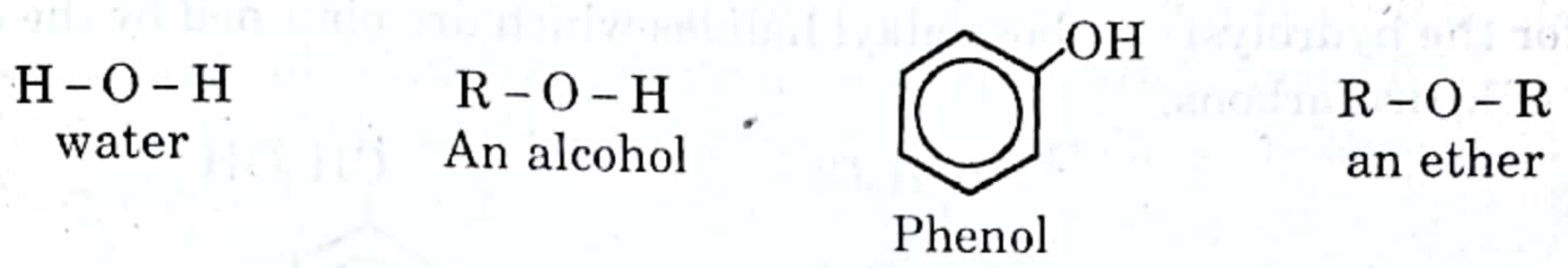


9. ALCOHOLS, PHENOLS AND ETHERS

Alcohols, phenols and ethers are structurally related compounds and may be regarded as derivatives of water. Alcohols and phenols are obtained from water by replacing one of its hydrogens by alkyl and aryl groups, respectively. Ethers are obtained from water by replacing both of its hydrogens by two alkyl, two aryl or one alkyl and one aryl groups.

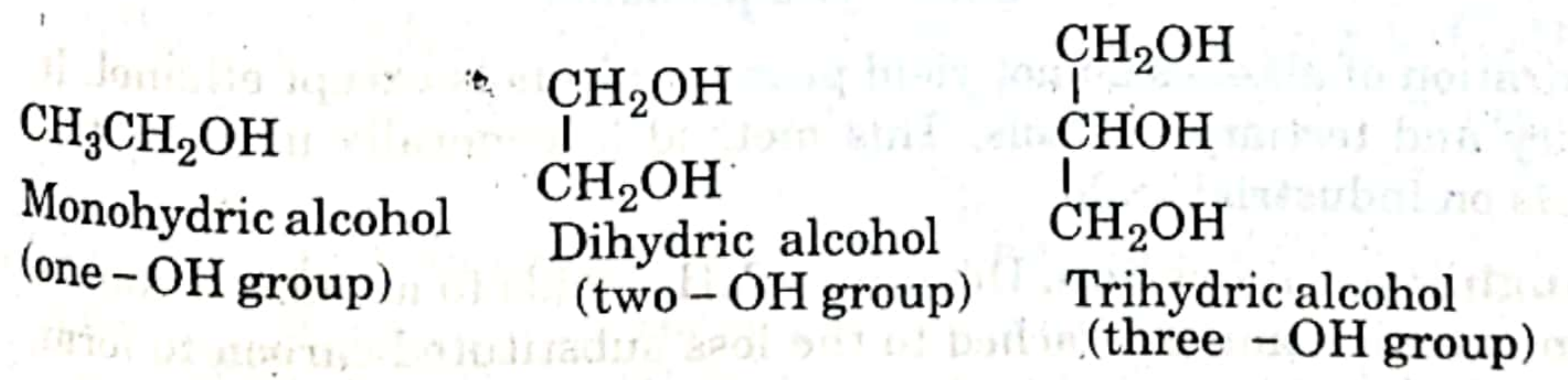


Both alcohols and phenols have the hydroxyl (-OH) functional groups while the functional group of ether is **oxo** (-O-). In alcohols the hydroxyl group is attached to an aliphatic carbon atom, while in phenols the hydroxyl group is directly attached to an aromatic ring.

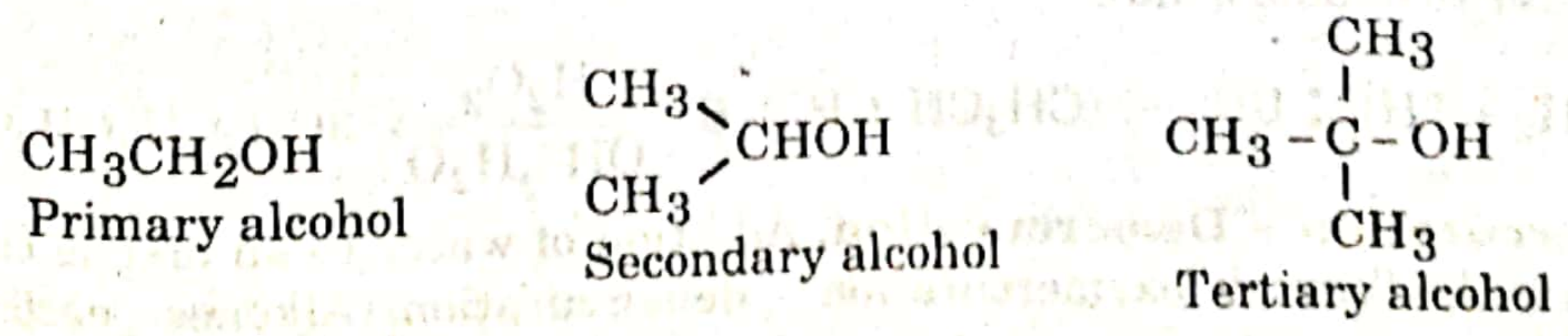
ALCOHOLS

9.1 Classification of Alcohols.

Compounds in which a hydroxyl group is attached to an aliphatic carbon atom are called **alcohols**. Alcohols are classified as monohydric, dihydric and trihydric, depending upon the number of hydroxyl groups they contain in their molecules. Alcohols containing one hydroxyl group in their molecules are called **monohydric alcohols** and the alcohols containing two and three hydroxyl groups on different carbon atoms in their molecules are called **dihydric** and **trihydric** alcohols, respectively. The alcohols having more than one hydroxyl group in their molecules are generally called **polyhydric alcohols**.

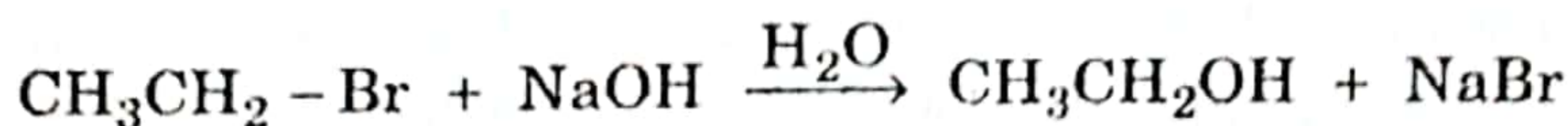


Monohydric alcohols are further classified as **primary** (prim-), **secondary** (sec-) and **tertiary** (tert-) **alcohols** depending on whether the - OH group is attached to a primary, secondary or a tertiary carbon atom.

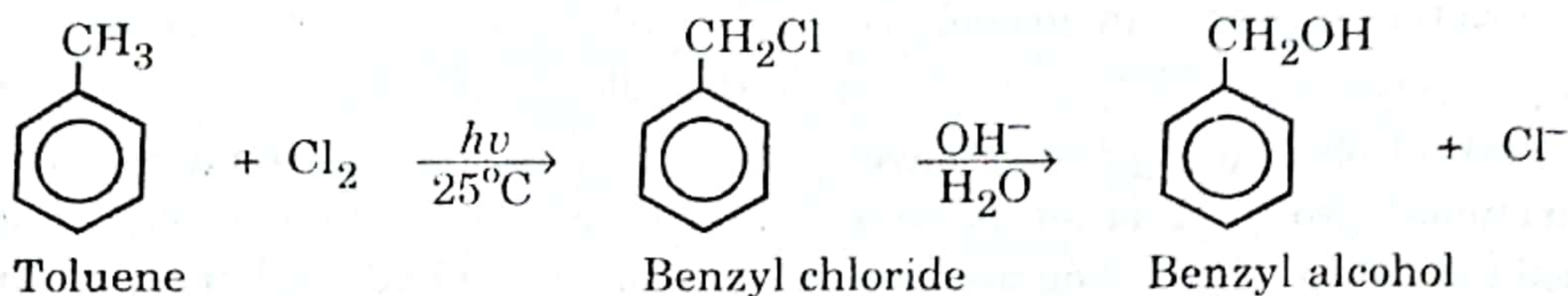


9.2 Methods of preparation of Alcohols

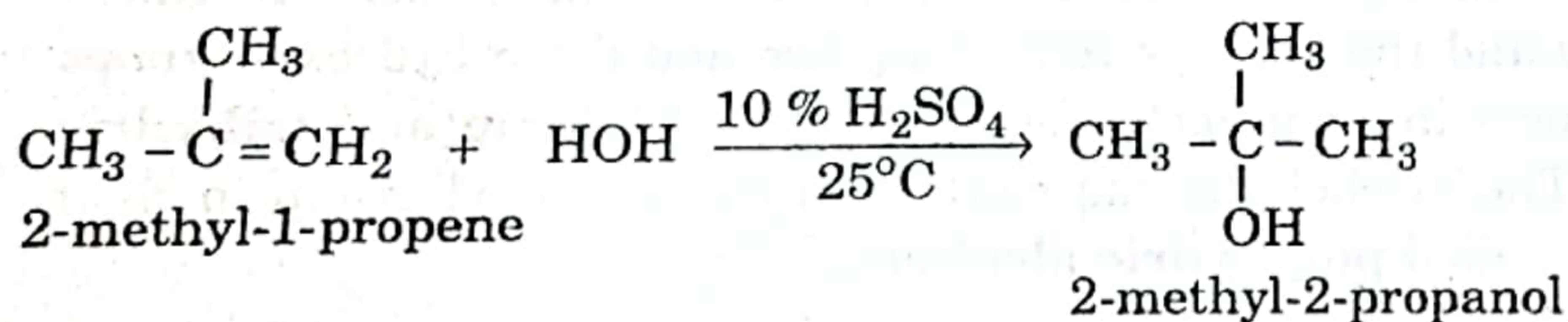
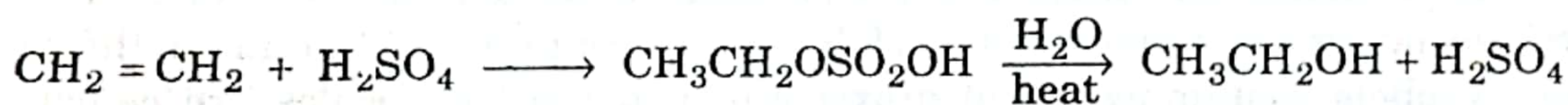
1. Hydrolysis of Alkyl Halides. Alkyl halides react with aqueous sodium hydroxide to form alcohols.



