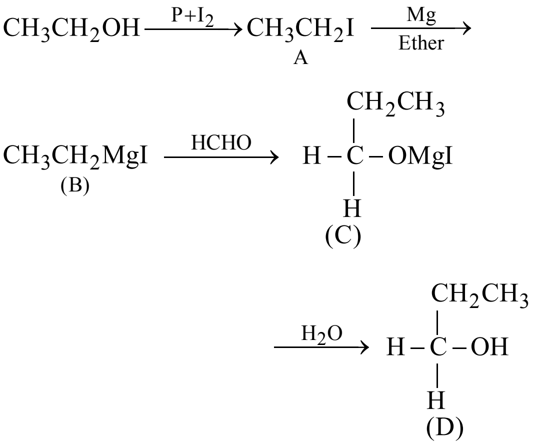


$$\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}+3HI\longrightarrow\begin{matrix}CH_2I\\|\\CHI\\|\\CH_2I\end{matrix}\xrightarrow{-I_2}\begin{matrix}CH_2\\\|\\CH\\|\\CH_2I\end{matrix}$$

$$\xrightarrow{+HI}\begin{matrix}CH_3\\|\\CHI\\|\\CH_2I\end{matrix}\xrightarrow{+I_2}\begin{matrix}CH_3\\|\\CH\\\|\\CH_2\end{matrix}\xrightarrow{+HI}\begin{matrix}CH_3\\|\\CHI\\|\\CH_3\end{matrix}$$

85. (b) Glycol is used as an antifreeze in automobiles.

86. (d)



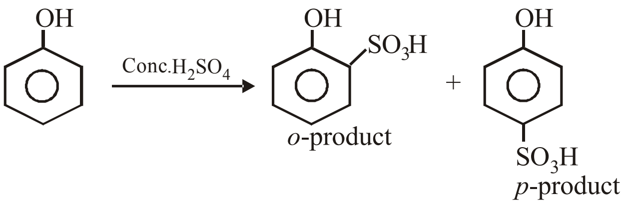
$$CH_3CH_2OH\xrightarrow{P+I_2}\underset{A}{CH_3CH_2I}\xrightarrow[\text{Ether}]{Mg}$$

$$\underset{(B)}{CH_3CH_2MgI}\xrightarrow{HCHO}\underset{(C)}{H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OMgI}$$

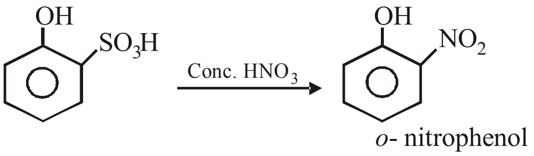
$$\xrightarrow{H_2O}\underset{(D)}{H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH}$$

n–propyl alcohol

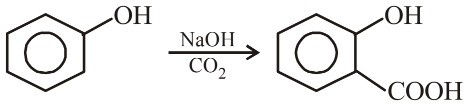
87. (b) Phenol on reaction with conc. H_2SO_4 gives a mixture of *o*- and *p*- products (i.e., $-SO_3H$ group, occupies *o*-, *p*- position). At room temperature *o*-product is more stable, which on treatment with conc. HNO_3 will yield *o*-nitrophenol.



At room temperature *o*- product is more stable



88. (b)

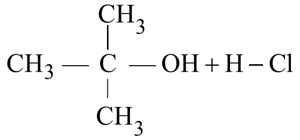


(salicylic acid)

89. (b) Tertiary alcohols react fastest with conc. HCl and anhydrous $ZnCl_2$ (lucas reagent) as its mechanism proceeds through the formation of stable tertiary carbocation.

Mechanism

Step 1 :



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH+H-Cl$$

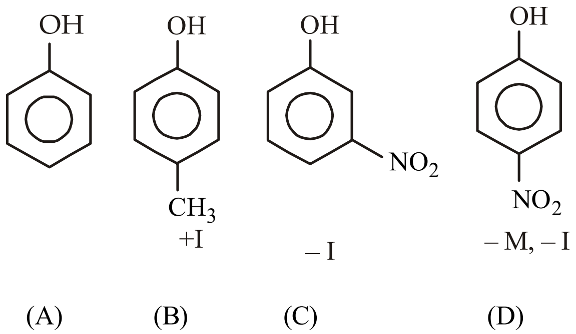
2-Methyl Propan-2-ol

$$\rightleftharpoons (CH_3)_3C-\overset{+}{O}H_2+Cl^-$$

Step 2 : $(CH_3)_3C-\overset{+}{O}H_2 \rightleftharpoons \underset{3^\circ\ \text{Carbocation}}{(CH_3)_3C^+} + H_2O$

Step 3 : $(CH_3)_3C^+ + Cl^- \rightleftharpoons \underset{\text{t-Butyl chloride}}{(CH_3)_3C-Cl}$

90. (a)



Electron withdrawing substituents increases the acidity of phenols; while electron releasing substituents decreases acidity. Further the particular effect (acidity increasing or decreasing) is more when a substituent is present in o-orp position to phenolic group. Thus the correct order will be D > C > A > B

