ALCOHOLS
PHENOLS
ETHERS

TOPIC-WISE STUDY MATERIAL

BY

EXAMS ROAD

"Bringing Excellence to Students"

Alcohols and Phenols

Alcohols and phenols are formed when a hydrogen atom from a hydrocarbon, aliphatic and aromatic respectively, is replaced by — OH group. The substitution of a hydrogen atom from a hydrocarbon by an alkoxy or aryloxy group (R — O / Ar — O) gives ethers.

Alcohols

The hydroxy derivatives of aliphatic hydrocarbons are called alcohols. They are obtained by replacing one or more hydrogen atoms of a hydrocarbon by the — OH group.

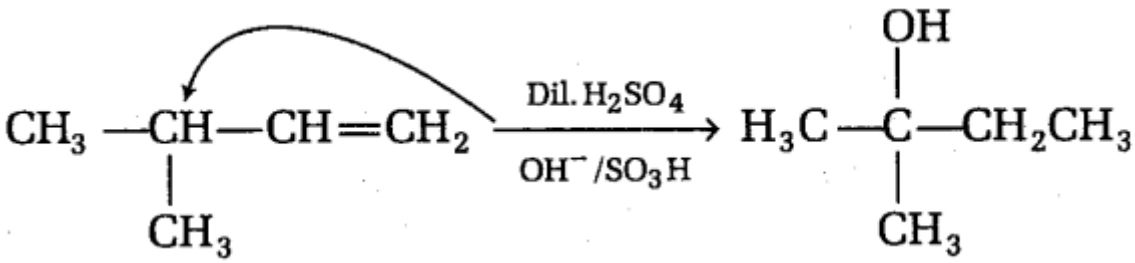
Preparation

The important methods used to prepare alcohols are as follows:

From Alkenes

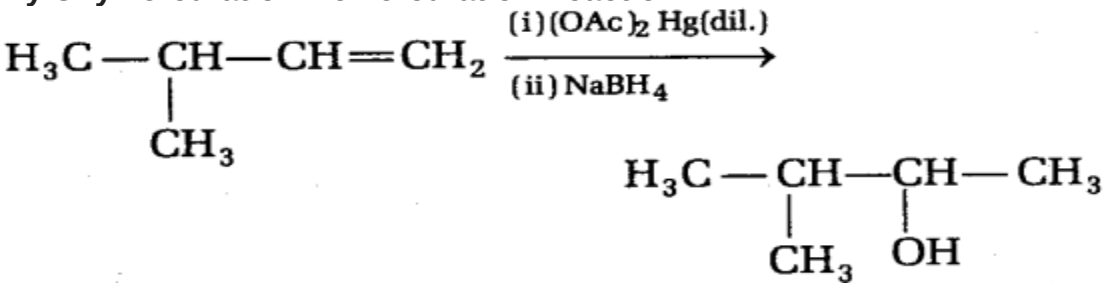
- **By Acid Catalysed Hydration**

It takes place in the presence of dilute H_2S0_4.



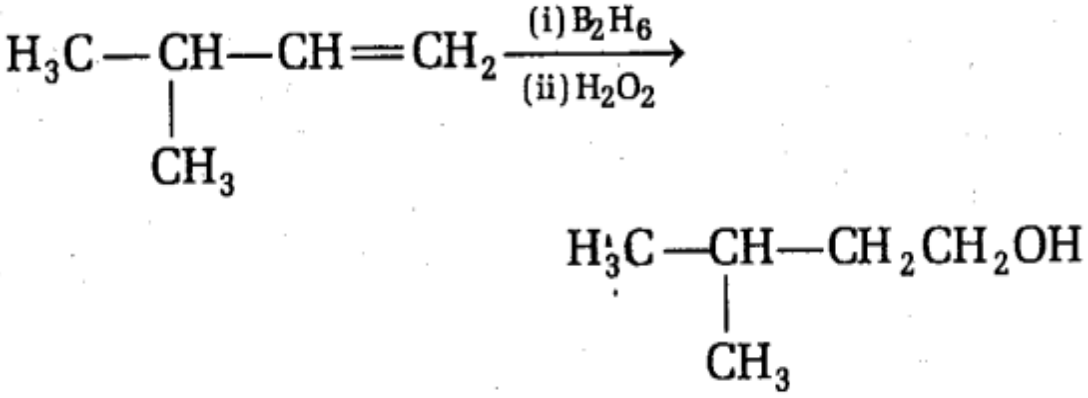
In this reaction, intermediate carbocation is formed and rearrange, therefore — OH gets attached at maximum degree of carbon.

- **By Oxymercuration-Demercuration Reaction**



Intermediate carbocation is not formed and alcohol is formed according to Markownikoffs rule.

- **By Hydroboration Oxidation Reaction**



Intermediate carbocation is not formed and alcohol is formed according to anti-Markownikoffs rule.

- **By Reduction of Carbonyl Compounds**

Aldehydes on reduction give primary alcohols and ketones give secondary alcohols in the presence of weak reducing agent **($NaBH_4$).**

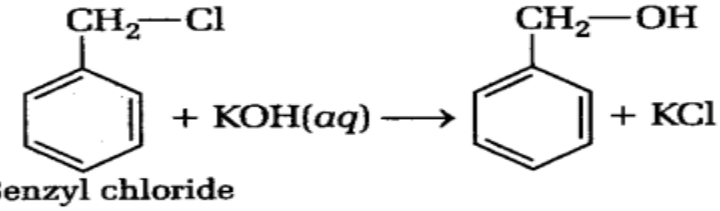
- $RCHO \xrightarrow[+2H]{NaBH_4} RCH_2OH$
- $RCOR' \xrightarrow{NaBH_4} R-\underset{\displaystyle OH}{\underset{|}{CH}}-R'$

- **By Reduction of Acids and Esters**

Carboxylic acids and esters on reduction, in the presence of strong reducing agent (LiAlH), give primary alcohols.

- $RCOOH \xrightarrow{LiAlH_4} RCH_2-OH$
- $CH_3COOCH_2-CH_2-CH_3 \xrightarrow[+4H]{LiAlH_4} CH_3CH_2OH + CH_3CH_2CH_2OH$

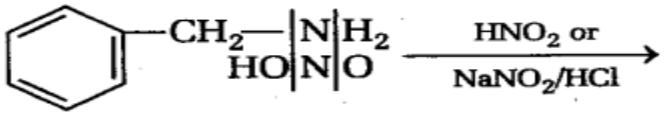
By Hydrolysis of Alkyl Halides



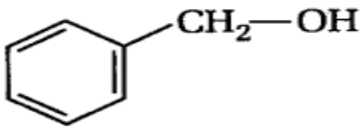
Benzyl chloride

$$CH_3—CH_2\,Br + NaOH(aq) \longrightarrow CH_3—CH_2—OH + NaBr$$

From Primary Aliphatic Amines



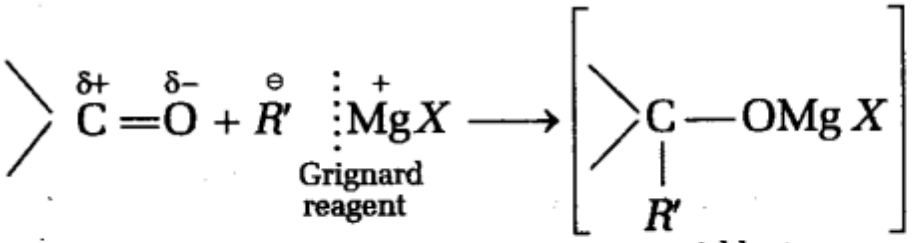
Benzyl amine

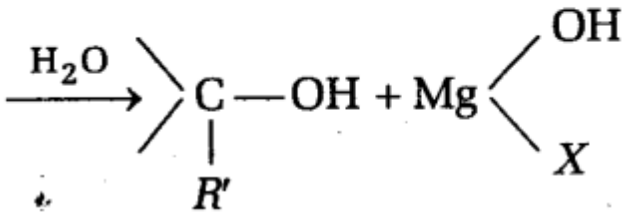


Benzyl alcohol

- **From Grignard Reagent**

Grignard reagent [R' Mg X) on reaction with aldehydes or ketones followed by hydrolysis gives alcohols.
The nature of alcohol formed depends upon the aldehyde or ketone taken, e.g. if the reacting aldehyde is formaldehyde, primary alcohol —CH_2OH is obtained while other aldehydes give secondary alcohols (— CHOH) with Grignard reagent. Ketones give tertiary alcohols with Grignard reagent.





Physical Properties of Alcohols

The detailed description of physical properties of alcohols, i.e. their boiling points, solubility are given below:

1. **Boiling Points**
   Alcohols have higher boiling point than haloalkanes of comparable molecular mass because alcohols have intermolecular hydrogen bonding. As the number of carbon atoms increases, boiling point increases.
   The boiling point decreases with increase of branching in carbon chain
2. **Solubility**
   Alcohols are soluble in water due to ability to form hydrogen bonds with water. As the number of carbon atoms increases, solubility decreases.

Chemical Properties of Phenols

The chemical properties of alcohol depend on the order of reactivity of alcohols as given below:

Order of reactivity of alcohols:
1° alcohol > 2° alcohol > 3° alcohol

Reactions Involving Cleavage of O—H Bond Reaction with Metals

$$2R-OH + 2Na \longrightarrow 2R-O-Na + H_2$$

Acidity of alcohols in decreasing order:
Primary alcohols > secondary alcohols > tertiary alcohols. Electron releasing group decreases the polarity of —OH bond. This decreases the acidic strength. Alcohols when react with carboxylic acids, acid chlorides and acid anhydrides, form esters. This reaction is called esterification

$$R\overset{\ominus}{O}:\overset{+}{H} + R'\overset{+}{C}O:\bar{O}H \overset{H^+}{\rightleftharpoons} R'COOR + H_2O$$

Alcohols when react with Grignard reagent give alkanes.

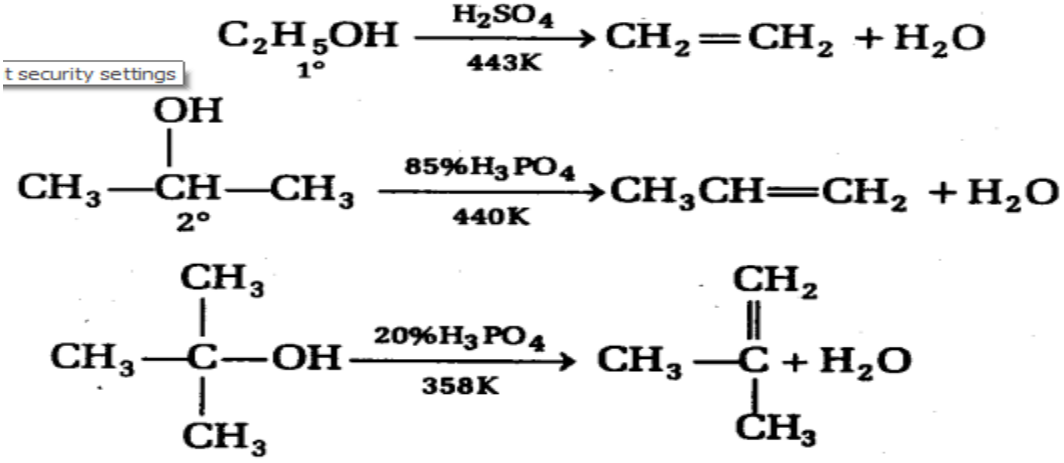
$$R\bar{O}:\overset{+}{H} + \bar{R}:\overset{+}{M}gBr \longrightarrow RH + Mg\begin{matrix}OR'\\ Br\end{matrix}$$

Reactions Involving Cleavage of Carbon Oxygen (C—O) Bond
Reaction with hydrogen halides

$$ROH + HX \longrightarrow R-X + H_2O$$

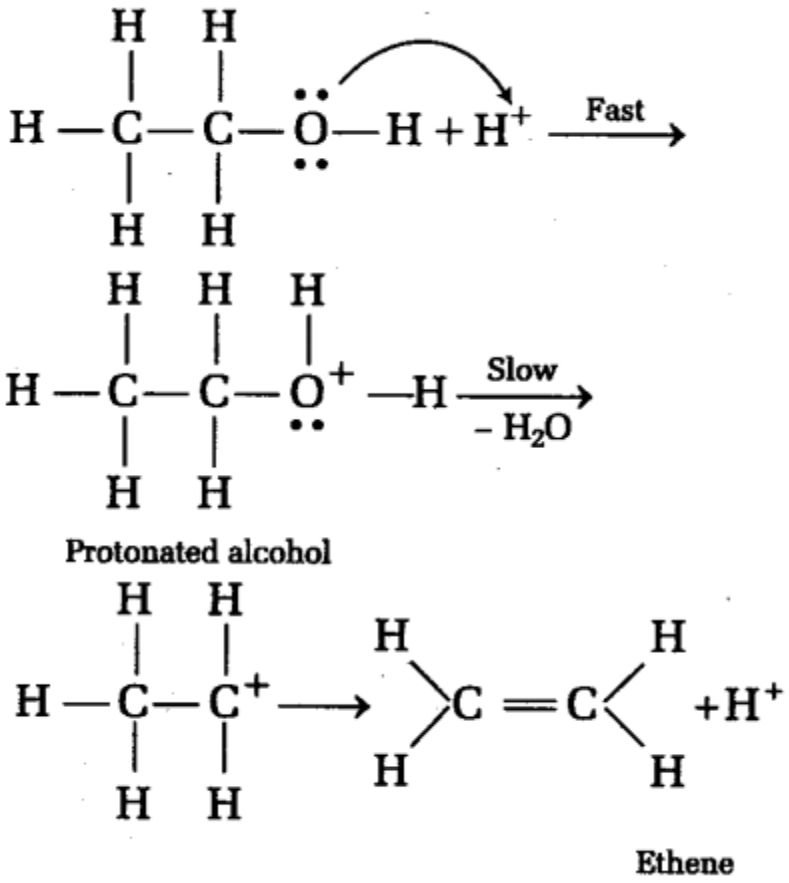
Reactivity in decreasing order 3°> 2°> 1°.