This method is of limited use because the alkyl halides are themselves are obtained from alcohols. However, this method does have some industrial importance, particularly for the hydrolysis of those alkyl halides which are obtained by the direct halogenation of hydrocarbons.

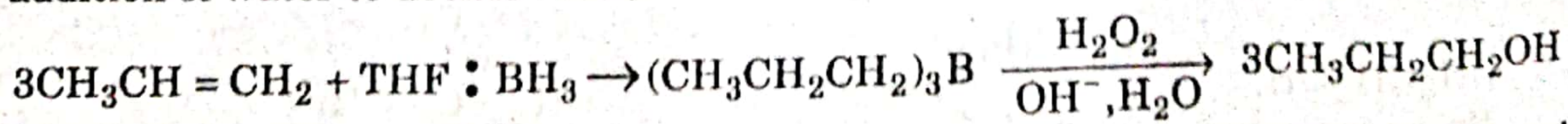


2. Hydration of Alkenes. The acid-catalyzed addition of water to an alkene gives an alcohol. The acids most commonly used to catalyze the hydration of alkenes are sulphuric acid and phosphoric acid. The addition of water to the double bond follows Markovnikov's rule. Alkenes react with sulphuric acid to produce alkyl hydrogen sulphates which on dilution with water followed by heating are hydrolyzed to alcohols.



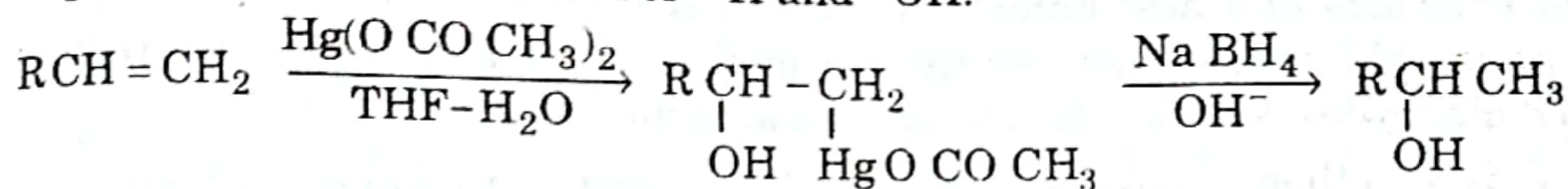
Acid-catalyzed hydration of alkenes do not yield primary alcohols except ethanol. It yields only secondary and tertiary alcohols. This method is generally used for the production of alcohols on industrial scale.

3. Hydration through Hydroboration. Diborane, B_2H_6 , adds to an alkene double bond with the boron atom becoming attached to the less substituted carbon to form trialkylboranes, which on oxidation with H_2O_2 in aqueous base give alcohols. Diborane adds as borane, BH_3 . Hydroboration reactions are usually carried out in diethyl ether or in tetrahydrofuran (THF). The result is an addition of $-\text{H}$ and $-\text{OH}$ with the $-\text{OH}$ being attached to the least substituted carbon (anti-Markovnikov addition of water to double bond).

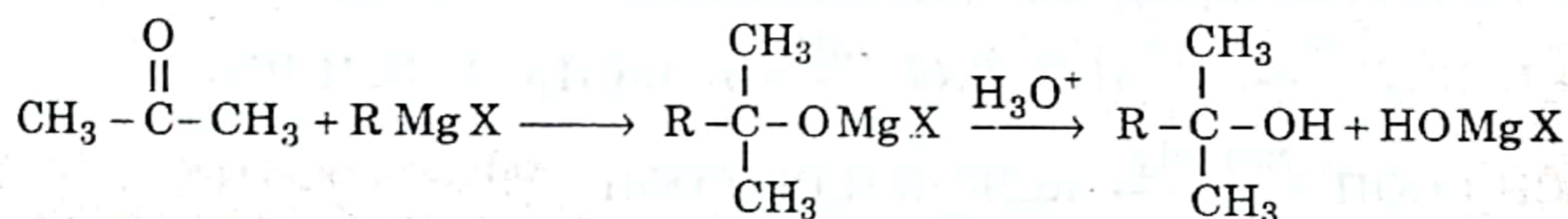
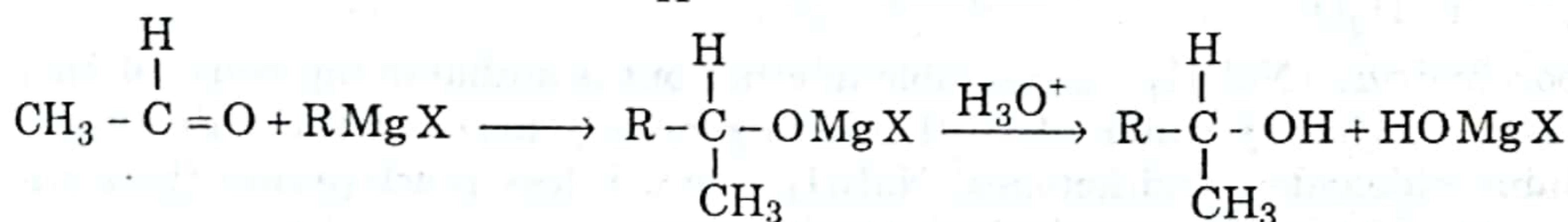
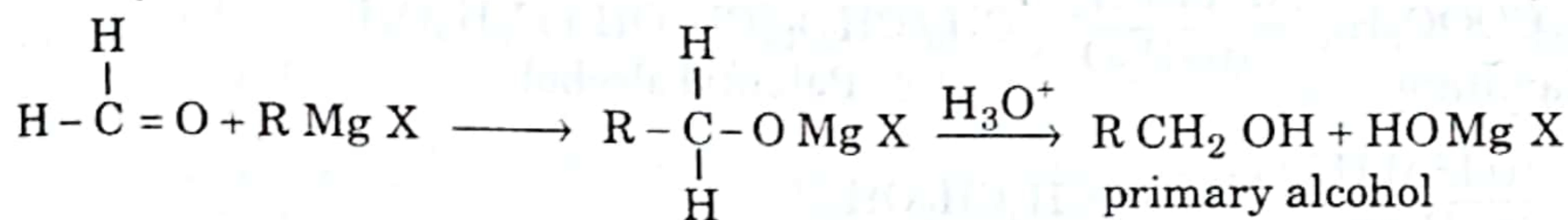


4. By Oxymercuration - Demercuration. Addition of water to an alkene can be achieved indirectly through oxymercuration - demercuration. Alkenes react with

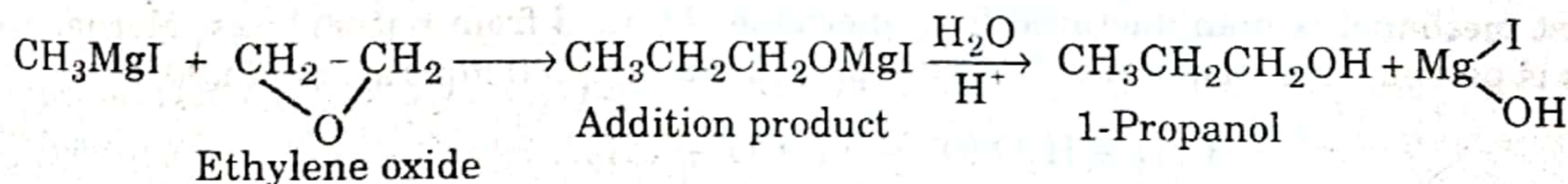
mercuric acetate in a water-tetrahydrofuran solution to form hydroxyalkylmercury compounds which on reduction with NaBH_4 yield alcohols. The net result of the two steps is Markovnikov addition of $-\text{H}$ and $-\text{OH}$.



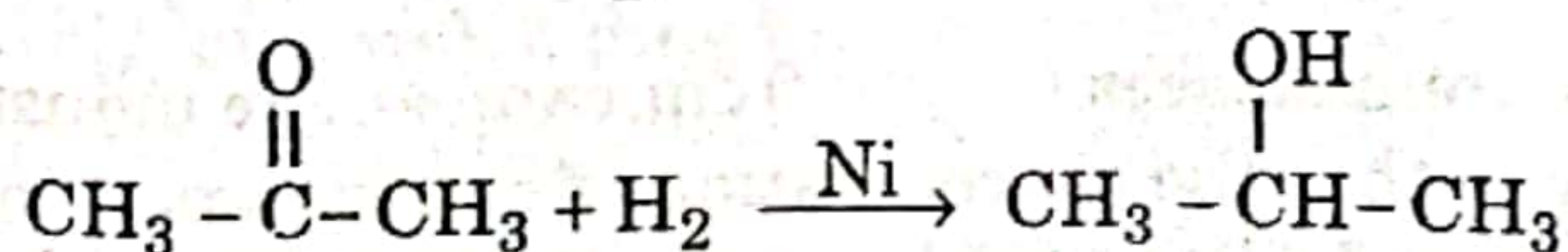
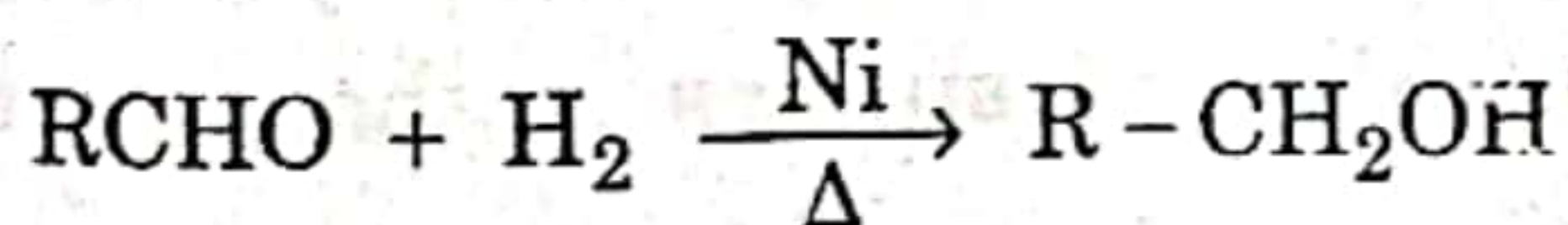
5. Alcohols from Grignard Reagent. Grignard reagent reacts with aldehydes or ketones to form an addition compound which on hydrolysis with dilute acid gives the corresponding alcohol. Formaldehyde with Grignard reagent gives primary alcohol. Aldehydes other than formaldehyde form secondary alcohols and ketones yield tertiary alcohols.