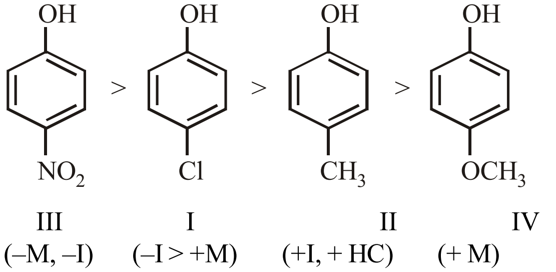
91. (b) $C_2H_5-OH+H_2SO_4 \xrightarrow{433K} CH_2=CH_2$ (ethylene)

$\xrightarrow{413\ K} CH_3-CH_2-O-CH_2-CH_3$ (di ethyl ether)

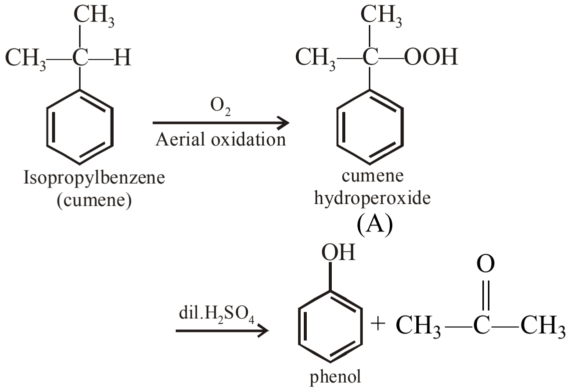
$\xrightarrow{383\ K} CH_3CH_2HSO_4+H_2O$ (ethyl hydrogen sulphate)

Acetylene is not formed under any conditions.

92. (c) Electron withdrawing substituents like $-NO_2$, Cl increase the acidity of phenol while electron releasing substituents like $-CH_3$, $-OCH_3$ decreases acidity. hence the correct order of acidity will be



93. (a)

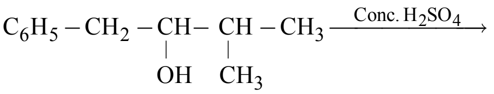


It is a commercial method for the manufacture of phenol.

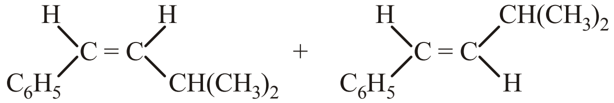
94. (a) Whenever dehydration can produce two different alkenes, major product is formed according to Saytzeff rule *i.e.* more substituted alkene (alkene having lesser number of hydrogen atoms on the two doubly bonded carbon atoms) is the major product.

Such reactions which can produce two or more structural isomers but one of them in greater amount than the other are called regioselective ; in case a reaction is 100% regioselective, it is termed as regiospecific.

In addition to being regioselective, alcohol dehydrations are stereoselective (*a reaction in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amount than any other).*



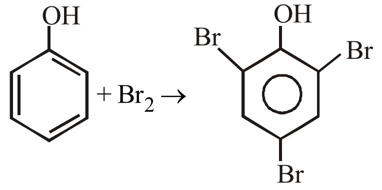
$$C_6H_5-CH_2-\underset{OH}{CH}-\underset{CH_3}{CH}-CH_3 \xrightarrow{\text{Conc. } H_2SO_4}$$



cis (minor) (less stable due to bulky groups lying on same side)

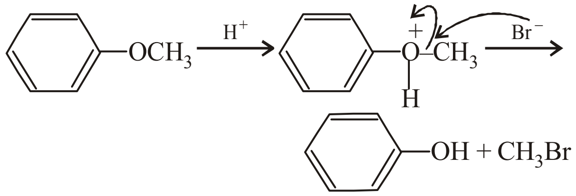
trans (major) (more stable)

95. (d) $5KBr + KBrO_3 + 3H_2O \rightarrow 3Br_2 + 6KOH$

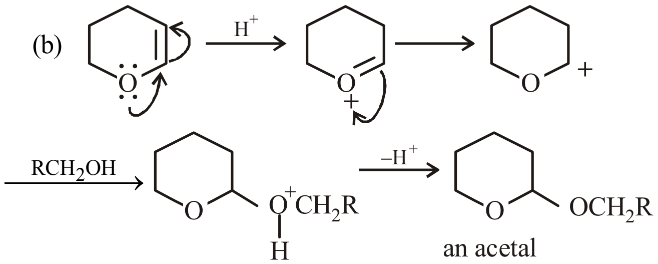


96. (d) Phenol gives a violet colour with neutral ferric chloride solution whereas benzoic acid does not give this test.

97. (d)



98. (b)



an acetal

99. (c) Due to strong electron-donating effect of the OH group, the electron density in phenol is much higher than that in toluene, benzene and chlorobenzene and hence phenol is readily attacked by the electrophile.