Dehydration in the presence of protic acids like cone. **H2S04 or H3P04** or in the presence of catalysts such as **anhy.$ZnCl_2$ or $A1_20_3$.**

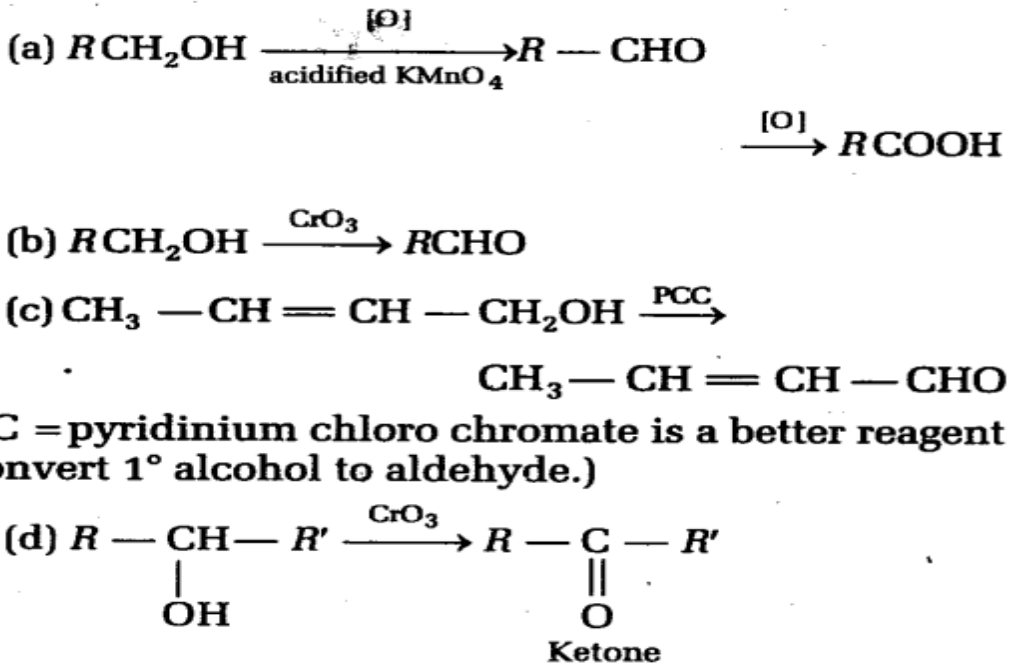


Ease of dehydration of alcohols 3°> 2°> 1°

Mechanism of Dehydration



Oxidation



Uses

- Methanol and ethanol are two commercially important alcohols. Methanol is used as a solvent in paints, varnishes and mainly for making formaldehyde.
- It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities cause even death.
- Ethanol is used as a solvent in paint industry and in preparation of a number of carbon compounds.
- Commercial alcohol is made unfit for drinking by mixing **$CuSO_4$** and pyridine (denaturation of alcohol).
- Ethanol is mainly used in alcoholic beverages.

Identification of Primary, Secondary and Tertiary Alcohols

With Lucas reagent (cone. HCl and $ZnCl_2$),

- tertiary alcohols give turbidity immediately.
- secondary alcohols give turbidity with in five minutes.
- primary alcohols do not produce turbidity at room temperature.

In Victor Meyer's test

- blood red colour indicates 1° alcohols.
- blue colour indicates 2° alcohols.

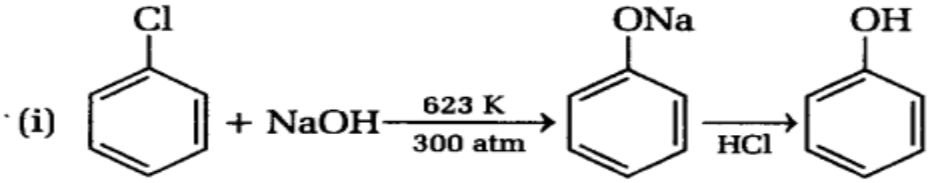
- colourless solution indicates 3° alcohols.

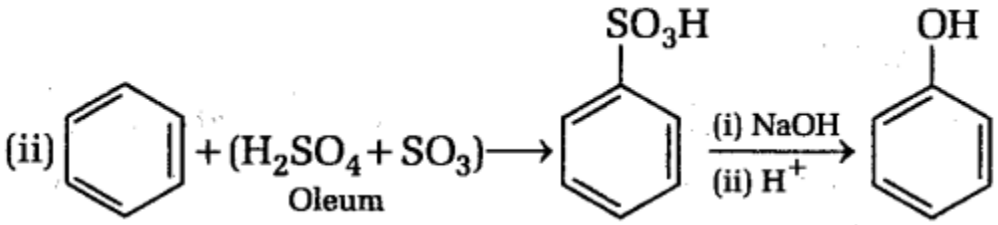
Phenols (C_6H_5OH)

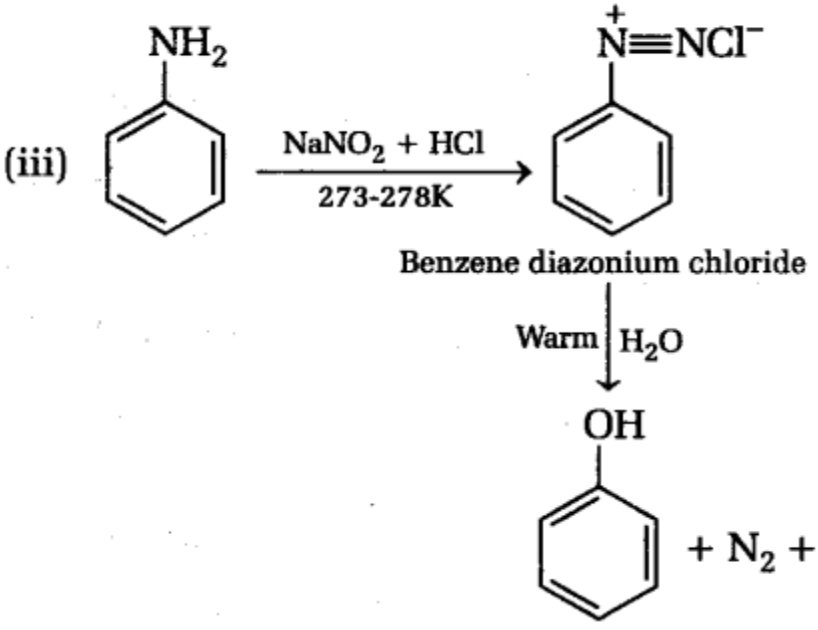
Aromatic compounds in which hydroxyl group (— OH) is directly attached with benzene nucleus are called phenols.

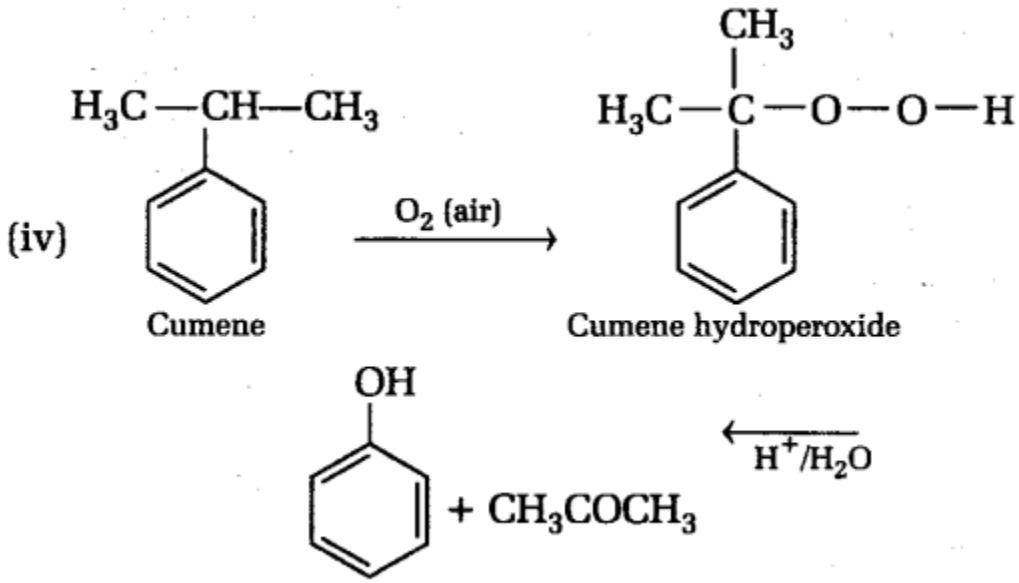
Preparation

Some general and important methods of preparation of phenols are discussed below:







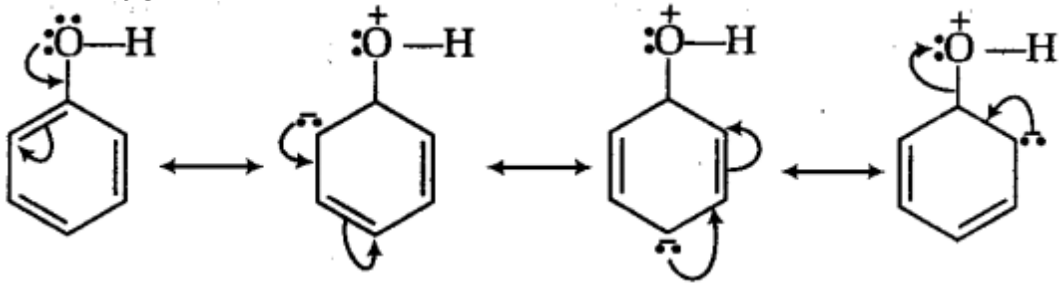


Physical Properties of Phenols

Phenol has higher boiling point and soluble in water due to its ability to form hydrogen bond with water.

Acidic Nature of Phenol

Phenols are acidic in nature, even more acidic than alcohols. The more acidic character of phenols (than corresponding aliphatic alcohols) is due to conjugation between lone pair of oxygen and benzene nucleus, i.e.



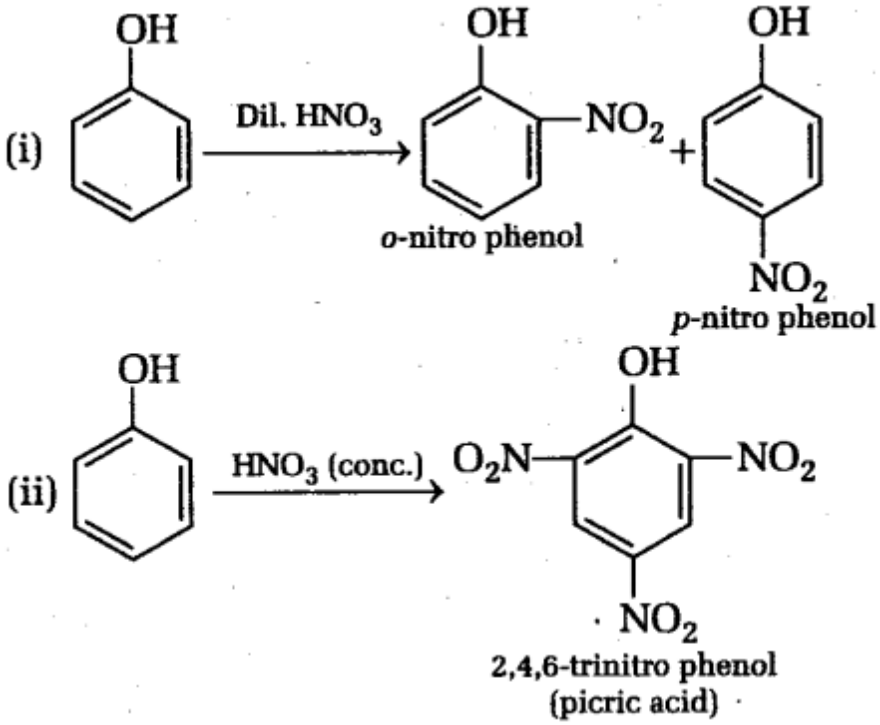
The positive charge on oxygen signifies the weakening of O—H bond. Presence of electron releasing group like **—CH_3, —C_2H_5** over benzene nucleus destabilises the phenoxide ion, thus, decreases the acidity of phenol whereas, presence of electron withdrawing groups like **—$N0_2$, —CN,** etc,, stabilises the phenoxide ion and thus, increases the acidity of phenol.