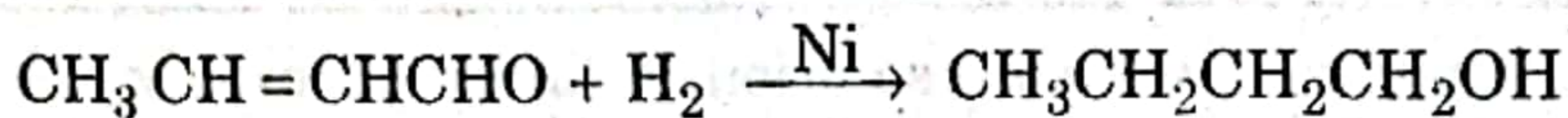
6. By the action of Grignard reagent on epoxides. Grignard reagents react with ethylene oxide (epoxide) to give an addition product which on hydrolysis yields primary alcohol.



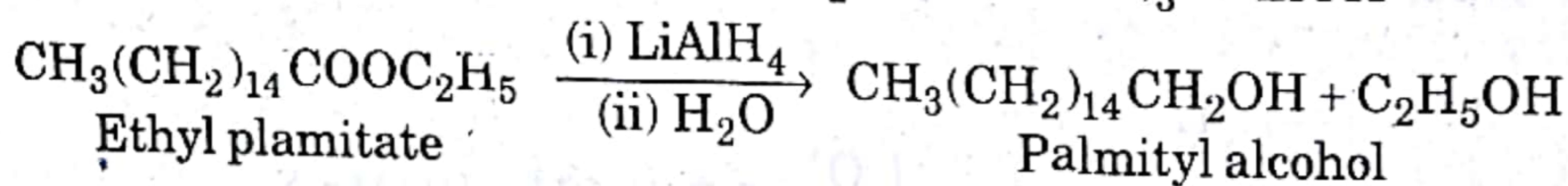
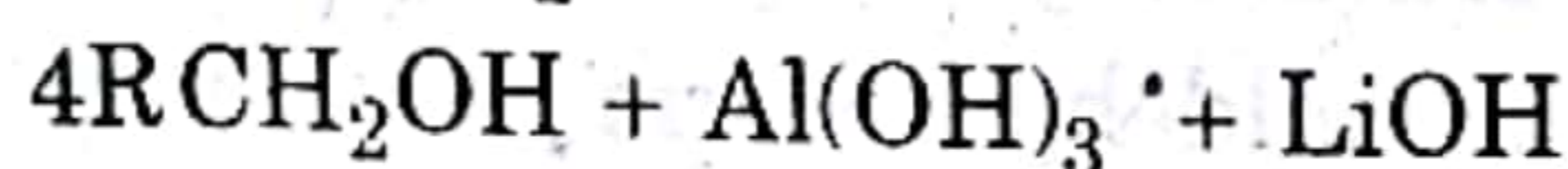
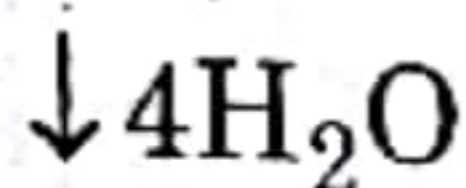
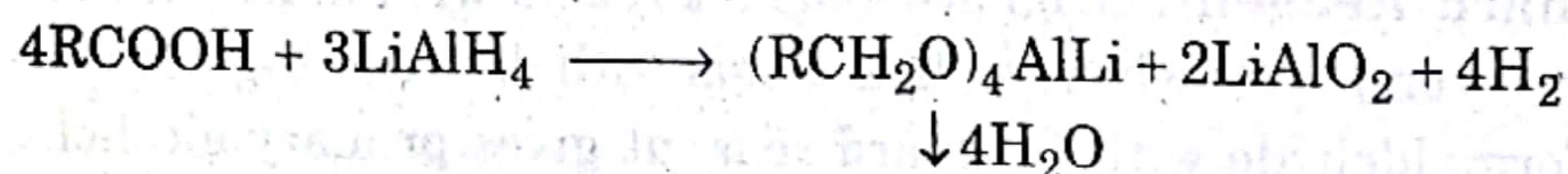
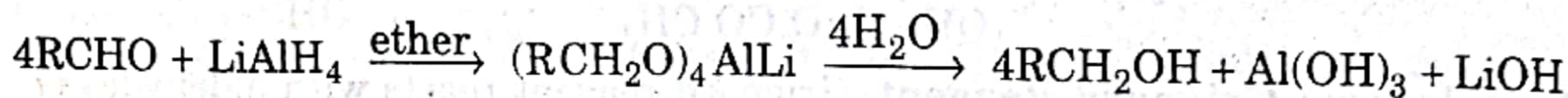
7. By the reduction of aldehydes, ketones, acids and esters. Alcohols can be easily prepared by the reduction of aldehydes and ketones either by hydrogenation in the presence of metal catalyst such as Ni, Pt or Pd or by the use of chemical reducing agents such as LiAlH_4 or NaBH_4 .



Catalytic hydrogenation has a drawback that it also reduces other functional groups such as $\text{>C}=\text{C}<$, $-\text{C}\equiv\text{C}-$, $-\text{C}\equiv\text{N}$, $-\text{NO}_2$ etc., if present in the molecule.

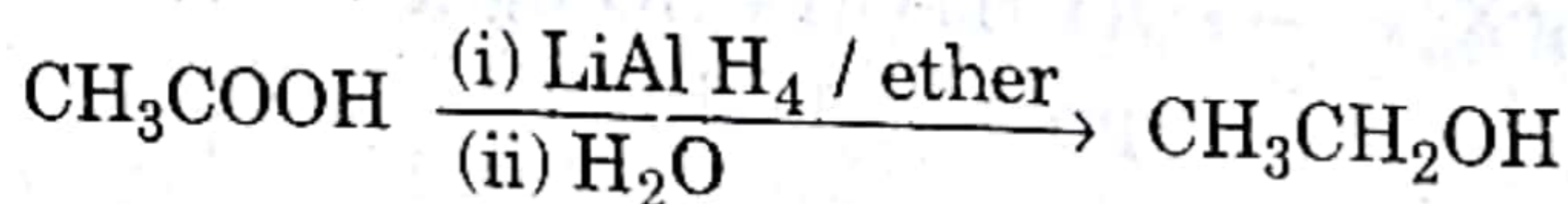


LiAlH_4 gives a very good yield of alcohols from aldehydes, ketones, acids, esters, acid chlorides and acid anhydrides in ethereal solution. One advantage of this reagent is that it does not reduce the olefinic bond and hence can reduce unsaturated aldehydes, ketones, etc., to unsaturated alcohols.

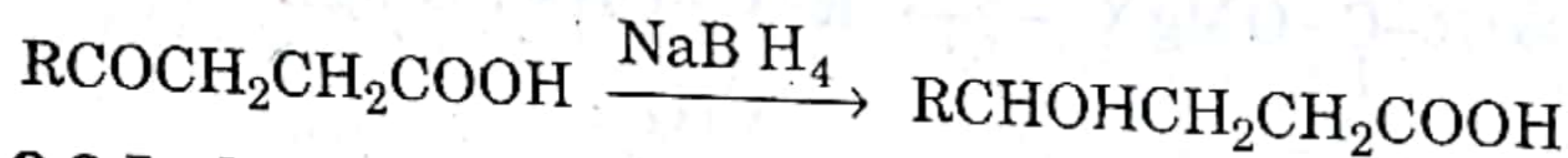
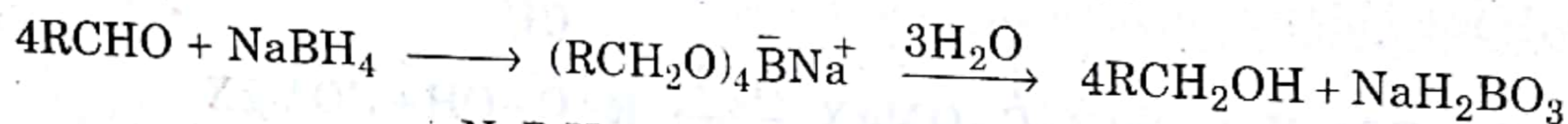


Ethyl palmitate

Palmityl alcohol

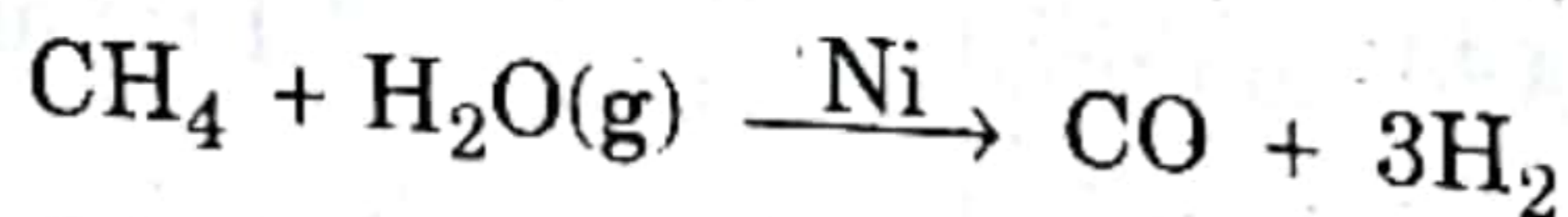


Sodium borohydride (NaBH_4) is insoluble in ether but is stable in aqueous solution (LiAlH_4 is destroyed by water). It is therefore generally used for the reduction of water-soluble aldehydes, and ketones. NaBH_4 is much less reactive and therefore more selective and reduces only aldehydes and ketones.

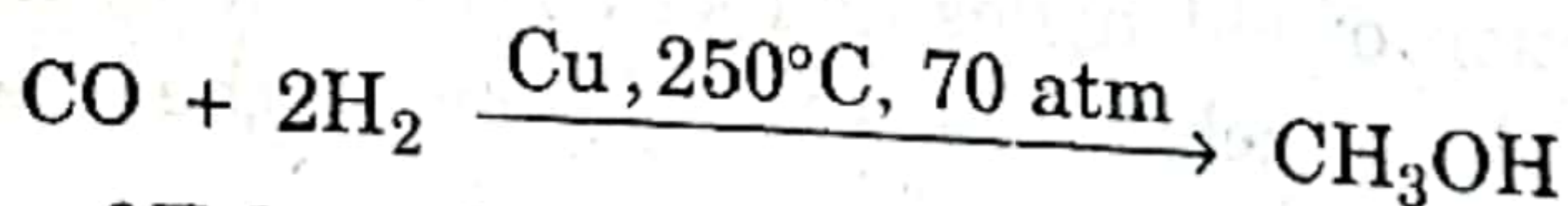


9.3 Industrial Preparation of Alcohols

Manufacture of Methanol. At one time, most methanol was produced by the destructive distillation of wood and therefore, was called "**wood alcohol**". Today, most methanol is manufactured from methane obtained from natural gas. Methane gas is passed with steam over Ni under pressure and at a temperature of 900°C .