100. (c) $KMnO_4$ (alkaline) and OsO_4 / CH_2Cl_2 are used for hydroxylation of double bond while O_3 /Zn is used for ozonolysis. Therefore, the right option is (c), i.e.,

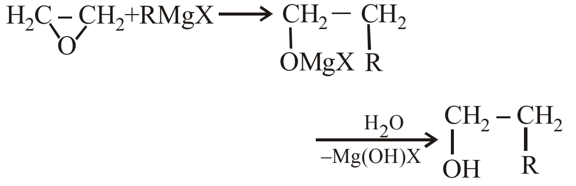
$$3CH_3CH=CH_2 \xrightarrow{BH_3 \text{ in THF}} (CH_3CH_2CH_2)_3B$$

$$\xrightarrow[NaOH]{3H_2O_2} \underset{\text{1-propanol}}{3CH_3CH_2CH_2OH} + H_3BO_3$$

EXERCISE - 2

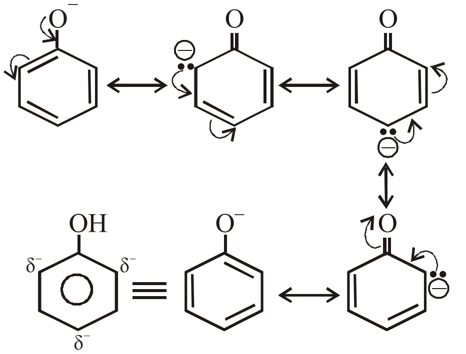
1. (c) $>C=O \xrightarrow{LiAlH_4} \underset{\text{primary alcohol}}{-CH_2OH}$

2. (c) We know that



3. (c) $C_6H_5OH + H_2O \rightleftharpoons \underset{\text{Phenoxide ion}}{C_6H_5O^-} + H_3O^+$

The phenoxide ion is stable due to resonance.



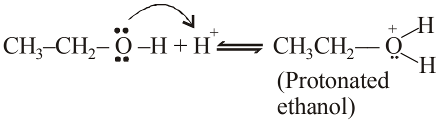
The negative charge is delocalized in the benzene ring which is a stabilizing factor in the phenoxide ion and because of this reason ionization constant of phenol is higher whereas no resonance is possible in alkoxide ions (RO^-)derived from alcohol. The negative charge is localized on oxygen atom in case of alcohols.

4. (c) $R-CH=CH_2 \xrightarrow[(ii)H_2O_2,\ OH^-]{(i)B_2H_6} R-CH_2-CH_2OH$ (oxidative hydroboration of alkene)

5. (c) $CH_3-CH=CH_2 \xrightarrow[NaOH/H_2O_2]{B_2H_6} \underset{\text{Propanol}}{CH_3-CH_2-CH_2-OH}$

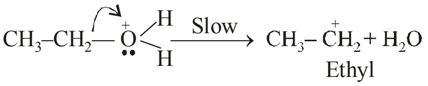
6. (d) The dehydration of alcohol to form alkene occurs in following three step. Step (1) is initiation step.

Step (1) Formation of protonated alcohol.



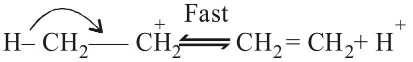
(Protonated ethanol)

Step (2) Formation of carbocation



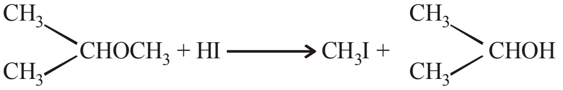
Ethyl carbocation

Step (3)Elimination of a proton to form ethene



ethene

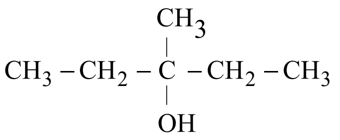
7. (b)



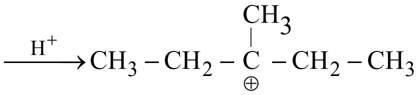
$$(CH_3)_2CHOCH_3 + HI \longrightarrow CH_3I + (CH_3)_2CHOH$$

2-propanol

8. (a) 3-methyl pentanol-3 will be dehydrated most readily since it produces tertiary carbonium ion as intermediate.

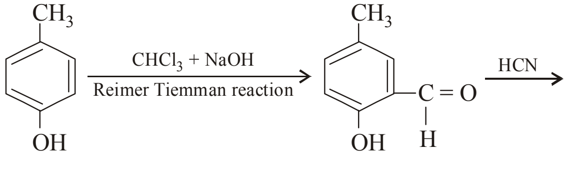


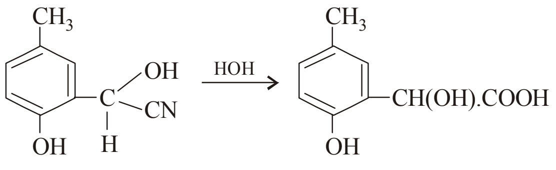
$$CH_3-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_3$$



$$\xrightarrow{H^+} CH_3-CH_2-\overset{CH_3}{\underset{\oplus}{C}}-CH_2-CH_3$$

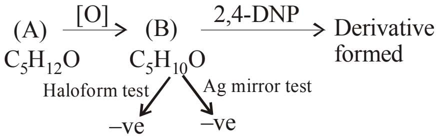
9. (c)





Cyanohydrin

10. (c) According to question

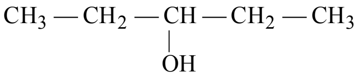


Since (B) on reaction with 2,4-DNP forms a derivative, it implies that (B) has carbonyl ($>C=O$)group (B) gives –ve Tollen's test, hence it is not an aldehyde, it is a ketone.