Chemical Properties of Phenols
Phenols exhibit the following chemical properties.

Electrophilic Substitution Reactions

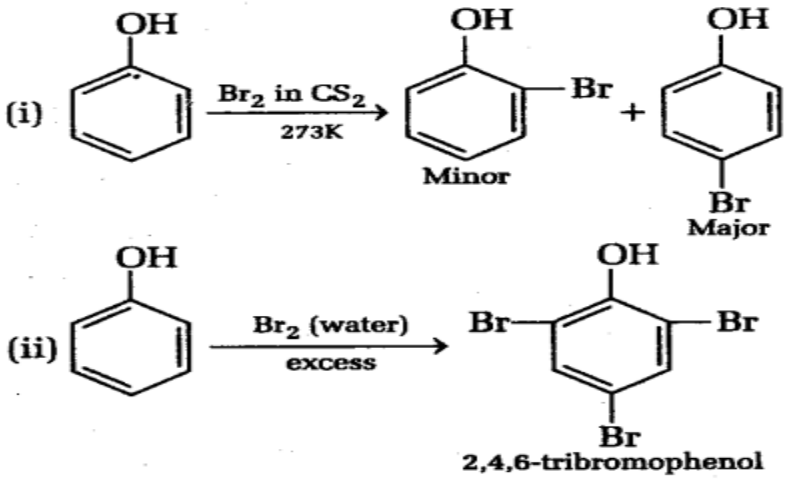
In phenol, the—OH group shows +R and -I effect and hence, highly activates the benzene ring towards electrophilic substitution reaction. It is ortho and para directing group.

Nitration

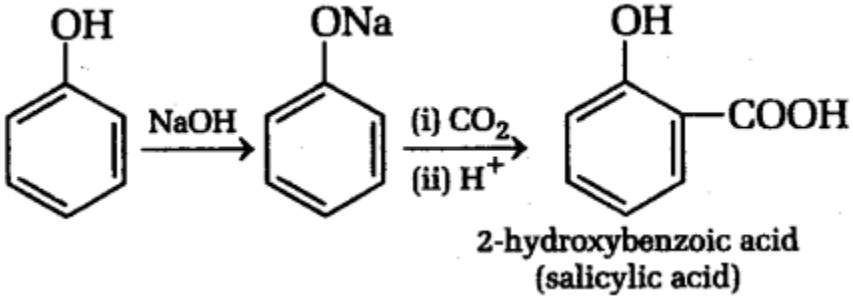


The ortho and para isomers can be separated by steam distillation, o-nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding.

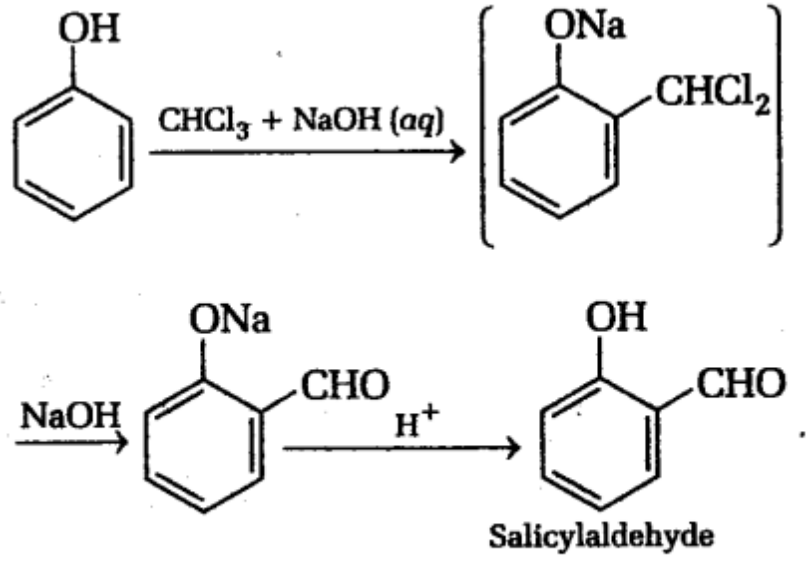
Halogenation



Kolbe's Reaction

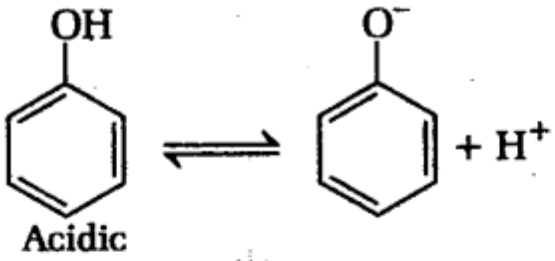


Reimer-Tiemann Reaction

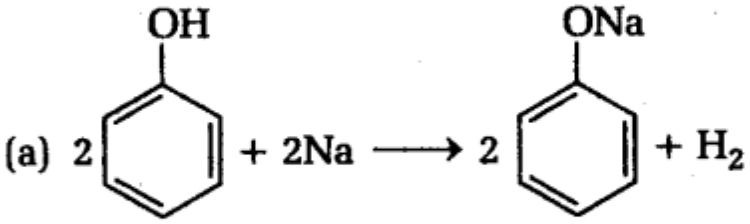


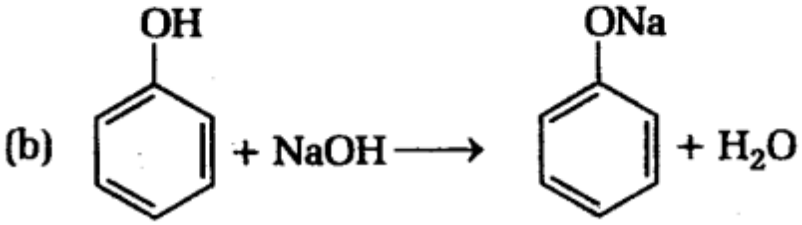
Electrophile : CCl_2 (dichlorocarbene) .

Reactions Involving Breaking of O—H Bond



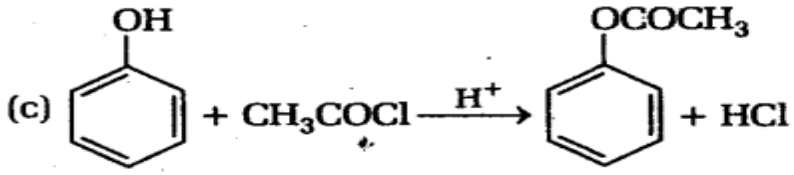
Acidic

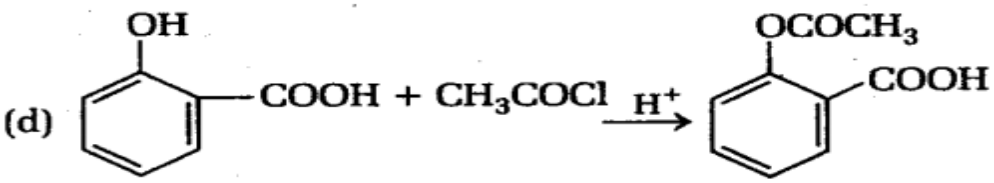




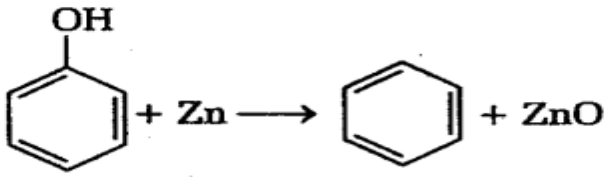
Sodium phenoxide

Both the above reactions show acidic nature of phenol.

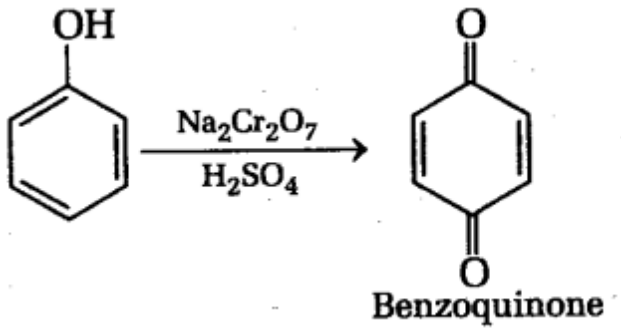




2-acetoxy benzoic acid (aspirin)



Oxidation



Benzoquinone

Uses

1. Phenol is used in the manufacture of bakelite, soaps, lotions, etc.
2. It is used in the manufacture of drugs like aspirin, salol, phenacetin, etc.

Ethers

Organic compounds having —O— functional group are called ethers. Thus, ethers may look like

R'—O—R"

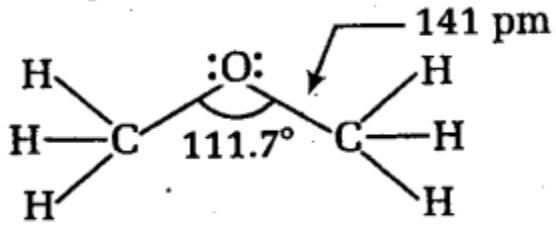
In other words, ethers are the derivatives of water as these are obtained when both the H-atoms of H20 are replaced by R groups. The R groups may be same or different. When both the R groups (alkyl groups) are same, the ethers are called simple or symmetrical ether and when both the groups are different, the ethers are called mixed or unsymmetrical ethers, e.g.

CH3— O — CH3 **CH3OC2H5**

(Simple or symmetrical ethers) **(Mixed ether)**

Structure of Ethers

In ethers, two bond pairs and two lone pairs of electrons on oxygen are arranged approximately in tetrahedral manner. The bond angle is slightly greater than tetrahedral angle due to the repulsive forces between the two bulky alkyl groups.

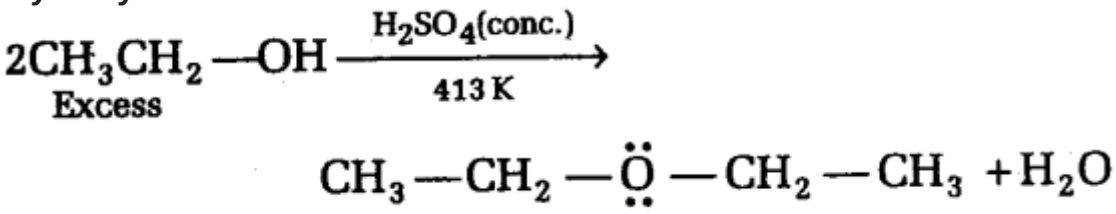


Structure of methoxy methane

Preparation of Ethers

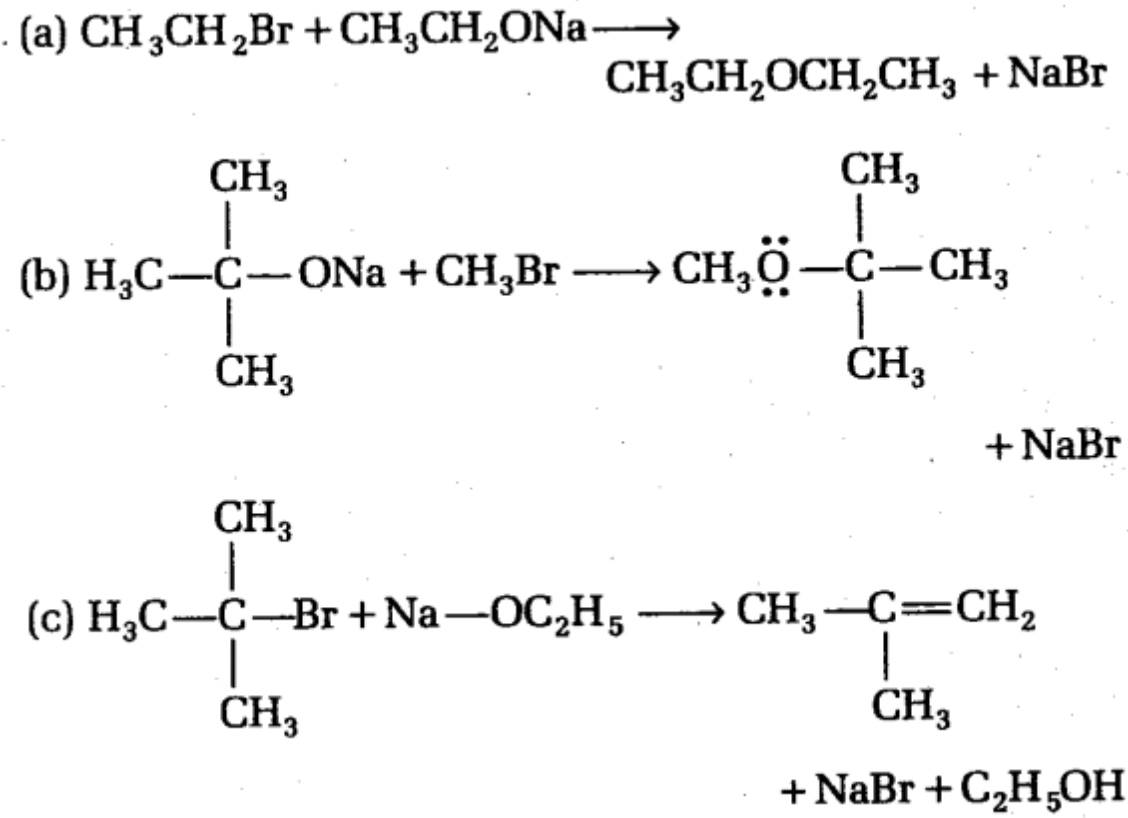
General methods used to synthesis ethers are as follows:

By Dehydration of Alcohols



Williamson's Synthesis

Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halide give alkene due to steric hindrance.