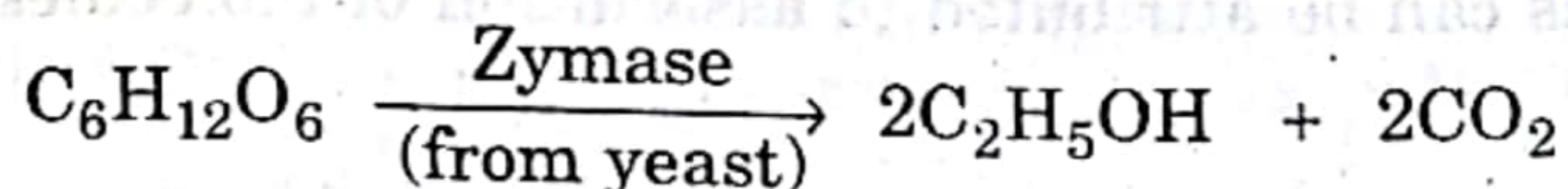
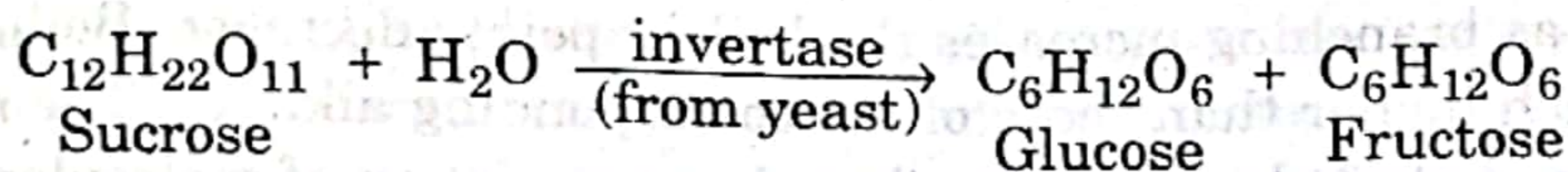


The mixture of CO and H_2 gases is passed over a heated copper catalyst under pressure to produce methanol.

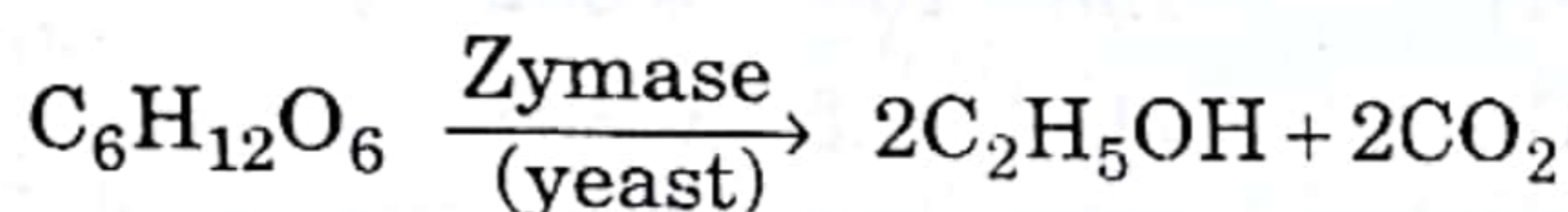
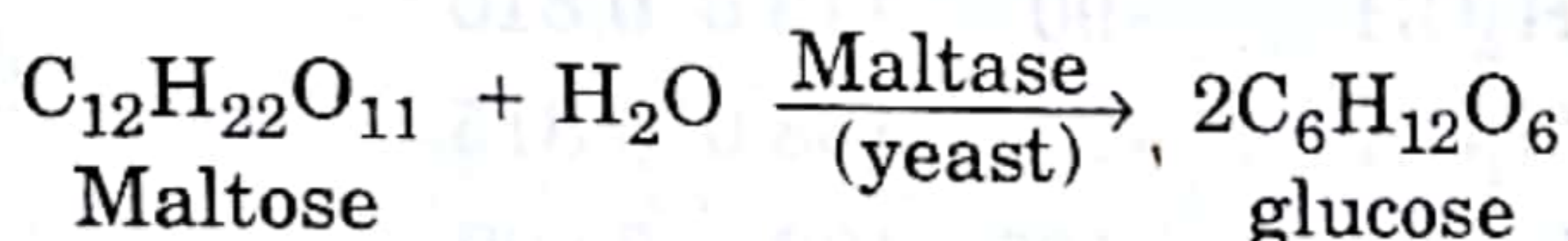
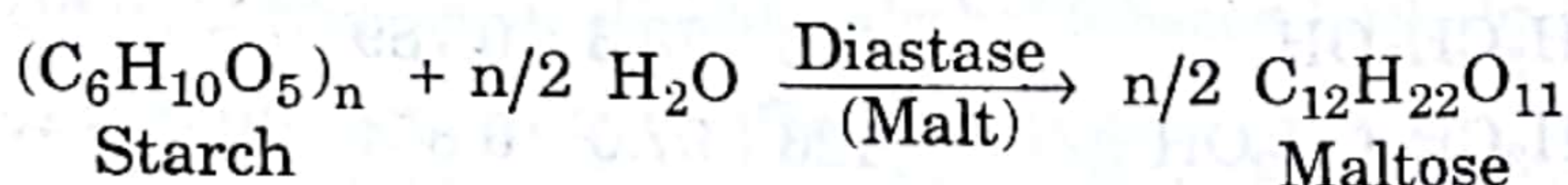


Manufacture of Ethanol. Ethanol is the alcohol of wine, beer, whiskey and similar beverages and can be made by the **fermentation of sugars** in the presence of yeast.

The main sources of sugars are molasses (waste from cane-sugar industries). The molasses is diluted with water so that the concentration of sugar comes down to about 10%. It is boiled and acid is added till its pH becomes 4. This solution known as **wort**, is mixed with yeast and kept at 35°C in large tanks. The following reactions are involved in the fermentation of sugars.

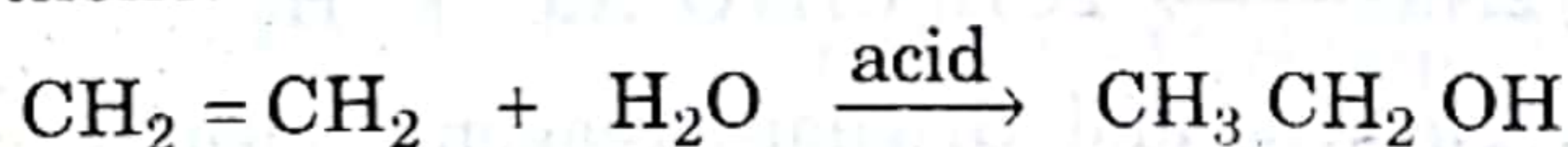


If the source for sugar is starch, then the starchy materials are converted into mash which is treated with malt, from germinating barley and contains the enzyme **diastase**. This enzyme converts starch into maltose which is then subjected to fermentation with yeast to get ethanol.



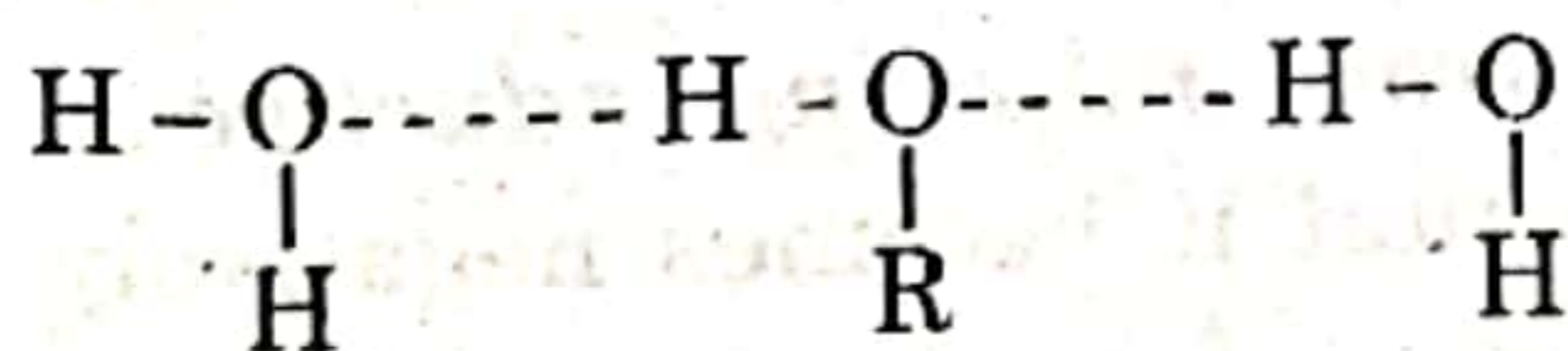
The crude alcohol thus obtained is subjected to fractional distillation whereby 95% ethanol called '**rectified spirit**' is obtained. To obtain 100% pure ethanol, called as **absolute alcohol**, it is mixed with benzene. Benzene forms an azeotrope with ethanol and water. Azeotropic distillation of the mixture gives three major fractions. The first fraction contains a mixture of benzene, ethanol and water, the second fraction contains benzene and ethanol and the final fraction is pure ethanol.

Most ethanol for industrial purposes is produced by the acid-catalyzed hydration of ethene.

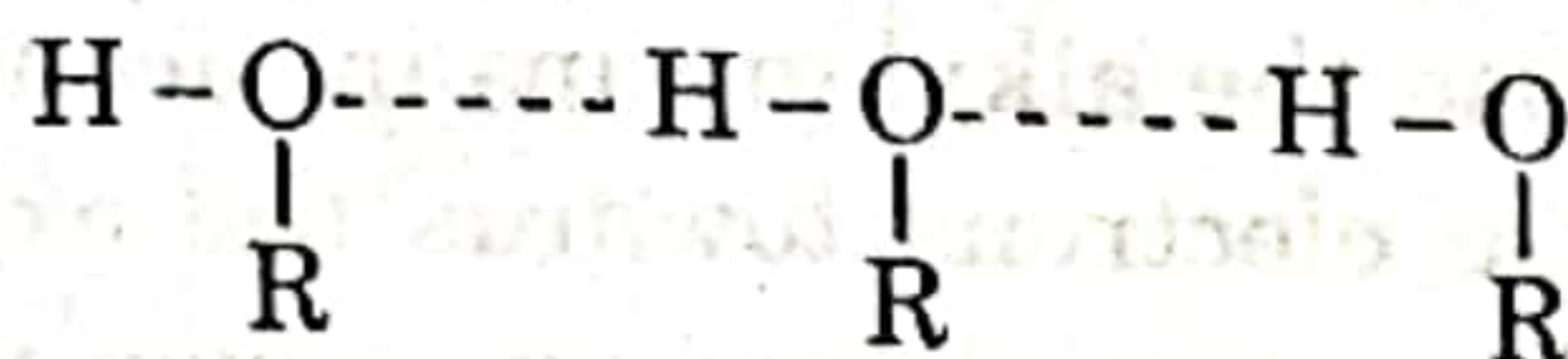


9.4 Physical Properties of Alcohols

Lower alcohols are colourless, toxic liquids and are miscible with water in all proportions. Their water solubility may be attributed to intermolecular hydrogen bonding between the molecules of alcohols and water. But with the increase in the number of carbon atoms, the solubility of alcohols in water decreases gradually. Among isomeric alcohols, the solubility increases with the increase in branching. For example, tert-butyl alcohol is completely miscible with water, but the other three butyl alcohols are only moderately soluble in water.