(B) gives –ve haloform test, thus it is not a methyl ketone.

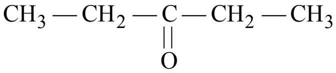
(B) is formed from the oxidation of (A), thus (A) is a 2° alcohol, and among the given options,

(A) is :



$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$

and ∴ (B) is



$CH_3-CH_2-\underset{\underset{O}{||}}{C}-CH_2-CH_3$

11. (b) Methyl vinyl ether under anhydrous condition at room temperature undergoes addition reaction.

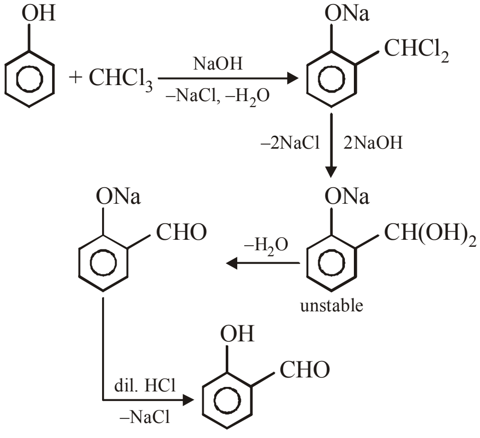
$CH_2=CH-OCH_3 \xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{CH}-O-CH_3$

12. (d) This is Reimer-Tiemann reaction and the electrophile is dichlorocarbene.

$$HCCl_3 + NaOH \longrightarrow \underset{\text{dichlorocarbene}}{Cl-\ddot{C}-Cl} + NaCl + H_2O$$

13. (a)

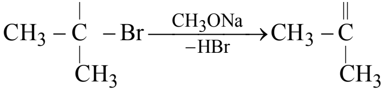
14. (b)



This reaction is called Reimer-Tiemann reaction.

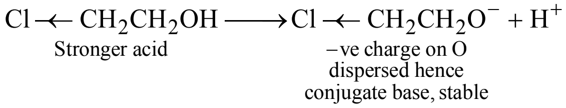
15. (b) By path 1 $(CH_3)_3C$–I and CH_3OH are formed and path 2 also form the same.

16. (d) tert-butylbromide undergoes elimination readily in presence of the base sodium methoxide to form 2-methylpropene

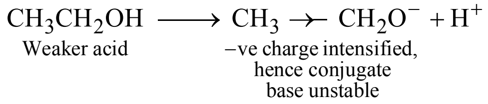


$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow[-HBr]{CH_3ONa} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{||}}{C}}$

17. (c) $ClCH_2CH_2OH$ is stronger acid than CH_3CH_2OH due to – I effect of Cl.

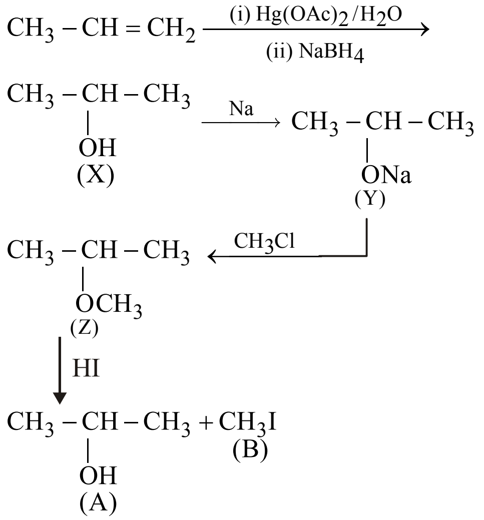


$\underset{\text{Stronger acid}}{Cl \leftarrow CH_2CH_2OH} \longrightarrow \underset{\substack{\text{–ve charge on O}\\ \text{dispersed hence}\\ \text{conjugate base, stable}}}{Cl \leftarrow CH_2CH_2O^-} + H^+$



$\underset{\text{Weaker acid}}{CH_3CH_2OH} \longrightarrow \underset{\substack{\text{–ve charge intensified,}\\ \text{hence conjugate}\\ \text{base unstable}}}{CH_3 \rightarrow CH_2O^-} + H^+$

18. (b)

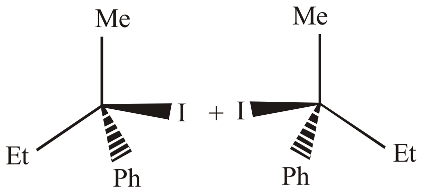


$CH_3-CH=CH_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg(OAc)}_2/H_2O}$

$\underset{\text{(X)}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow{Na} \underset{\text{(Y)}}{CH_3-\underset{\underset{ONa}{|}}{CH}-CH_3}$

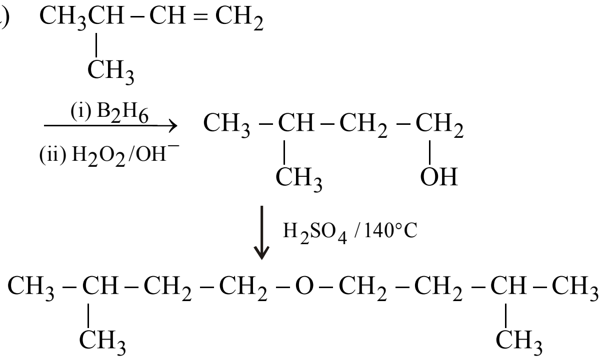
$\xrightarrow{CH_3Cl} \underset{\text{(Z)}}{CH_3-\underset{\underset{OCH_3}{|}}{CH}-CH_3} \xrightarrow{HI} \underset{\text{(A)}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} + \underset{\text{(B)}}{CH_3I}$