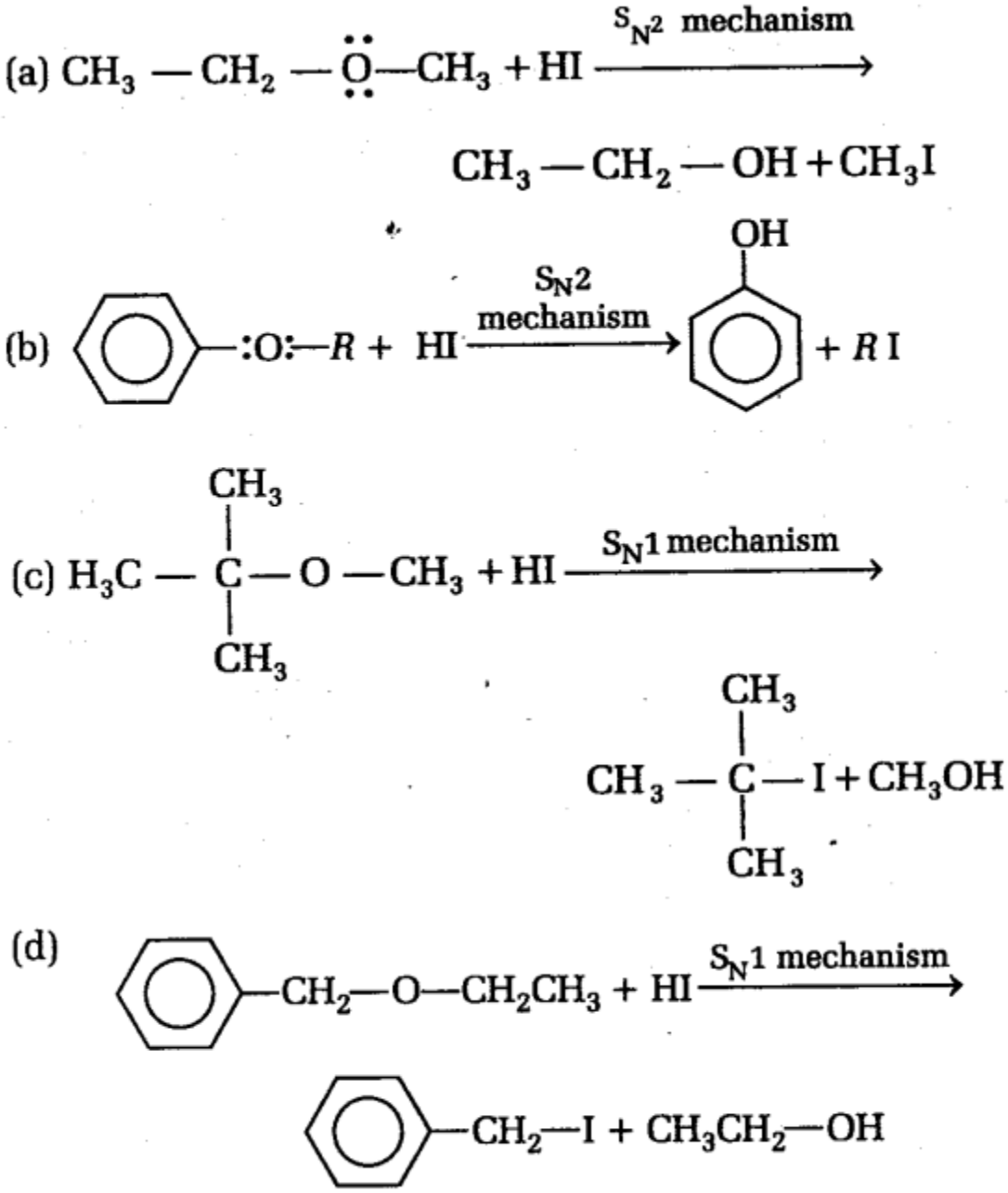
Physical Properties of Ethers

Ethers are polar but insoluble in **H_2O** and have low boiling point than alcohols (having comparable molecular mass) because ethers do not form hydrogen bond with water.

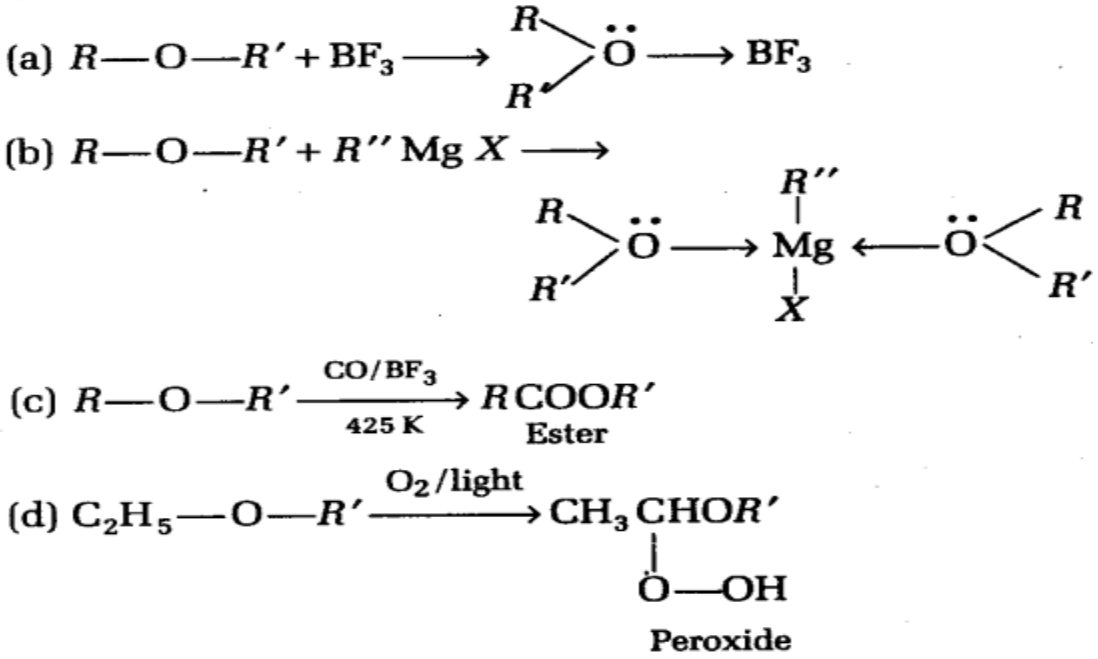
Chemical Properties of Ethers

The reactions of ethers are mainly due to lone pair of ethereal oxygen, cleavage of C—O bond and —R group.

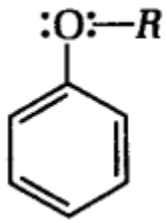
Reactions Involving Cleavage of C—O Bond



Addition Reactions

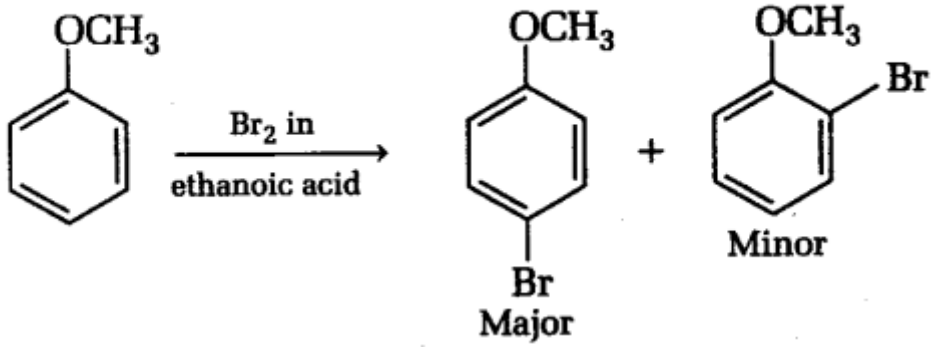


Electrophilic Substitution Reactions

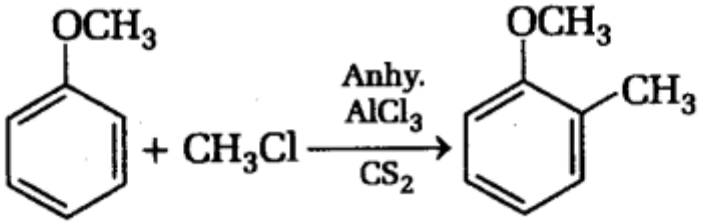


—OR is ortho, para directing group and activates the aromatic ring towards electrophilic substitution reaction.

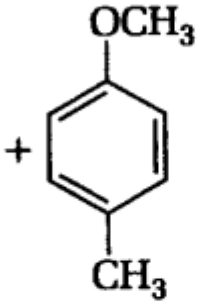
(a) Halogenation



(b) Friedel-Crafts Alkylation

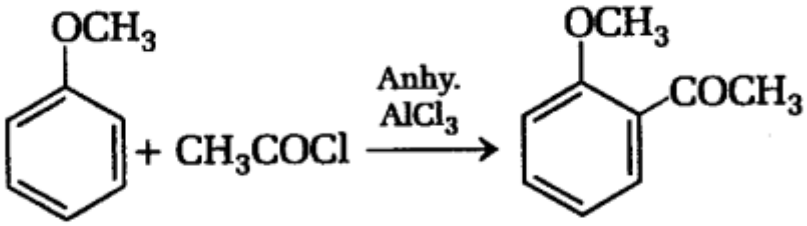


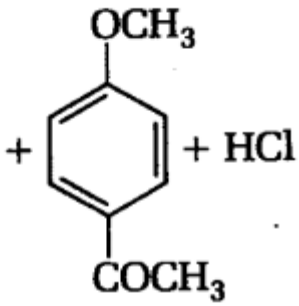
Minor



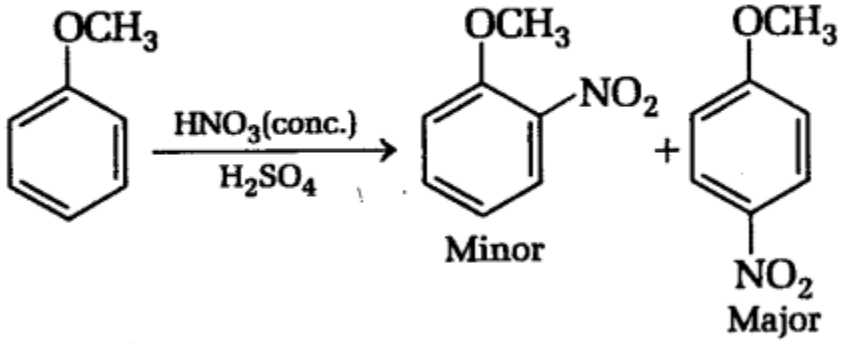
Major

(c) Friedel-Crafts Acylation





(d) Nitration



Uses

1. Ethers are used asya solvent for oils, fats and Grignard reagent, etc.
2. It is used as general anaesthetic. It provides inert and moisture free medium for various reactions.

Question 1.
Industrially ethyl alcohol is prepared from ethylene by
(a) permanganate oxidation
(b) fermentation
(c) catalytic reduction
(d) absorbing in H_2S0_4 followed by hydrolysis

Question 2.
For the sequence of reactions,

$$A \xrightarrow{C_2H_5MgI} B \xrightarrow{H_2O/H^+} \textit{tert}\text{-pentyl alcohol.}$$

The compound A in the sequence is
(a) 2-butanone
(b) acetaldehyde
(c) acetone
(d) propanal

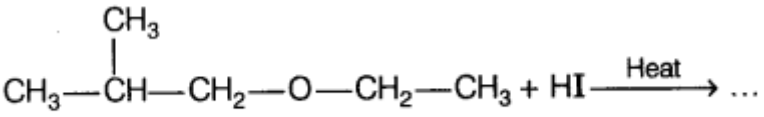
Question 3.
Ethylene oxide when treated with Grignard reagent yield
(a) secondary alcohol
(b) tertiary alcohol
(c) cyclopropyl alcohol
(d) primary alcohol

Question 4.
Which of the following is not a characteristic of alcohol?
(a) They are lighter than water
(b) Their boiling points rise fairly uniformly with rising molecular weight
(c) Lower members are insoluble in water and organic solvents but the solubility regularly increases with molecular mass
(d) Lower members have a pleasant smell and burning taste, higher members are colourless and tasteless

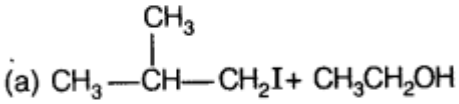
Question 5.
Arrange the following compounds in increasing order of boiling point. Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1 -ol.
(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol
(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
(d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

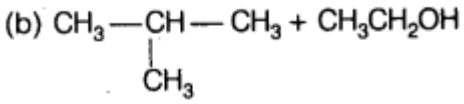
Question 6.