Hydrogen bonding between alcohol and water molecules



Hydrogen bonding in alcohol molecules

The boiling points of alcohols show a regular increase with the increase in the number of carbon atoms due to increase in van der Waals interactions. Among

isomeric alcohols, as branching increases the boiling points decrease. Boiling points of alcohols are much higher than those of the corresponding alkanes. The relatively high boiling points of alcohols can be attributed to association of molecules through hydrogen bonding.

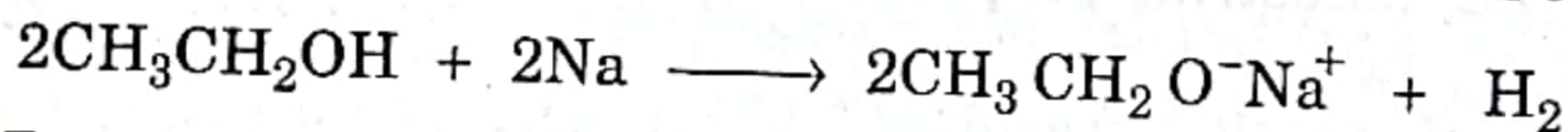
Table 9.1 Physical Properties of Alcohols

Name	Formula	M.pt. (°C)	B.pt. (°C)	Density (at 20°C)	Solubility (g/100cm ³ H ₂ O)
Methanol	CH ₃ OH	-97	65	0.792	∞
Ethanol	CH ₃ CH ₂ OH	-115	78.3	0.789	∞
1-Propanol	CH ₃ CH ₂ CH ₂ OH	-126	97.0	0.804	∞
1-Butanol	CH ₃ (CH ₂) ₂ CH ₂ OH	-90	118.0	0.810	7.9
1-Pentanol	CH ₃ (CH ₂) ₃ CH ₂ OH	-79	138.0	0.815	2.3
isobutyl alcohol	(CH ₃) ₂ CHCH ₂ OH	-108	108	0.802	10.0
sec - butyl alcohol	CH ₃ CH ₂ CHOHCH ₃	-114	99.5	0.807	12.5
tert - butyl alcohol	(CH ₃) ₃ COH	+25.5	82.5	0.789	∞

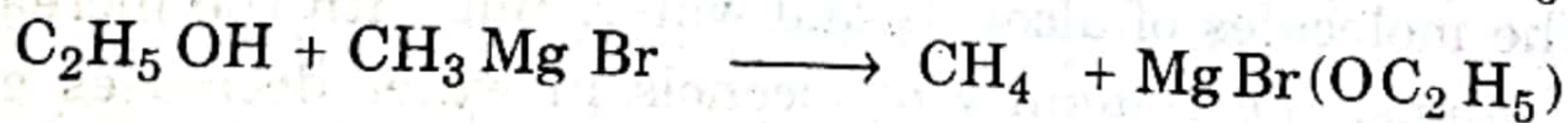
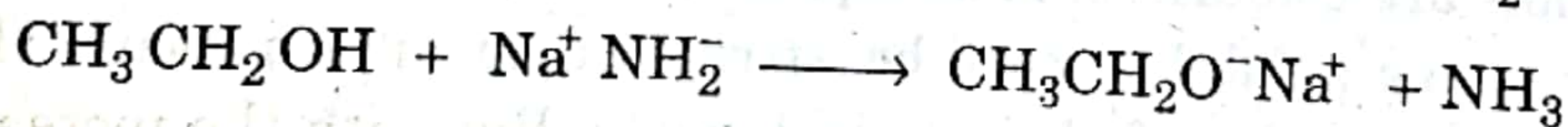
9.5 Chemical Reactions of Alcohols

Chemical reactions of alcohols involve either O-H or C-O bond cleavage. Some of the important reactions of alcohols are described below.

1. Reaction with Active Metals (Alcohols as acids). Alcohols react with active metals like Na, K or Mg to form alkoxides with the evolution of hydrogen gas.



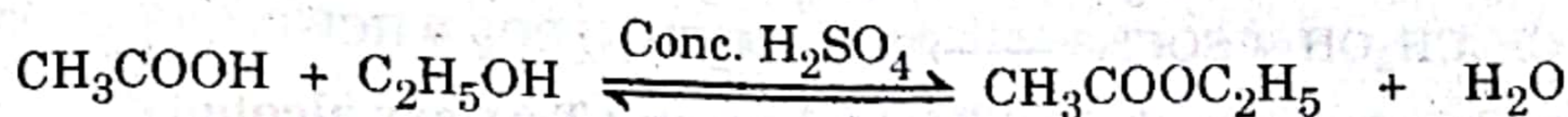
Bases like NaH, NaNH₂ and Grignard reagents also react with alcohols forming alkoxide ions.



The above reactions show that alcohols are acidic in nature. This is because that the O - H bond in alcohols is polar and allows the release of the hydrogen atom as proton (H⁺). However, alcohols are slightly weaker acids than water. This is because the alkyl groups in alcohols have a *electron-releasing inductive effect*. They release electrons towards the oxygen atom so that it becomes negatively charged. This negative charge on oxygen makes the release of positive proton more difficult. The order of acidity of alcohols is methyl > primary > secondary > tertiary alcohol.

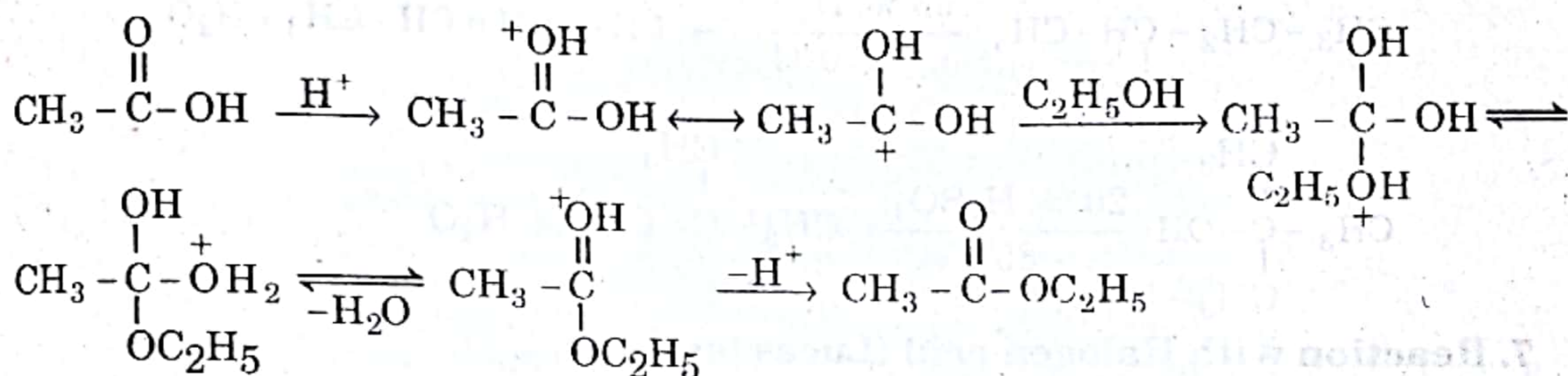
2. Reaction with carboxylic acids (esterification). Alcohols react with carboxylic acids on heating in the presence of catalytic amount of sulphuric acid to

form esters. The reaction is known as **esterification**. The reaction is reversible and can be shifted in the forward direction by removing water as soon as it is formed.



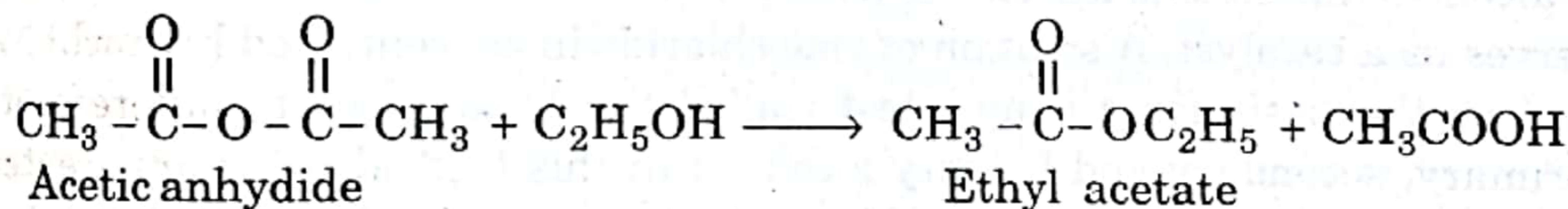
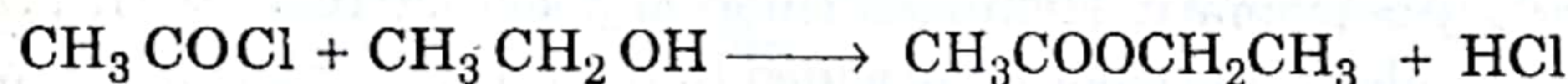
Conc. H_2SO_4 acts as a protonating agent as well as dehydrating agent. Only primary alcohols give good yields of esters. Steric hindrance is an important factor in esterification. A highly branched alkyl group in either the alcohol or the acid will show down the rate of esterification and also shift the equilibrium more to the left side of the esterification reaction. The order of reactivity of an alcohol with given organic acid is, therefore, as: Primary alcohol > Secondary alcohol > Tertiary alcohol.