19. (b)



[Two]

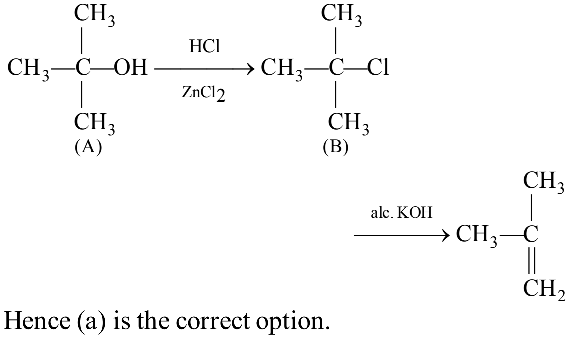
20. (a)



$CH_3\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow[\text{(ii) }H_2O_2/OH^-]{\text{(i) }B_2H_6} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH_2}$

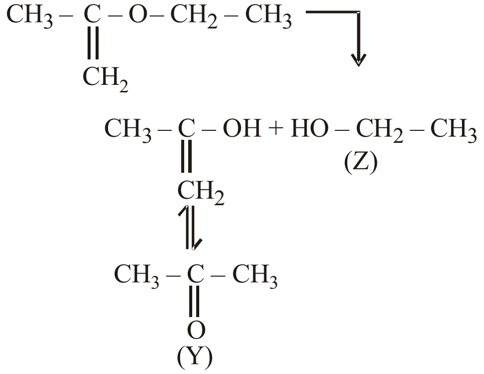
$\xrightarrow{H_2SO_4/140°C} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-O-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

21. (a) Reaction involved is given as :



$\underset{\text{(A)}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH} \xrightarrow[ZnCl_2]{HCl} \underset{\text{(B)}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl} \xrightarrow{\text{alc. KOH}} CH_3-\underset{\underset{CH_2}{||}}{\overset{\overset{CH_3}{|}}{C}}$

Hence (a) is the correct option.

22. (c) 
$$CH_3-\underset{\underset{CH_2}{\|}}{C}-O-CH_2-CH_3 \longrightarrow CH_3-\underset{\underset{CH_2}{\|}}{C}-OH + \underset{(Z)}{HO-CH_2-CH_3}$$
$$\rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3\ (Y)$$

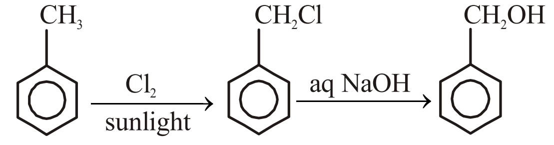
23. (c)

24. (c) It is correct that sodium phenoxide (sodium salt of phenol) and CO_2 on heating form sodium salicylate. This is known as Kolbe's reaction. Ethanol does not respond to this reaction. Therefore, statement-1 is true. But the statement-2 that phenoxide ion is more basic than ethoxide ion is not correct.

25. (c) Lucas reagent is a mixture of anhydrous $ZnCl_2$ and conc. HCl. It is used for the distinction of monohydric alcohol. Tertiary alcohols on addition produce a precipitate immediately while secondary alcohols produce ppt. after 5 minutes. Primary alcohols do not produce any precipitate. Therefore, statement-1 is true but statement-2 is false.

EXERCISE - 3

Exemplar Questions

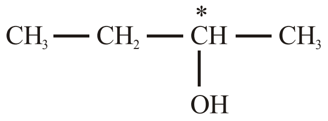
1. (d) 

Toluene Benzyl chloride Benzyl alcohol

2. (a) Following are the three possible isomers of butanol.

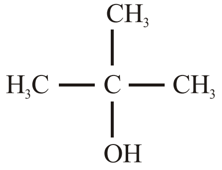
(i) $\underset{\text{Butan}-1-\text{ol}}{CH_3CH_2-CH_2-CH_2OH}$

no chiral carbon.

(ii) 
$$CH_3-CH_2-\overset{*}{\underset{\underset{OH}{|}}{CH}}-CH_3$$

Butan –2 – ol

1-Chiral Carbon

(iii) 
$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

2 – methylpropan – 2 – ol

No Chiral Carbon

3. (c) HCl + An. $ZnCl_2$ is known as lucas reagent. It is used to determine degree of an alcohol.

The reaction follow nucleophilic substitution reaction in which — OH group is replaced by — Cl. In this reaction carbocation is formed as intermediate. Higher the stability of intermediate carbocation higher will be the reactivity of reactant molecule. Since 3° carbocation is more stable than 2° carbocation as well as 1° carbocation.

Hence, the order of reactivity of alcohols is 3° > 2° > 1°.