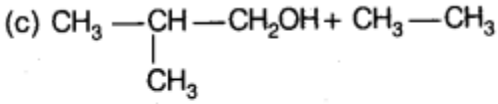
The reaction,

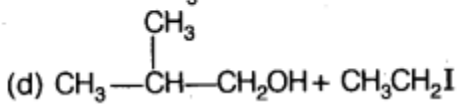


Which of the following compounds will be formed?

(a) 

(b) 

(c) 

(d) 

Question 7.

Conversion of ethyl alcohol into acetaldehyde is an example of

(a) molecular rearrangement
(b) oxidation
(c) reduction
(d) hydrolysis

Question 8.

Ethyl alcohol on oxidation with $K_2Cr_2O_7$ gives

(a) acetic acid
(b) acetaldehyde
(c) formaldehyde
(d) formic acid

Question 9.

When primary alcohol is oxidised with Cl_2, it gives

(a) CH_3CHO
(b) CH_3COCH_3
(c) CH_3COCl
(d) $COCl_2$

Question 10.

A compound is soluble in cone. H_2SO_4 It does not decolourise Br_2 in CCl_4 but oxidised by chromic anhydride in sulphuric acid, within two seconds, turning orange solution to blue

green, then opaque. The original solution contains
(a) secondary alcohol
(b) an ether
(c) an alkene
(d) a primary alcohol

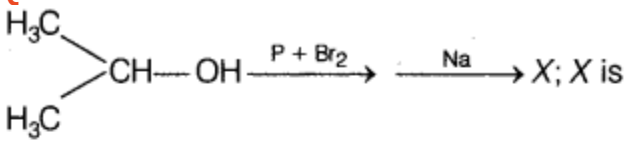
Question 11.
The most suitable reagent for the conversion of
RCH_2OH ———> R CHO is
(a) $KMn0_4$
(b) $K_2Cr_2O_7$
(c) CrO_3
(d) PCC (pyridinium chloro chromate)

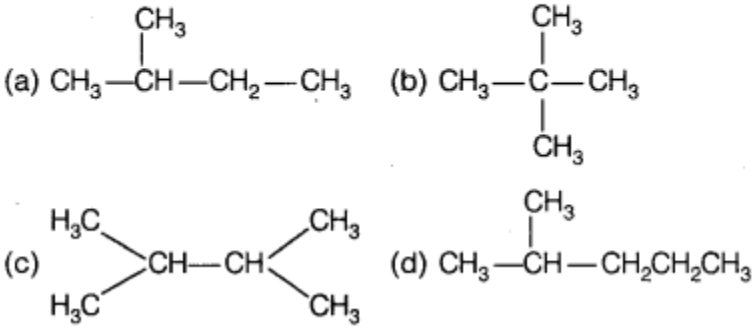
Question 12.
Isopropyl alcohol on oxidation gives
(a) acetone
(b) ether
(c) ethylene
(d) acetaldehyde

Question 13.
The alcohol that produces turbidity immediately with $ZnCl_2$/conc. HCl at room temperature is
(a) 1-hydroxy butane
(b) 2-hydroxy butane –
(c) 2-hydroxy-2-methyl propane
(d) 1-hydroxy-2-methyl propane

Question 14.
$R-OH + HX \longrightarrow RX + H_2O$;
In this reaction, the reactivity of alcohol is
(a) tertiary > secondary > primary
(b) primary > secondary > tertiary
(c) tertiary > primary > secondary
(d) secondary > tertiary > primary

Question 15.





Question 16.

During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4, the initiation step is

(a) protonation of alcohol molecule
(b) formation of carbocation
(c) elimination of water
(d) formation of an ester

Question 17.

When compound *X* is oxidised by acidified potassium dichromate, compound *Y* is formed. Compound *Y* on reduction with $LiAlH_4$ gives *X*. *X* and *Y* respectively are

(a) C_2H_5OH, CH_3COOH (b) CH_3COCH_3, CH_3COOH
(c) C_2H_5OH, CH_3COCH_3 (d) CH_3CHO, CH_3COCH_3

Question 18.

Dehydration of glycerol gives

(a) propane (b) propene (c) acrolein (d) benzene

Question 19.

The dehydration of butan-1-ol gives

(a) 1-butene as the main product
(b) 2-butene as the main product
(c) equal amount of 1-butene and 2-butene
(d) 2-methyl propene

Question 20.

Lucas reagent is

(a) anhydrous $ZnCl_2$ and NH_3

(b) anhydrous $ZnCl_2$ and $CaCl_2$

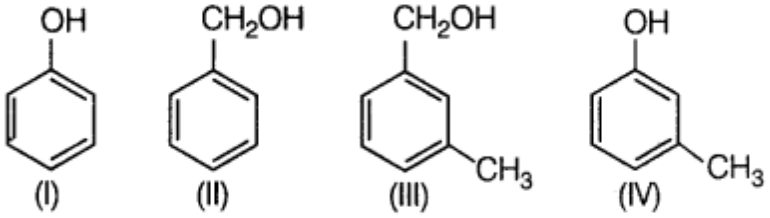
(c) anhydrous $ZnCl_2$ and conc. HCl

(d) anhydrous $ZnCl_2$ and HCl gas

Question 21.

Which of the following compounds is aromatic alcohol?

[NCERT Exemplar]



(I) (II) (III) (IV)

(a) I, II, III and IV (b) I and IV

(c) II and III (d) Only I

Question 22.

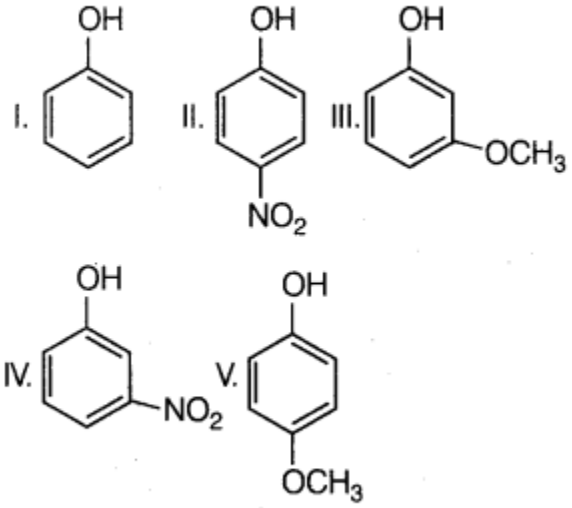
The strongest acid among the following aromatic compound is

(a) *o*-nitrophenol (b) *p*-chlorophenol

(c) *p*-nitrophenol (d) *m*-nitrophenol

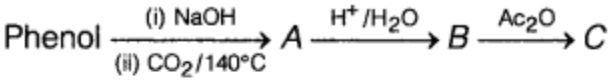
Question 23.

Mark the correct order of decreasing acidic strength of the following compounds. **[NCERT Exemplar]**



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

Question 24.



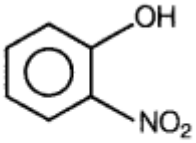
In this reaction, the end product *C* is

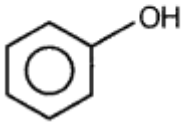
(a) salicylaldehyde
(b) salicylic acid
(c) phenyl acetate
(d) aspirin

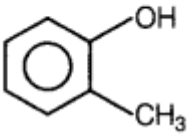
Question 25.

Which one of the following is most acidic?

(a) Cl—CH_2—CH_2OH

(b) 

(c) 

(d) 

Question 26.

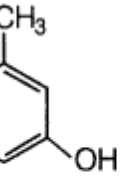
The correct order of acidic strength of the following compounds is

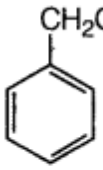
I. Phenol
II. *p* -cresol
III. *m*-nitrophenol
IV. *p*-nitrophenol

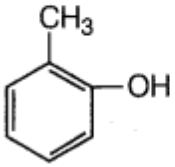
(a) III>II>I>IV (b) IV>III>I>II (c) II>IV>I>III (d) I>II>IV>III

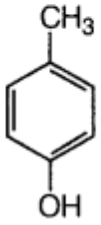
Question 27.

The structure of the compound that gives a tribromo derivative on treatment with bromine water is

(a) 

(b) 

(c) 

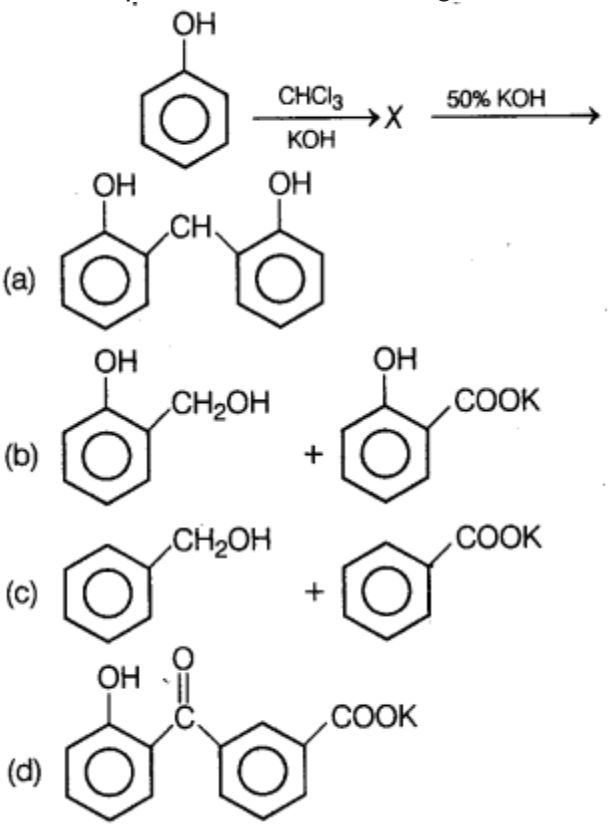
(d) 

Question 28.

Salicylic acid is prepared from phenol by

(a) Reimer-Tiemann reaction
(b) Kolbe's reaction
(c) Kolbe's electrolysis reaction
(d) None of the above

Question 29.
The final product of the following reaction is/are



Question 30.
When methyl f-butyl ether is formed?
(a) $(C_2H_5)_3CONa+CH_3Cl$
(b) $(CH_3)_3CONa+C_2H_5Cl$
(c) $CH_3ONa+(CH_3)_3CCl$
(d) $(CH_3)_3CONa+ CH_3Cl$

Question 31.
From Williamson's synthesis preparation of which of the following is possible?
(a) Only symmetrical ethers
(b) Only asymmetrical ethers
(c) Both (a) and (b)
(d) None of these

Question 32.
Tert-butyl methyl ether on heating with HI gives a mixture of
(a) Tert-butyl alcohol and methyl iodide
(b) Tert-butyl iodide and methanol

(c) isobutyleneand methyl iodide
(d) isobutylene and methanol

Question 33.
Which one of the following reaction does not yield an alkyl halide?
(a) Diethyl ether+Cl_2 (in the dark)
(b) Diethyl ether+PCl_5
(c) Diethyl ether+HI
(d) Divinyl ether $\xrightarrow{\text{Reduction}} X \xrightarrow{SOCl_2}$

Direction (Q.No. 34-35): In the following questions more than one of the answers given may be correct. Select the correct answers and mark it according to the codes.
Codes
(a) 1, 2 and 3 are correct
(b) 1 and 2 are correct
(c) 2 and 4 are correct
(d) 1 and 3 correct

Question 34.
Choose the correct statement about crotyl alcohol.
1. It is a primary alcohol
2. It contains one -CH_2 unit more than allyl alcohol
3. It gives test of unsaturation
4. It is an isomer of allyl alcohol

Question 35.
Diethyl ether is obtained by the reaction of
1. sodium ethoxide with methyl iodide
2. sodium ethoxide with ethyl chloride
3. ethanol with red phosphorus
4. ethanol with cone. H_2S0_4

Question 36.

Match the Column I with Column II and choose the correct codes given below.

	Column I		Column I
A	Propane -1, 2, 3-triol	1	Absolute ethanol + petrol
B	Ethane -1, 2-diol	2	Dynamite
C	Power alcohol	3	Terylene
D	Methylated spirit	4	Denaturated alcohol

Codes

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

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

Direction (Q.Nos. 37-42): Each of these questions contains two statements : Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b) ,(c) and (d) given below.
(a) Assertion is true, Reason is true; Reason is the correct explanation for Assertion
(b) Assertion is true, Reason is true; Reason is not the correct explanation for Assertion
(c) Assertion is true, Reason is false
(d) Assertion is false, Reason is true

Question 37.
Assertion: Primary and secondary alcohols can be distinguished by Victor-Meyer's test.
Reason: Primary alcohols form nitrolic acid which dissolved in NaOH to form blood red colouration but secondary alcohols form pseudonitroles which gives blue colouration with NaOH.