The **mechanism of esterification** is as follows:

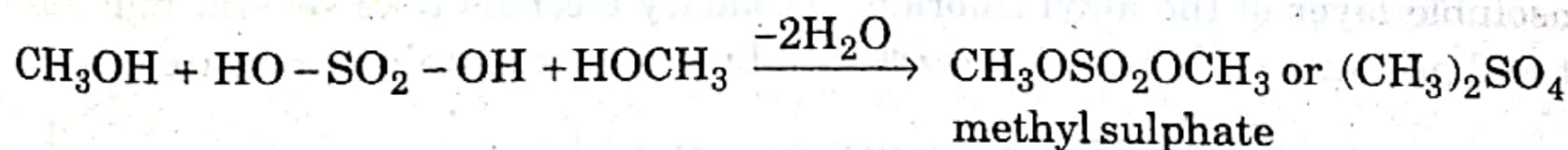


3. Reaction with Acid Halides and Acid Anhydrides (Acetylation)

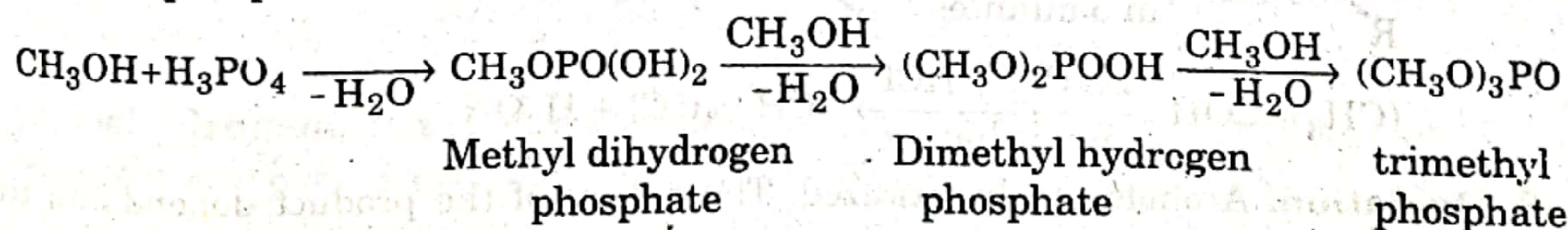
Alcohols react with acid halides and acid anhydrides to form esters.



4. Formation of Inorganic Esters. Alcohols react with inorganic acids containing oxygen such as sulphuric acid and phosphoric acid, to form esters.



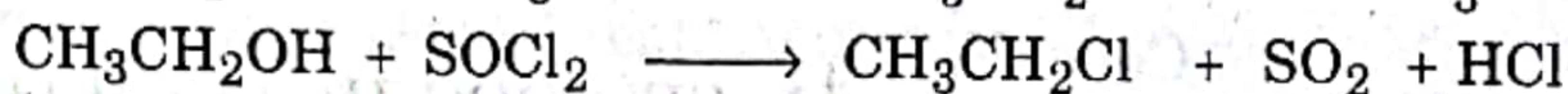
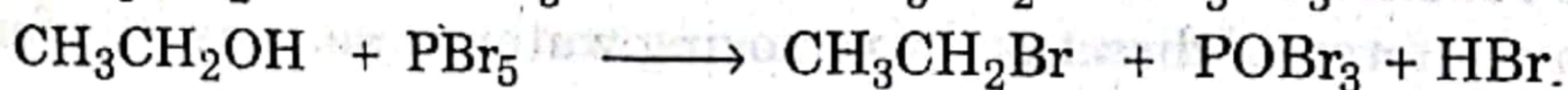
Methyl sulphate (an ester) is used as a methylating agent. Phosphoric acid with alcohols yield alkyl phosphates. If excess of alcohol is used, dialkyl and trialkyl esters of phosphoric acid are produced.



Esters of phosphoric acid are extremely important in biochemical reactions.

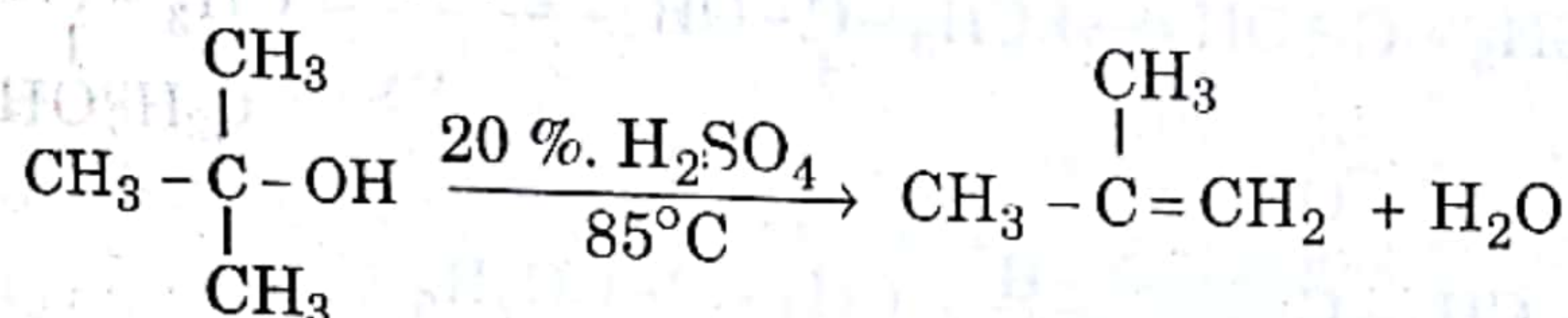
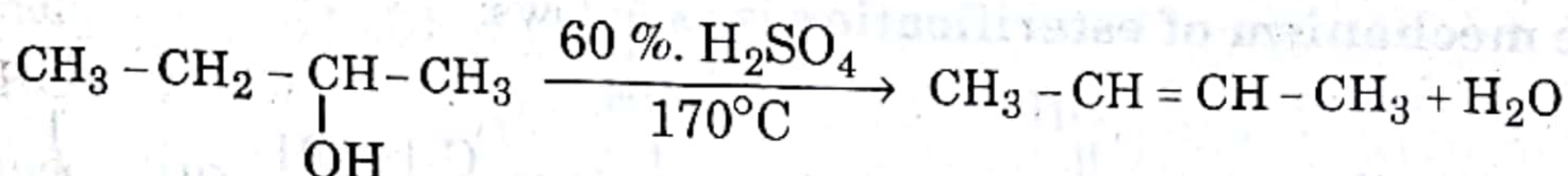
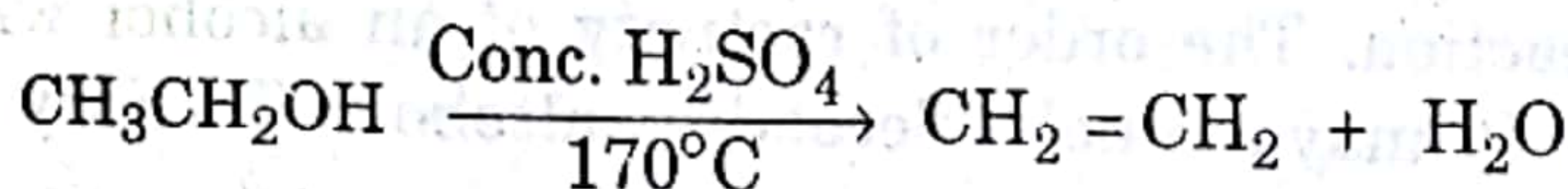
5. Reactions of Alcohols with phosphorus halides or Thionyl chlorides.

Alcohols react with phosphorus tri- or pentahalides or thionyl chlorid to form alkyl halides.



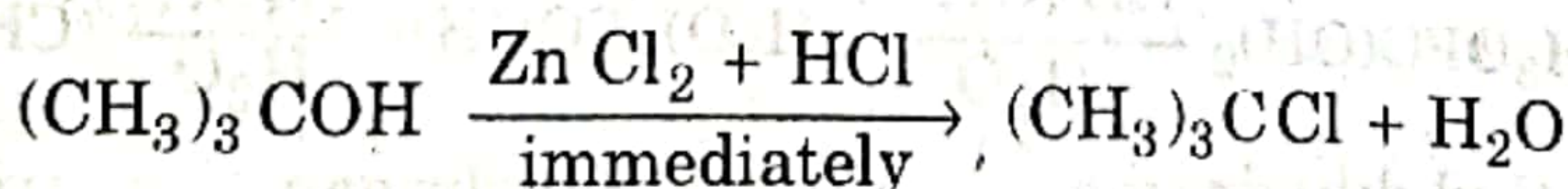
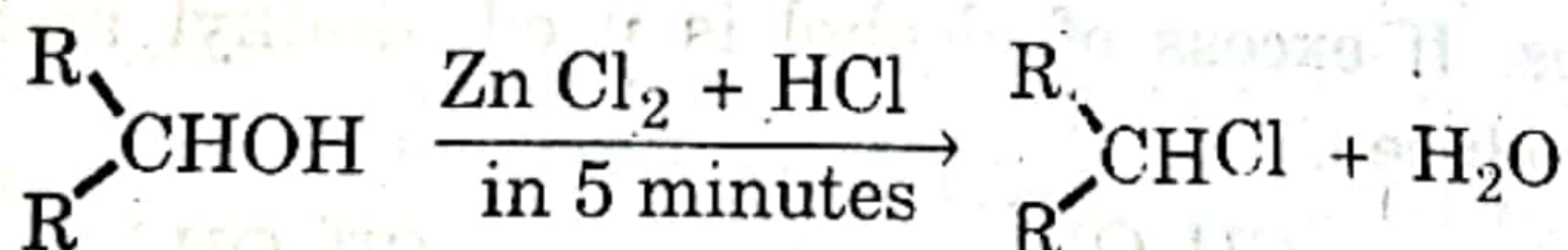
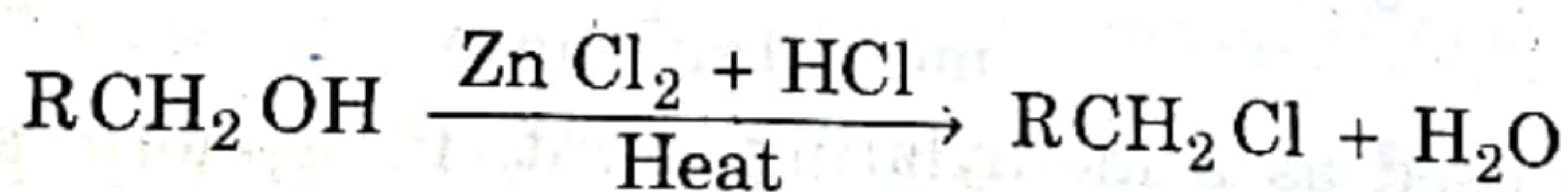
Distinguish between primary, secondary and Tertiary alcohols

6. Dehydration of Alcohols. When alcohols are heated with strong acids such as sulphuric acid, they undergo dehydration (elimination of water) to form alkenes. The ease of dehydration is tert- > sec- > primary which is also the order of stability of the carbonium ions.