4. (c) Less powerful oxidizing agent, Pyridinium chlorochromate $\left(C_5H_5\overset{+}{N}HCl\overset{-}{C}rO_3\right)$ oxidises primary alcohols to aldehydes.

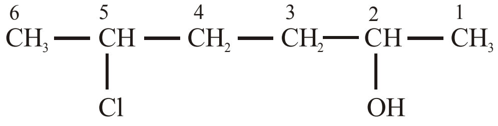
$$\underset{\text{Ethanol}}{CH_3CH_2OH}\xrightarrow{PCC}\underset{\text{Ethanal}}{CH_3CHO}$$

5. (b) The process of conversion of alkyl halides into alcohols involves substitution reaction.

$$\underset{\text{Alkyl halide}}{R-X}\xrightarrow{OH^-}\underset{\text{Alcohol}}{R-OH}$$

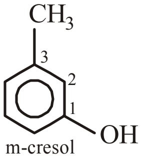
6. (c) Compound (A) i.e., phenol and compound (D) i.e., a derivative of phenol cannot be considered as aromatic alcohol.

On the other hand. In compounds (B) and (C), — OH group is bonded to sp^3 hybridised carbon which inturn is bonded to benzene ring. Hence, are considered as aromatic.

7. (c) 
$$\overset{6}{CH_3}-\overset{5}{\underset{\underset{Cl}{|}}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{\underset{\underset{OH}{|}}{CH}}-\overset{1}{CH_3}$$

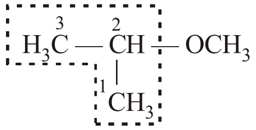
5-chlorohexan-2-ol

8. (a) The structure of *m* – cresol is



m-cresol

Here – OH is the functional group and the methyl is substituents. Hence the IUPAC name is 3-methylphenol.

9. (c) 
$$\overset{3}{H_3C}-\overset{2}{\underset{\underset{\overset{1}{CH_3}}{|}}{CH}}-OCH_3$$

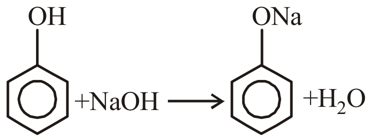
IUPAC name of the above compund is 2-methoxypropane.

10. (b) Weakest acid has the strongest conjugate base.

Among all these acids, ROH is the weakest acid.

Therefore, the strongest base is RO^-.

11. (a) Phenol being more acidic in nature reacts with sodium hydroxide solution and by the loss of one proton, it give phenoxides ion. This phenoxide ion is resonance stabilised.



12. (b) Presence of electron withdrawing group at ortho position increase the acidic strength. In *o*-nitrophenol, nitro group is present at ortho position. On the other hand, in *o*-methylphenol and in *o*-methoxyphenol, electron releasing group (—CH_3, —OCH_3) are present. Presence of these groups at ortho & Para positions of phenol decreases the acidic strength of phenols. So, phenol is less acidic than *o*-nitrohenol.

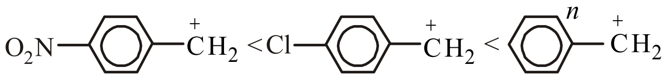
13. (d) Presence of electron withdrawing group increases the acidic strength. So, *m*-chlorophenol is most acidic among all the given compounds.

14. (b) Electron withdrawing substituents increase the acidic strength of phenols. so, *p*-nitrophenol (II) and *m*-nitrophenol (IV) are stronger acid than Phenol (I). If — NO_2 group is present at *p*-position, then it exerts both — I and — R effect but if it is present at meta position, then it exerts only–I effect. Therefore, *p*-nitrophenol is stronger than *m*-nitrophenol.
On the other hand, electron releasing substituents decreases the acidic strength of phenol. If — OCH_3 group is present at meta position, it will exert – I effect only.
But, if it is present at para position, it will exert + R effect. Thus, *m* - methoxy phenol is more acidic than *p*- methoxy phenol. Hence, the correct order of decreasing acidic strength will be : II > IV > I > III > V.

15. (c) Nucleophilic substitution reactions depends upon the stability of carbocation. As, presence of electron withdrawing group decreases the stability of carbocation in compound (II) and (III). Therefore, will give less stable carbocation than (I).
Now NO_2 group is a stronger EWG than — Cl.

Thus, $NO_2-C_6H_5-\overset{+}{C}H_2$ will be less stable than $Cl-C_6H_5-\overset{+}{C}H_2$

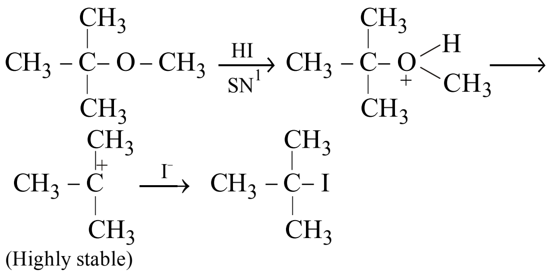
Hence, the order of reactivity of carbocatiors will be:



16. (a) With increase in molecular mass boiling point increases. Thus the b.p. of pentan-1-ol will be more than other given compounds. Now, among isomeric alcohols 1° alcohols will have higher boiling points than 2° alcohols due of higher surface area.
Hence, increasing order of b.pts. will be
Propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol.