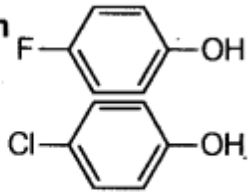
Question 38.
Assertion: t-butyl methyl ether is not prepared by the reaction of t-butyl bromide with sodium methoxide.
Reason: Sodium methoxide is a strong nucleophile.

Question 39.
Assertion: Solubility of n-alcohol in water decreases with increase in molecular weight.
Reason: The reactive proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permits enhanced hydrogen bonding with water.

Question 40.
Assertion: Phenoxide ion on treatment with active alkyl halide (e.g. CH_2=CH—CH_2Cl)

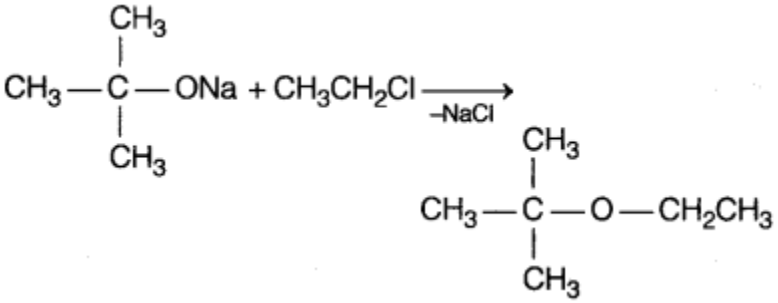
gives two products viz O-substituted and C-substituted.
Reason: Phenoxide ion is an ambident nucleophile.

Question 41.

Assertion  is less acidic than

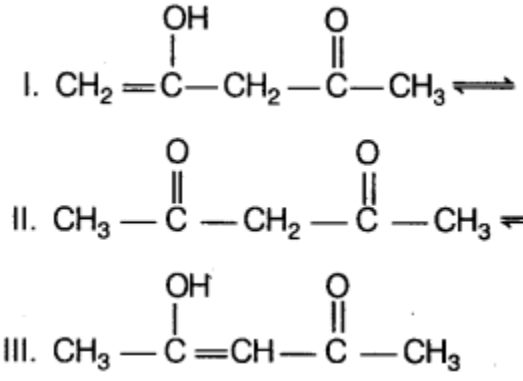
Reason —F exerts better (+) mesomeric effect than —Cl.

Question 42.
The reaction



is called
(a) Williamson synthesis
(b) Williamson continuous etherification process
(c) Etard reaction
(d) Gattermann-Koch reaction

Question 43.
The order of stability of the following tautomeric compounds is



(a) III > II > I
(b) II > III > I

(c) II > I > III
(d) I > II >111

Question 44.
Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?

(a) $CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{|}{CH}}-O-CH_3$

(b) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3$

(c) $CH_3-\underset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-O-CH_3$

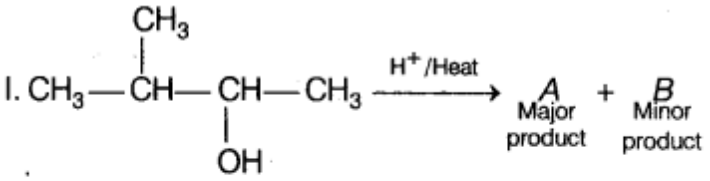
(d) $CH_3-CH_2-CH_2-CH_2-O-CH_3$

Question 45.
On shaking H_2O_2 with acidified potassium dichromate and ether, etheral layer becomes
(a) green
(b) red
(c) blue
(d) brown

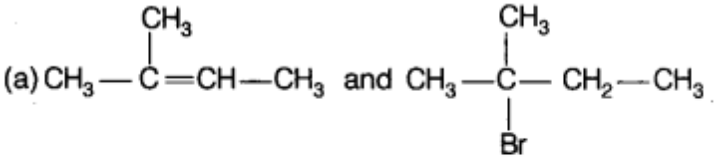
Question 46.
Dunston's test is used for identification of
(a) glycerol
(b) acetone
(c) glycol
(d) ethanol

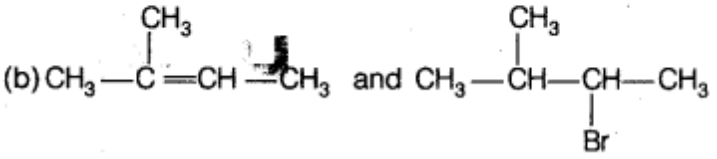
Question 47.
Etherates are
(a) ethers
(b) solution in ether
(c) complexes of ethers with Lewis acid
(d) complexes of ethers with Lewis base

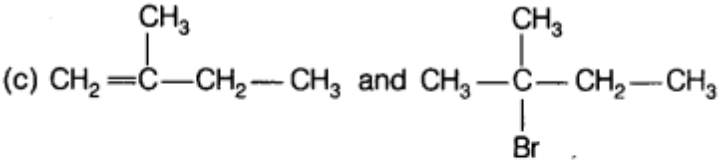
Question 48.
In the following reactions,

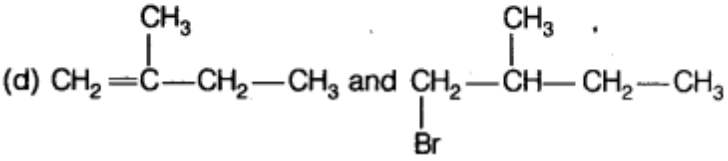


the major products *A* and *C* respectively are





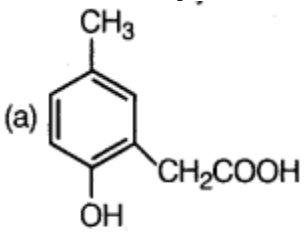


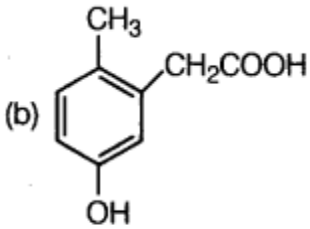


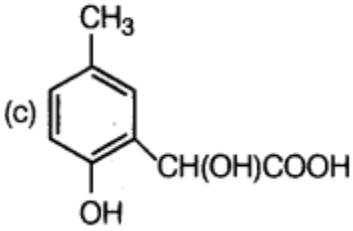
Question 49.
Dehydration of alcohol is an example of which type of reaction?
(a) Substitution
(b) Elimination
(c) Addition
(d) Rearrangement

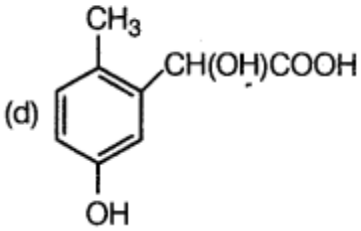
Question 50.
p-cresol reacts wfth chloroform in alkaline medium to give a compound A which adds hydrogen cyanide to form another compound B. This latter on acidic hydrolysis gives

chiral carboxylic acid. The structure of the carboxylic acid is

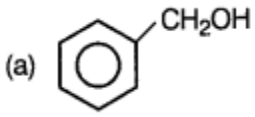
(a) 

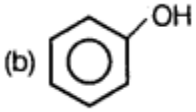
(b) 

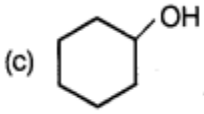
(c) 

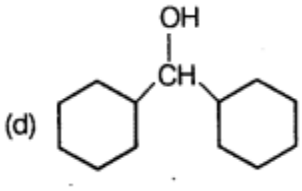
(d) 

Question 51.
Which one of the following compounds has the most acidic nature?

(a) 

(b) 

(c) 

(d) 

Question 52.
Among the given compounds, one which can be distinguished by $AgN0_3$ is
(a) ethane
(b) ethylene
(c) acetylene
(d) diethyl ether

Answers:

1. (d)	2. (c)	3. (d)	4. (c)	5. (a)	6. (d)	7. (b)	8. (a)	9. (a)	10. (d)
11. (d)	12. (a)	13. (c)	14. (a)	15. (c)	16. (a)	17. (a)	18. (c)	19. (b)	20. (c)
21. (c)	22. (c)	23. (b)	24. (d)	25. (b)	26. (b)	27. (a)	28. (a)	29. (b)	30. (d)
31. (c)	32. (b)	33. (a)	34. (a)	35. (c)	36. (d)	37. (a)	38. (b)	39. (c)	40. (a)
41. (a)	42. (a)	43. (a)	44. (b)	45. (c)	46. (a)	47. (c)	48. (a)	49. (b)	50. (c)
51. (b)	52. (c)								

Hints And Solutions:

1. $CH_2{=}CH_2 + H_2SO_4 \longrightarrow C_2H_5HSO_4 \xrightarrow[-H_2SO_4]{H_2O/H^+} C_2H_5OH$

2. $H_3C{-}\underset{\underset{CH_3}{|}}{C}{=}O \xrightarrow[\text{Ether}]{C_2H_5MgI} H_3C{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OMgI}{|}}{C}}{-}CH_3$

A (Acetone) B

$\xrightarrow[-Mg(OH)I]{H_2O/H^+} H_3C{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_3$

t-pentyl alcohol

3. Ethylene oxide on treatment with Grignard reagent to give additive product which on hydrolysis to give primary alcohol as final product.

$$\underset{\diagdown\,O\,\diagup}{CH_2{-}CH_2} + RMgX \longrightarrow RCH_2CH_2{-}OMgX \xrightarrow{H_3O^+} \underset{\text{Primary alcohol}}{RCH_2CH_2OH} + Mg(OH)X$$

4. Lower members are soluble in water as they form H-bonding with water molecules.
Solubility of alcohols in water decreases with increase in molecular masses.

5. Boiling point of alcohols increases with molecular weight. Alcohols with same molecular weight are expected to have almost same boiling point however two more factor other than molecular weight are important, they are namely H-bonding and surface area. Both these factors are least in 3° alcohols and maximum in 1° alcohols.

Therefore, the correct order of boiling points of alcohols will be

$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} < \underset{\text{Butan-2-ol}}{CH_3CH_2CH(OH)CH_3} < \underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} < \underset{\text{Pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH}$$

6. When conc. HI or HBr react with mixed ether, the halogen atom attaches to the smaller alkyl group due to steric effect.

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-CH_3 + HI \xrightarrow{\Delta} CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2OH + CH_3CH_2I$$

7. $CH_3CH_2OH \xrightarrow{[O]} CH_3CHO + H_2O$

8. $\underset{\text{Ethyl alcohol}}{C_2H_5OH} + 2[O] \xrightarrow{K_2Cr_2O_7/H^+} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$

9. A primary alcohol on oxidation with Cl_2 gives an aldehyde (CH_3CHO).

$$RCH_2OH \xrightarrow[\text{oxidation}]{Cl_2} RCHO + 2HCl$$

10. Since, oxidation is easier and occurs very quickly. Hence, it must be a 1° alcohol. The dichromate solution changes from orange to blue green.

11. Pyridinium chloro chromate (PCC) prevents further oxidation of aldehydes to carboxylic acid,

$$RCH_2OH \xrightarrow[CH_2Cl_2 \text{ solvent}]{PCC} RCHO + H_2O$$

12. $CH_3-\underset{\text{Iso-propyl alcohol}}{\underset{|}{\overset{OH}{|}}CH}-CH_3 \xrightarrow[\text{Mild oxidation}]{[O]} CH_3-\underset{\text{Acetone}}{\overset{O}{\overset{||}{C}}}-CH_3$

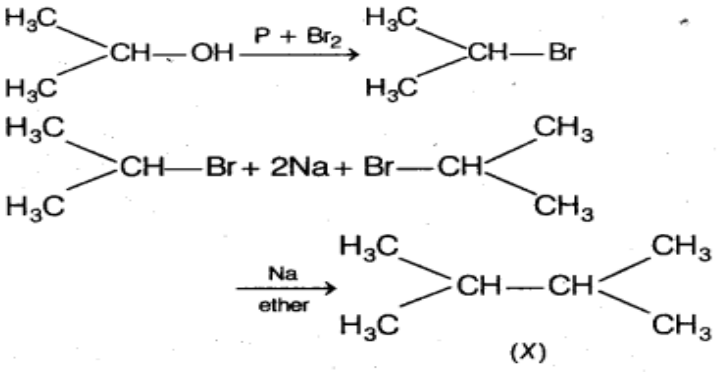
13. Mixture of anhydrous $ZnCl_2$ and conc. HCl is known as Lucas reagent. Lucas test is used for the distinction between primary, secondary and tertiary alcohols.

The tertiary alcohol reacts immediately with Lucas reagent producing turbidity.

The secondary alcohol gives turbidity within 5 -10 min and primary alcohol dose not give turbidity at room temperature. In the given alternates, 2-hydroxy-2-methyl propane is a 3° alcohol, so it is more reactive.