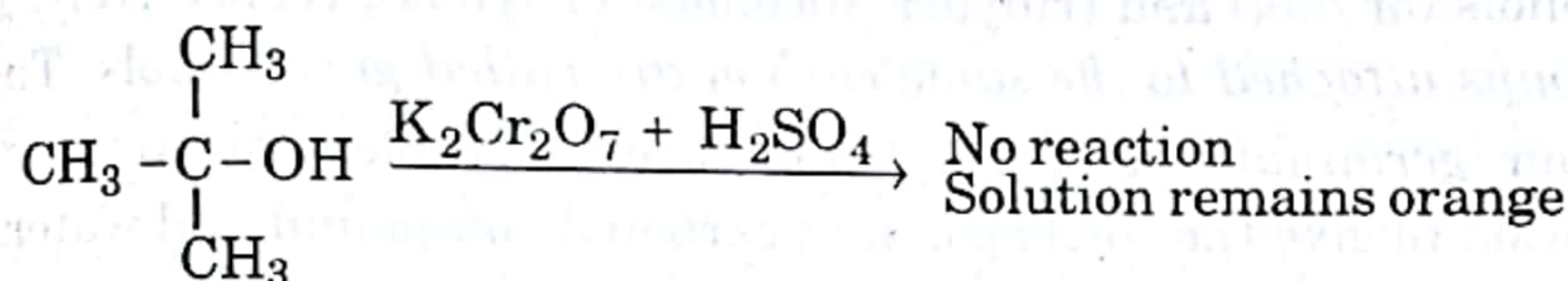
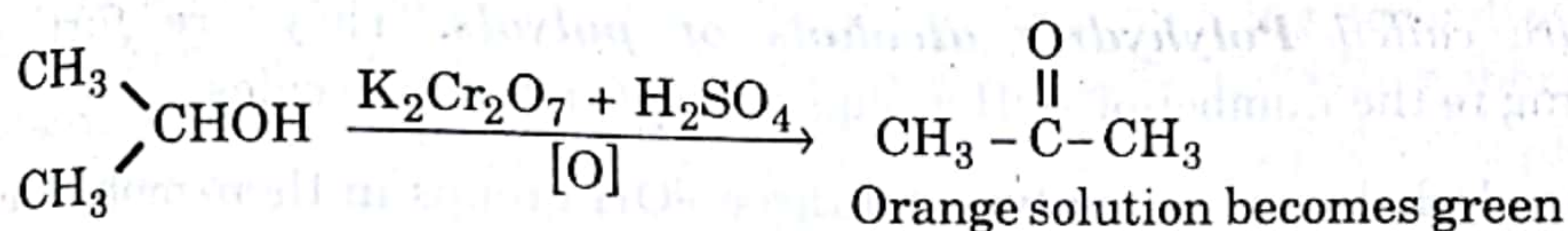
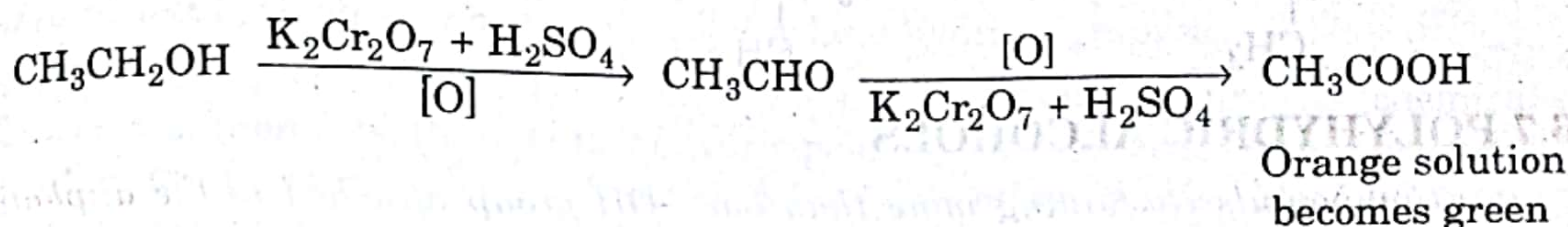
7. Reaction with Halogen acid (Lucas test)

Alcohols react with halogen acid to form alkyl halides. The order of reactivity of the halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$ and the order of reactivity of alcohols is tertiary > secondary > primary. Hydrogen chloride does not react with primary or secondary alcohols unless zinc chloride is added to the reaction mixture as well. Zinc chloride serves as a catalyst. A solution of zinc chloride in concentrated hydrochloric acid is used as the basis for a simple test (called the Lucas test) to differentiate between primary, secondary and tertiary alcohols. In this test, alcohols are treated with a solution of zinc chloride in conc. HCl (Lucas reagent) to form alkyl halides. Tertiary alcohols react with Lucas reagent immediately at room temperature to give an insoluble layer of the alkyl chloride. Secondary alcohols take several minutes to react and primary alcohols do not react with Lucas reagent unless they are heated.

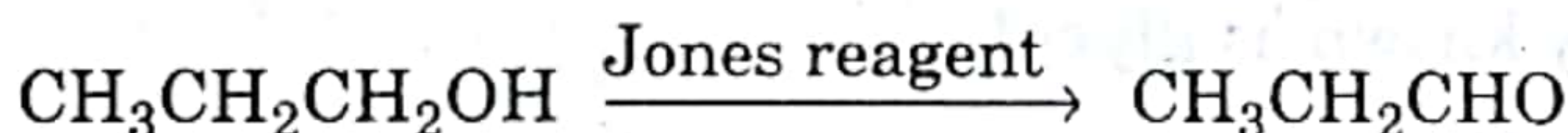


8. Oxidation. Alcohols can be oxidized. The nature of the product depends on the type of alcohols and conditions of the reaction. Most widely used oxidizing agents are $\text{CrO}_3 + \text{CH}_3\text{COOH}$, $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ or $\text{KMnO}_4 + \text{KOH}$. Oxidation of alcohols can be used to distinguish between primary, secondary and tertiary alcohols. The alcohol is treated at room temperature with $\text{K}_2\text{Cr}_2\text{O}_7$ in sulphuric acid (orange solution).

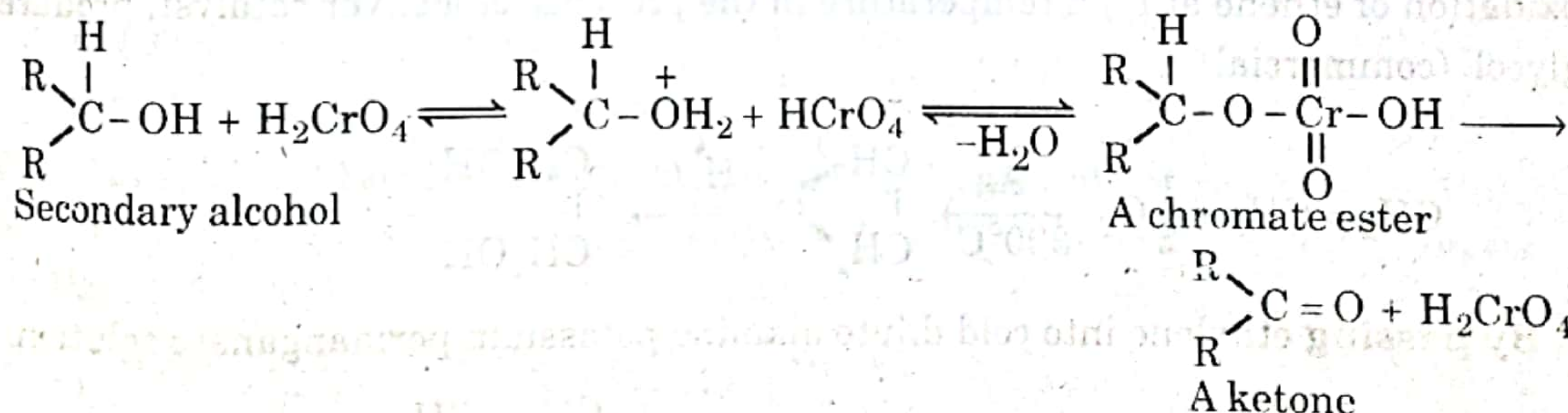
Primary alcohols are first oxidized to aldehydes and then to carboxylic acids containing the same number of carbon atoms and the orange solution turns green. Secondary alcohols give a ketone containing the same number of carbons and the orange solution turns green. Tertiary alcohols are resistant to oxidation and solution will remain orange.



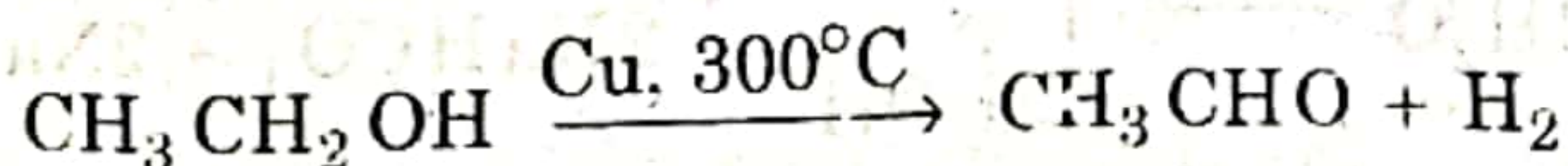
Most oxidizing reagents oxidizes a primary alcohol to the carboxylic acid directly. Chromic oxide CrO_3 in dilute H_2SO_4 and acetone called the **Jones reagent** is milder enough to change the prim-alcohol to aldehyde and secondary alcohol to ketone only. The Jones reagent has no effect on the double bonds present in the molecule.