NEET/AIPMT (2013-2017) Questions

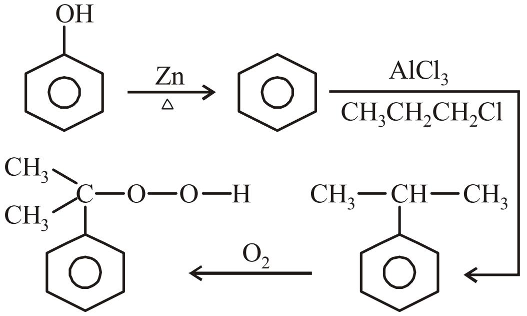
17. (b) The reaction will proceed via $S_N{}^1$ mechanism because alkyl group attached is 3°.



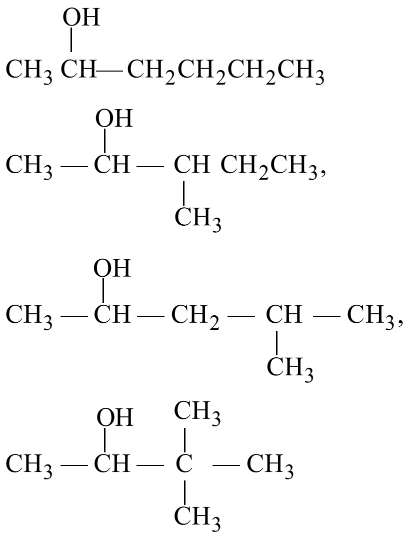
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 \xrightarrow[SN^1]{HI} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{O}{<}^{H}_{CH_3} \longrightarrow$$

$$\underset{\text{(Highly stable)}}{CH_3-\underset{CH_3}{\overset{CH_3}{\overset{+}{C}}}} \xrightarrow{I^-} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I$$

18. (c)



19. (c) Compound containing $CH_3CH(OH)$ or CH_3CO–group give positive iodoform test.



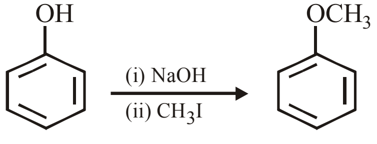
$$CH_3\overset{OH}{CH}-CH_2CH_2CH_2CH_3$$

$$CH_3-\overset{OH}{CH}-\underset{CH_3}{CH}\,CH_2CH_3,$$

$$CH_3-\overset{OH}{CH}-CH_2-\underset{CH_3}{CH}-CH_3,$$

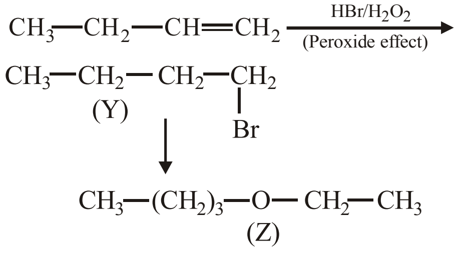
$$CH_3-\overset{OH}{CH}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

20. (b) Phenols react with alkyl halides in alkaline medium to form ethers. Therefore,



21. (c) *o*-nitrophenol will not be soluble in $NaHCO_3$. Due to intramolecular hydrogen bonding hydrogen on OH is strongly bound. So it can not be have as an acid and can not react with sodium bicarbonate.

22. (a)



$$CH_3-CH_2-CH=CH_2 \xrightarrow[\text{(Peroxide effect)}]{HBr/H_2O_2}$$

$$\underset{(Y)}{CH_3-CH_2-CH_2-\underset{Br}{CH_2}}$$

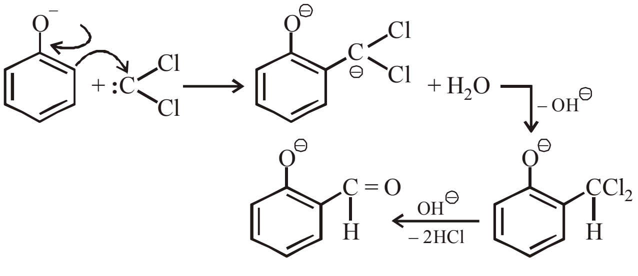
$$\downarrow$$

$$\underset{(Z)}{CH_3-(CH_2)_3-O-CH_2-CH_3}$$

23. (d) Williamson synthesis is one of the best methods for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.

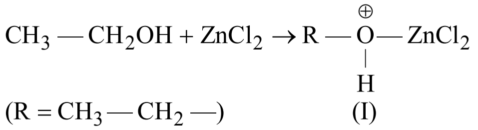
24. (d) $CHCl_3 + NaOH \rightleftharpoons :\overset{\ominus}{C}Cl_3 + H_2O$

$:\overset{\ominus}{C}Cl_3 \longrightarrow :CCl_2 + Cl^{\ominus}$



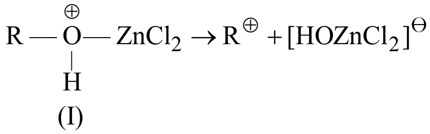
Therefore functional group – CHO is introduced.