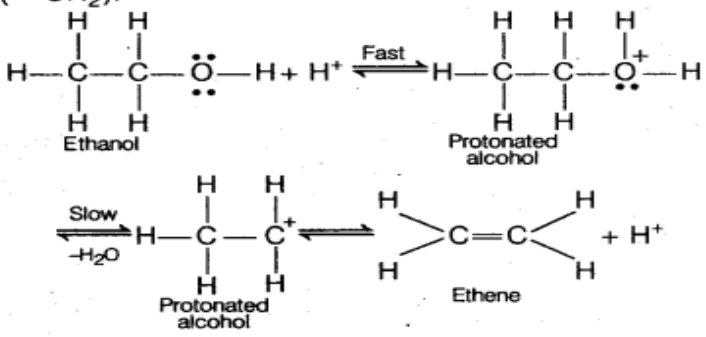
14. The presence of three electron releasing group (alkyl groups) at α-carbon atom repel the bond pair of C — OH bond and facilitate its replacement. Hence, the reactivity order is 3° > 2° > 1°.

15.



(X)

16. Protonation of —OH is first step. In this step, conversion of poor leaving group (—OH) into good leaving group ($-\overset{+}{O}H_2$).



17. When ethyl alcohol is oxidised by acidified potassium dichromate, CH_3COOH(Y) is obtained as

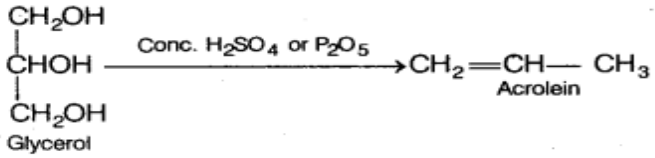
$$\underset{(X)}{3C_2H_5OH} + 2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow \underset{(Y)}{3CH_3COOH} + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$$

Carboxylic acid undergoes reduction with $LiAlH_4$ to give primary alcohol as

$$\underset{Y}{CH_3-\overset{\overset{O}{\|}}{C}-OH} \xrightarrow[(Ether)]{LiAlH_4} \underset{X}{CH_3CH_2OH}$$

So, X is CH_3CH_2OH and Y is CH_3COOH.

18.

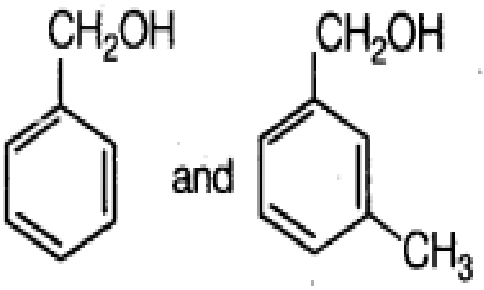
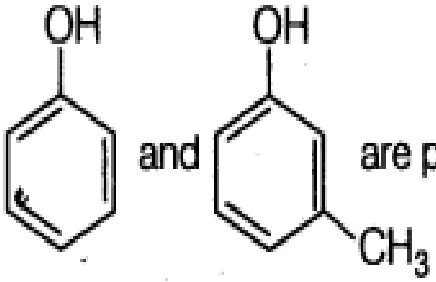


19. The dehydration of 1-butanol gives 2-butene as the main product because 2-carbocation is stable than 1°.

$$CH_3-CH_2-CH_2-CH_2OH \xrightarrow[H_2O]{H^+} \underset{1° \text{ carbocation}}{CH_3CH_2-CH_2\overset{+}{C}H_2}$$

$$\xrightarrow{\text{H-shift}} \underset{2° \text{ carbocation}}{CH_3CH_2-\overset{+}{C}H-CH_3} \longrightarrow \underset{2\text{-butene}}{CH_3-CH=CHCH_3}$$

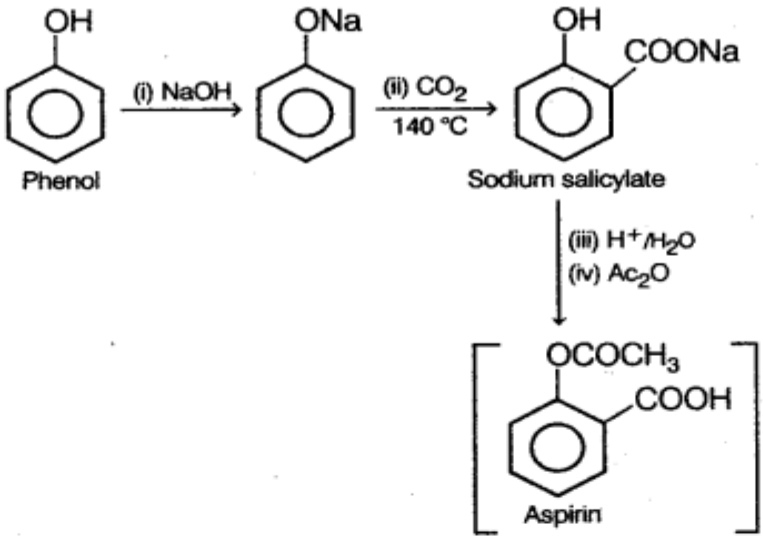
20. Anhy. $ZnCl_2$ and conc. HCl is called Lucas reagent.
It is used to distinguish the primary, secondary and tertiary alcohol.

21.  and are aromatic alcohols due to the presence of benzene ring and —OH group is attached with aliphatic carbon.  and are phenols.

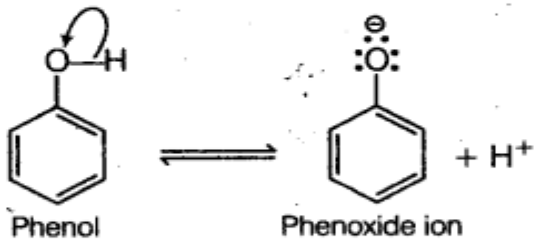
22. *p*-nitrophenol is more acidic because presence of electron withdrawing group at *o* or *p*-positions increases the acidic strength.

23. Phenols are acidic in nature due to resonance stabilisation of phenoxide ion. Presence of electron withdrawing groups (such as $-NO_2$, $-X$, $-NR_3^+$, $-CHO$, $-COX$, $-COOR$, $-CN$) in the ring stabilise phenoxide ion and increase the acidic nature of phenols. On the other hand, presence of electron releasing groups (such as $-CH_3$, $-OR$) in the ring destabilises the phenoxide ion and decreases the acidic nature of phenols.

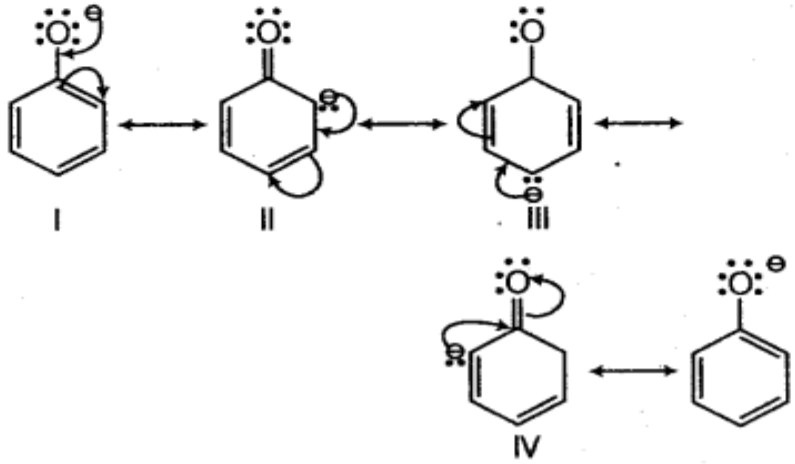
24.



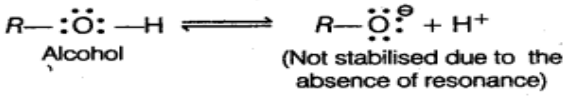
25. Phenols are much more acidic than alcohol due to the stabilisation of phenoxide ion resonance.



Phenoxide ion is stabilised due to the following resonating structures.



While, in alcohols

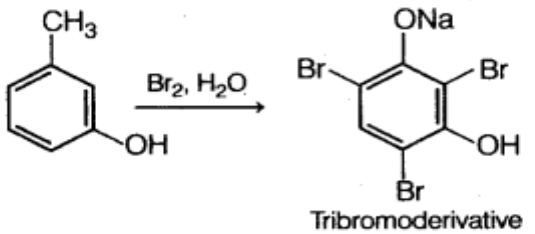


Ortho-nitrophenol is most acidic because in it, $—NO_2$ electron attracting group is attached at *ortho* position which helps in stabilising the negative charge on the oxygen of phenoxide ion. Hence, due to this reason, acidic character of phenol is increased, while on attachment of $—CH_3$ group (electron donating group) acidic strength of phenol is decreased in cresol due to the destabilisation of phenoxide ion.

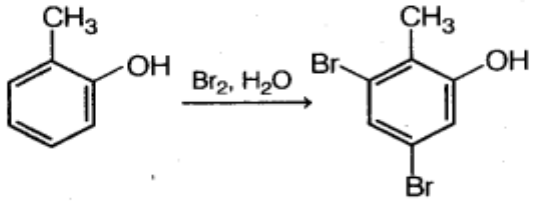
26. Phenols are acidic in nature due to resonance stabilisation of phenoxide ion. Presence of electron releasing groups such as $—CH_3$ destabilises ion and decreases the acidic nature of phenols. On the other hand presence of electron withdrawing group in the ring stabilise phenoxide ion and increases the acidic nature of phenols. Further more *meta*-isomer is less acidic than *para*, because it is stabilised by inductive effect only. Thus, correct order is

IV > III > I > II.

27. *m*-cresol due to phenoxide ion in H_2O solvent, gives tribromo derivative at all *ortho* and *para* positions.

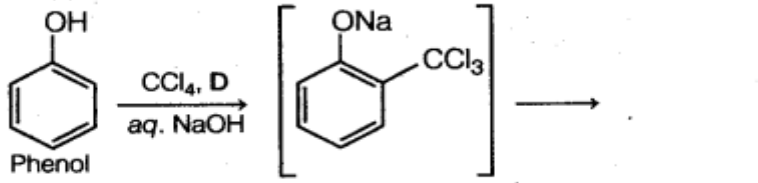


Tribromoderivative

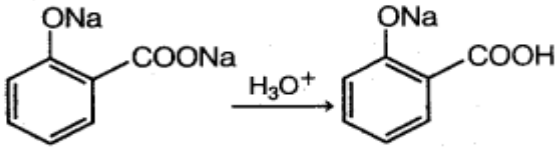


Dibromoderivative

28.

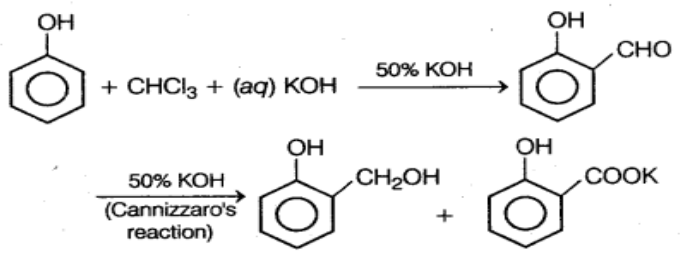


Phenol



Salicylic acid

29. Phenol on reaction with chloroform and KOH gives salicylaldehyde, which with 50% KOH solution undergoes Cannizaro's reaction.



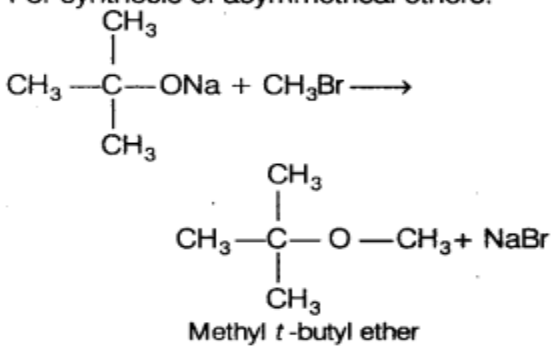
30. $(CH_3)_3C—ONa + CH_3Cl \longrightarrow (CH_3)_3C—O—CH_3 + NaCl$

Methyl-*t*-butyl ether

31. For synthesis of symmetrical ethers

$$CH_3ONa + BrCH_3 \longrightarrow \underset{\text{Dimethyl ether}}{CH_3OCH_3} + NaBr$$

For synthesis of asymmetrical ethers.



Methyl *t*-butyl ether

32. $\underset{t\text{-butyl methyl ether}}{(CH_3)_3C—O—CH_3} + HI \longrightarrow \underset{t\text{-butyl iodide}}{(CH_3)_3C—I} + \underset{\text{Methanol}}{CH_3OH}$

33. $CH_3CH_2—O—CH_2CH_3 + Cl_2 \xrightarrow{\text{Dark}} CH_3CH_2—O—\underset{Cl}{CH}—CH_3$

34. The structure of crotyl alcohol is $CH_3—CH=CH—CH_2OH$.

Here, it is clear that it is a primary alcohol. Due to the presence of double bond, it gives test for unsaturation.

Crotyl alcohol and allyl alcohol ($CH_2=CHCH_2OH$) have a difference of $—CH_2$ unit, so they are not isomers.