25. (a) $ZnCl_2$ is a lewis acid and interact with alcohol.



$$CH_3-CH_2OH + ZnCl_2 \rightarrow R-\underset{\substack{|\\H}}{\overset{\oplus}{O}}-ZnCl_2$$

(R = CH_3-CH_2-) (I)



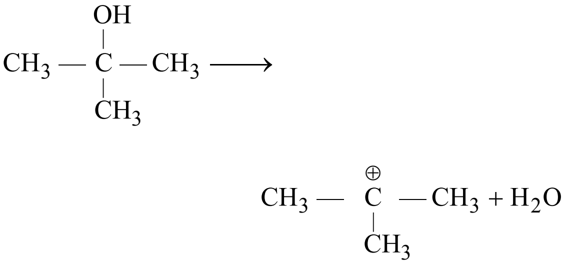
$$R-\underset{\substack{|\\H}}{\overset{\oplus}{O}}-ZnCl_2 \rightarrow R^{\oplus} + [HOZnCl_2]^{\ominus}$$

(I)

Carbocation is formed as intermediate in the S_N^1 mechanism which these reaction undergoes.

In the absence of $ZnCl_2$ formation of primary carbocation is difficult which is the case with (ii) while (i) undergoes reaction.

(iii) Tertiary carbocation casily formed due to the stability.

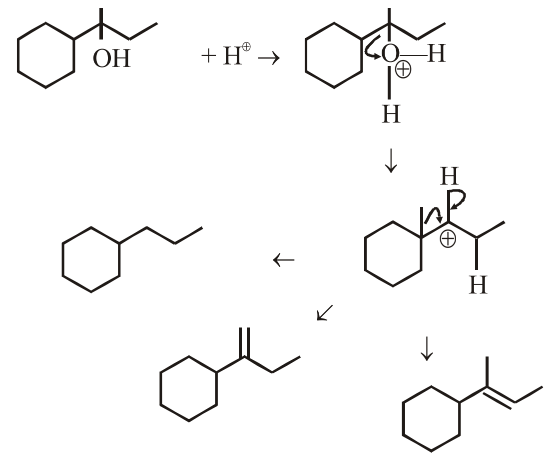


$$CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{OH\\|}}{C}}-CH_3 \longrightarrow CH_3-\underset{\substack{|\\CH_3}}{\overset{\oplus}{C}}-CH_3 + H_2O$$

(iv) In the presence of $ZnCl_2$, 2° carbocation is formed from $(CH_3)_2-\underset{\substack{|\\H}}{C}-OH$

i.e., $CH_3-\overset{\oplus}{C}H-CH_3$

26. (b)

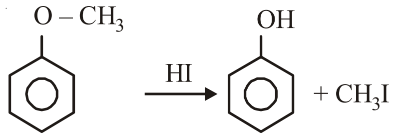


27. (a)

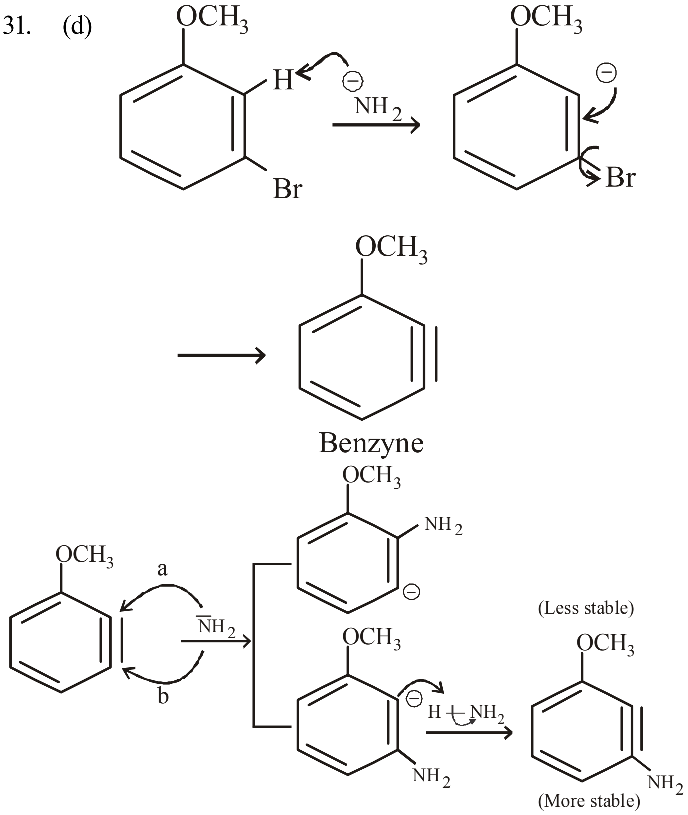
28. (a) This is an example of Williamson ether synthesis reaction in which sodium alkoxide reacts with alkyl halide and gives ether.

29. (c) Electron withdrawing – NO_2 group has very strong –I and –R effects so, compound 3 will be most acidic.

30. (b) When Ar – O – R ethers are reacted with HI, they are cleaved at weaker O – R bond to give phenol and alkyl iodide.



31. (d)



More stable as –ve charge is close to electron withdrawing group.

Also, incoming nucleophile gets attached on same 'C' on which 'Br' (Leaving group) was present.

∴ not a cine substitution reaction