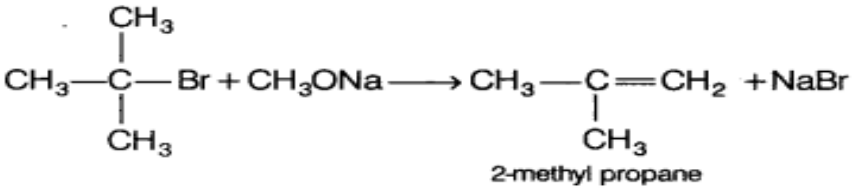
35. (1) $\underset{\text{Sodium ethoxide}}{C_2H_5ONa} + \underset{\text{Methyl iodide}}{CH_3I} \longrightarrow \underset{\text{Methyl ethyl ether}}{C_2H_5OCH_3} + NaI$

(2) $\underset{\text{Sodium ethoxide}}{C_2H_5ONa} + \underset{\text{Ethyl chloride}}{C_2H_5Cl} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + NaCl$

(3) $\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{\text{Red P/HI}} \underset{\text{Ethane}}{C_2H_6}$

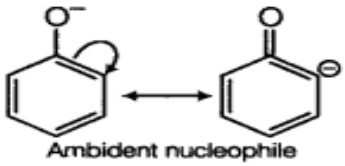
(4) $\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{(conc.)}}{H_2SO_4} \xrightarrow{140°C} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2O$

38. *t*-butyl methyl ether cannot be prepared by reaction of *t*-butyl bromide with sodium methoxide because sodium methoxide is a strong base hence, *t*-halide undergo elimination reaction rather instead of nucleophilic substitution reaction.



CH_3ONa is also a nucleophile (CH_3O^-).

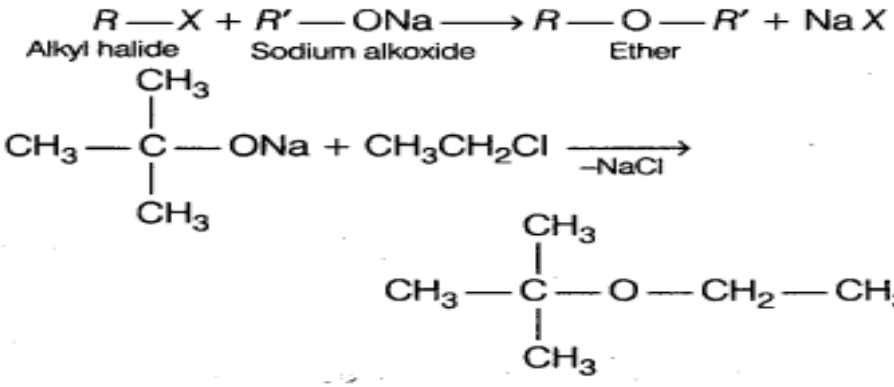
39. Phenoxide ion is given as



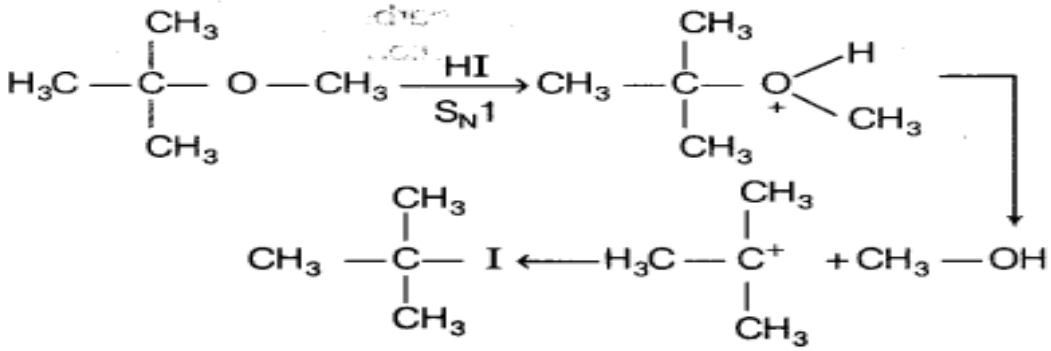
Thus, it gives two products, i.e. O-substituted and C-substituted with active alkyl halide.

41. —F has stronger +*M*-effect than —Cl, thus,

42. The reaction of alkyl halides with sodium alkoxide or sodium phenoxide to form ethers is called Williamson synthesis. Here, in this reaction alkyl halide should be primary and alkoxide, e.g. should be bulkier as shown below:



44.



45. $K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2Cr_2O_7$

$$4[H_2O_2 \longrightarrow H_2O + O]$$

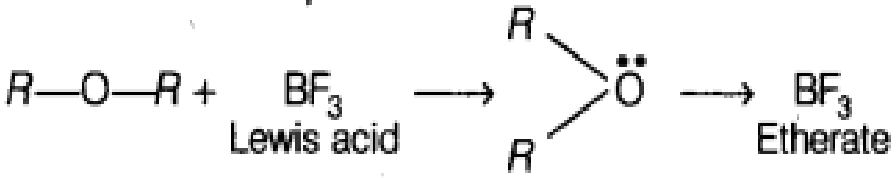
$$H_2Cr_2O_7 + 4O \longrightarrow 2CrO_5 + H_2O$$

$$K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O$$

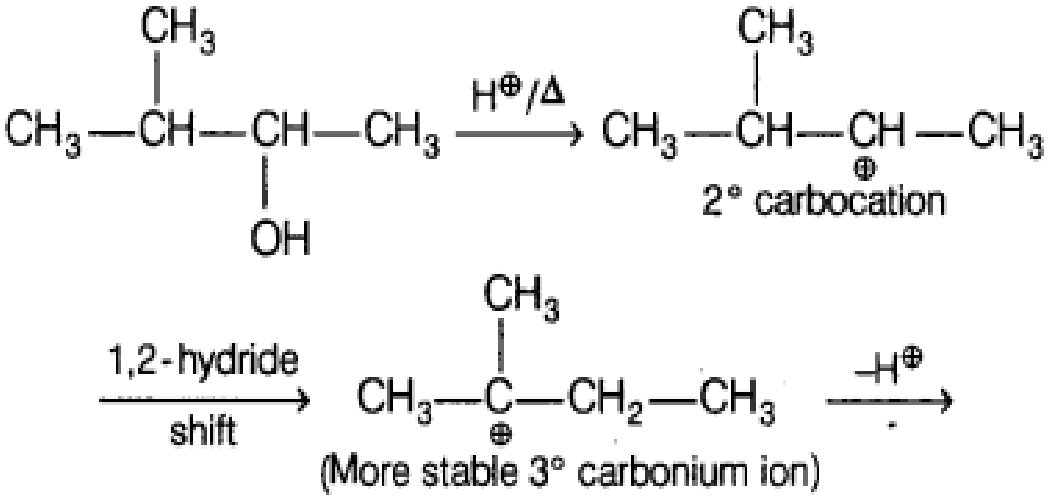
Acidified $K_2Cr_2O_7$ is oxidised to blue peroxide of chromium (CrO_5) which is soluble in ether and produces blue coloured solution.

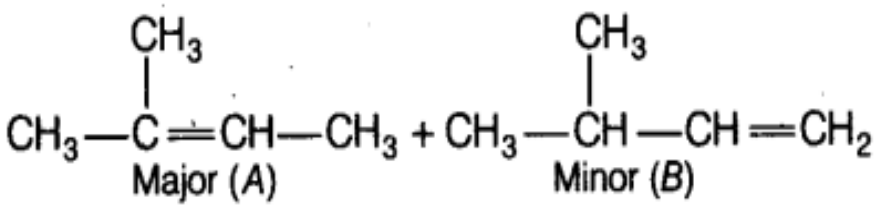
46. Dunstan's test is used for identification of glycerol.

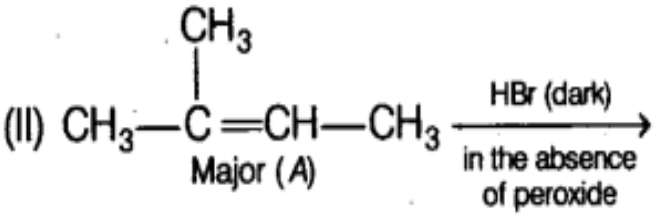
47. Etherates are complexes of ethers with Lewis acid.

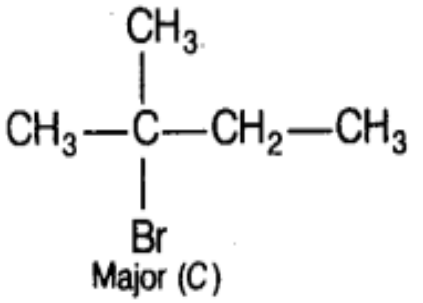


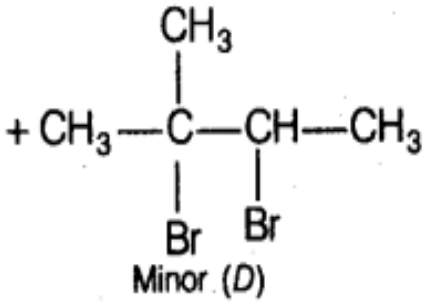
48. (I)



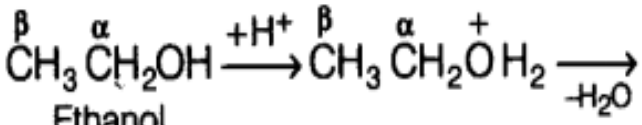


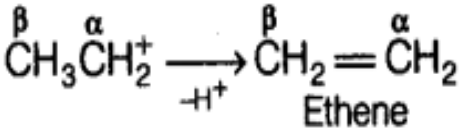




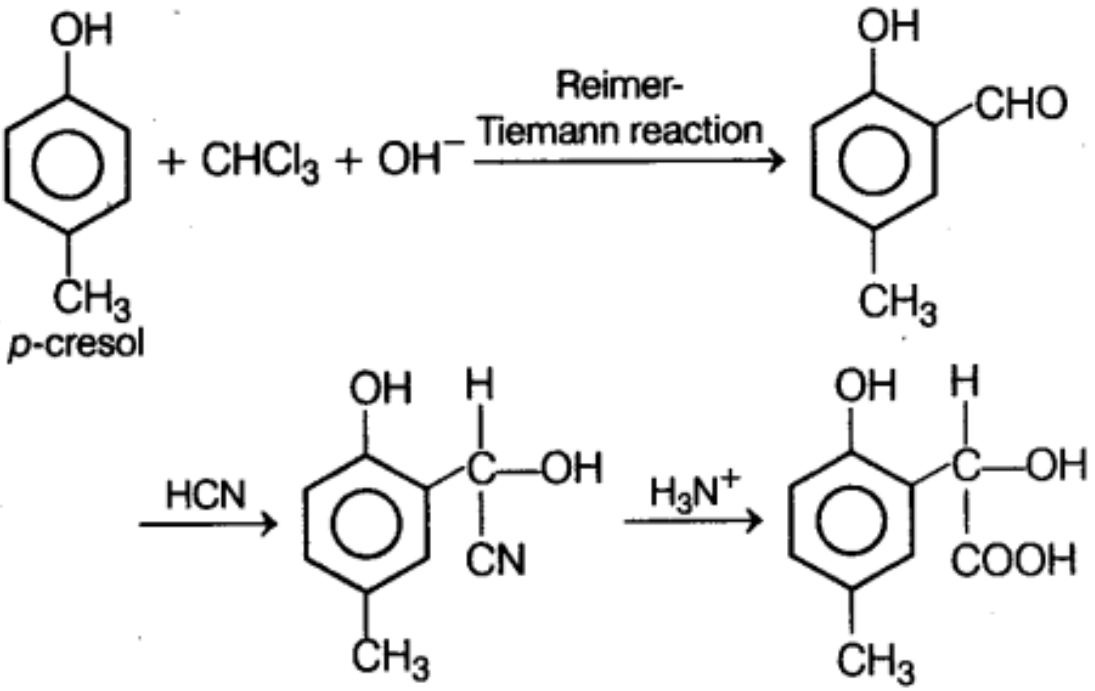


49. Dehydration of alcohol involves the loss of two atoms or groups from the adjacent carbon atoms, hence, it is an example of β-elimination reaction.





50.



(—OH is more activating than —CH_3 in *o*, *p*-directing, thus, —CHO goes to *o*-position w.r.t —OH).

51. Presence of electron withdrawing substituent increases the acidity while electron releasing substituent, when present, decreases the acidity. Phenyl is an electron withdrawing substituent while —CH_3 is an electron releasing substituent. Moreover, phenoxide ion is more resonance stabilised as compared to benzyloxide ion, thus releases proton more easily. That's why it is a strong acid among the given.

52. Only acetylene reacts with $AgNO_3$ and gives white precipitate of silver acetylide among the given compounds.

$$CH{\equiv}CH \xrightarrow[+\ NH_4OH]{AgNO_3} \underset{\text{White ppt}}{CAg{\equiv}CAg}$$

Thus, it is distinguished by $AgNO_3$.