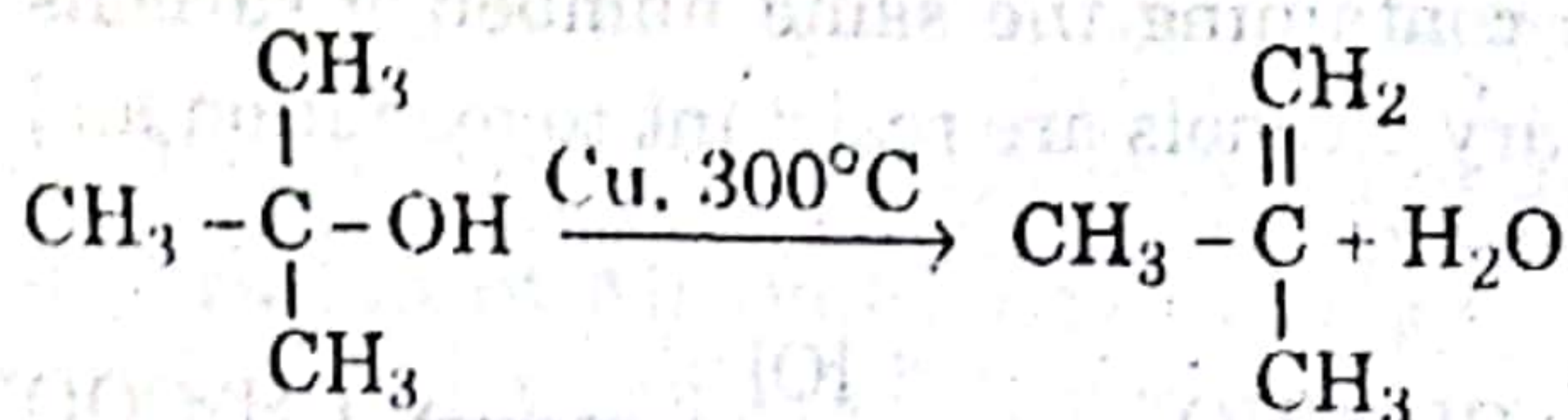
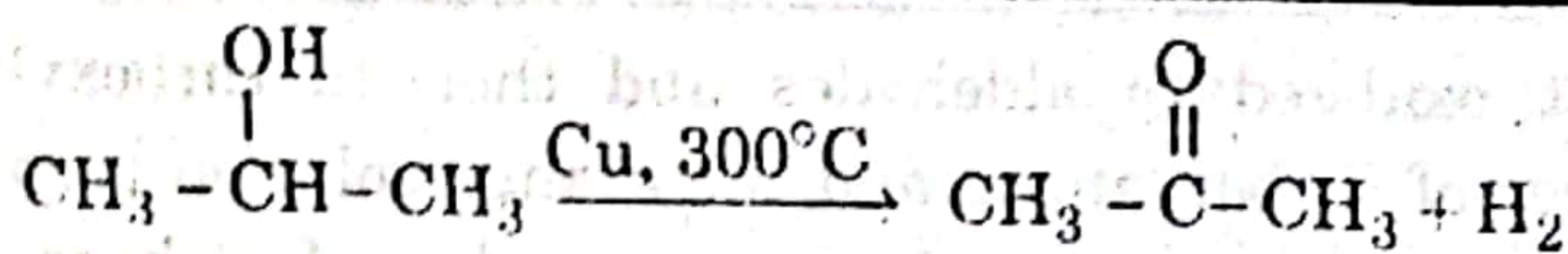


Chromic acid oxidation is particularly useful for secondary alcohols due to the stability of the product, ketones, to these conditions. The reaction proceeds through an initially formed chromate ester.



9. Dehydrogenation. Different types of alcohols give different products when their vapours are passed over copper gauze at 300°C . Primary and secondary alcohols undergo dehydrogenation forming aldehydes and ketones, respectively. Tertiary alcohols are not dehydrogenated but undergo dehydration forming alkenes.

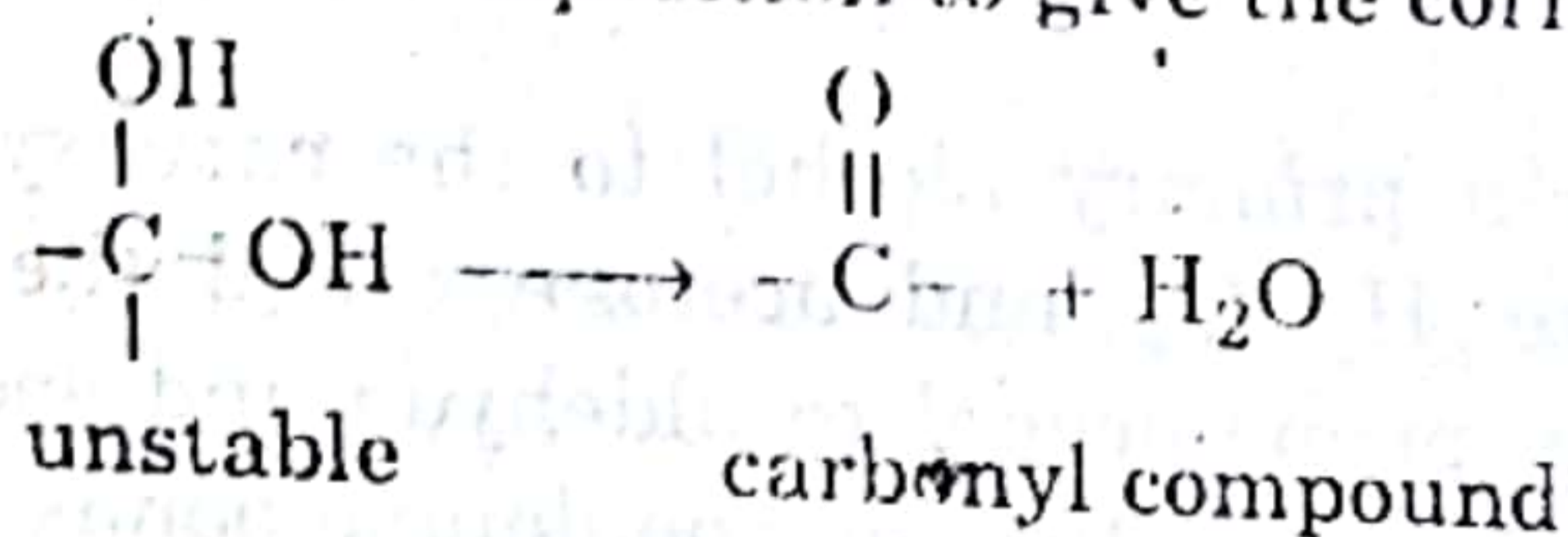




6.7 POLYHYDRIC ALCOHOLS

Compounds containing more than one -OH group attached to the aliphatic carbon atoms are called **Polyhydric alcohols or polyols**. They are further classified according to the number of -OH groups present in the molecules.

Polyhydric alcohols containing two and three -OH groups in their molecules are called dihydric alcohols (or diol) and trihydric alcohols (or triols), respectively. A diol with both -OH groups attached to the same carbon are called gem - diols. The prefix gem comes from *germinal*. Most gem diols are unstable and undergo spontaneous decomposition to give the corresponding carbonyl compound and water.

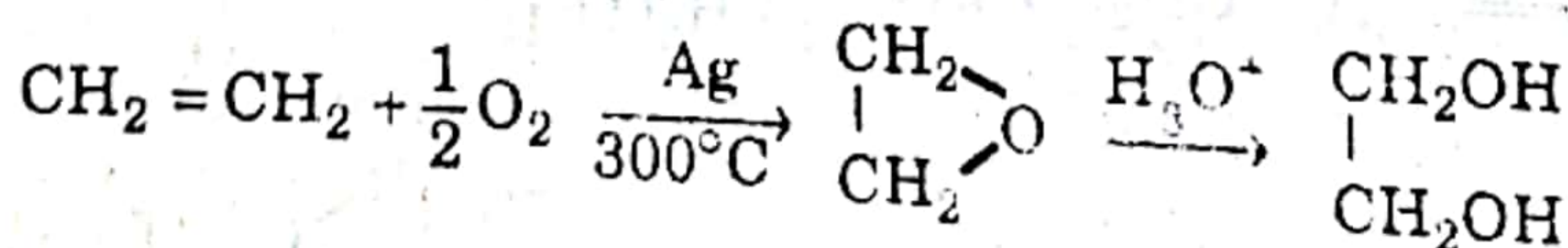


A diol having two hydroxyl groups present at 1,2-positions are called 1,2-diol or vicinal diol and commonly known as **glycol**.

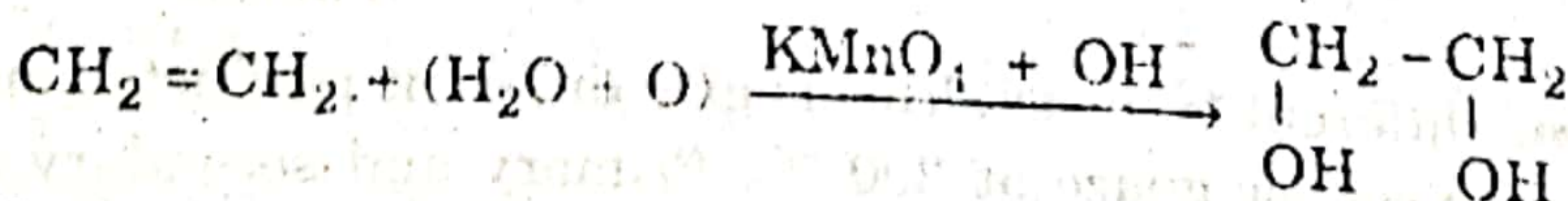
9.7 Glycol (Ethylene glycol)

Glycol is prepared as follows:

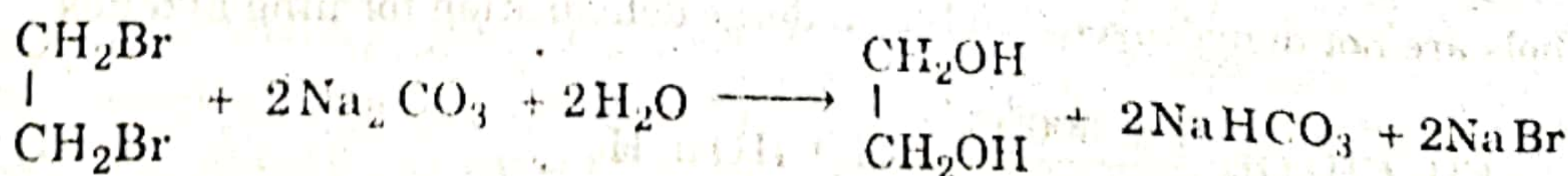
1. **Acid-catalyzed hydrolysis of ethylene oxide** which is made by the air oxidation of ethene at high temperature in the presence of a silver catalyst, produces glycol. (commercial)



2. **By passing ethylene into cold dilute alkaline potassium permanganate solution.**



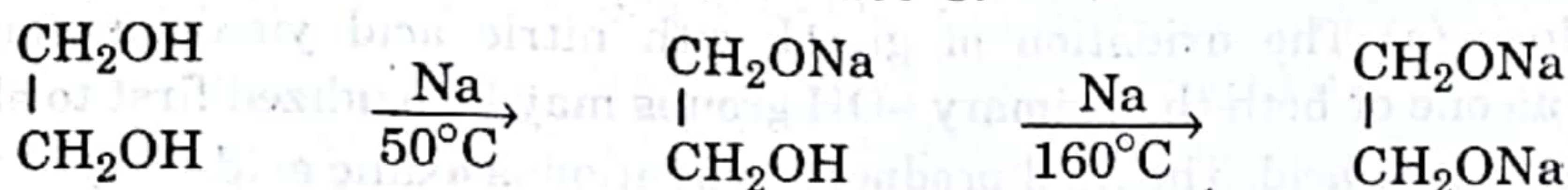
3. **By Hydrolysis of 1,2 -dibromoethane with aq. Na₂CO₃ solution.**



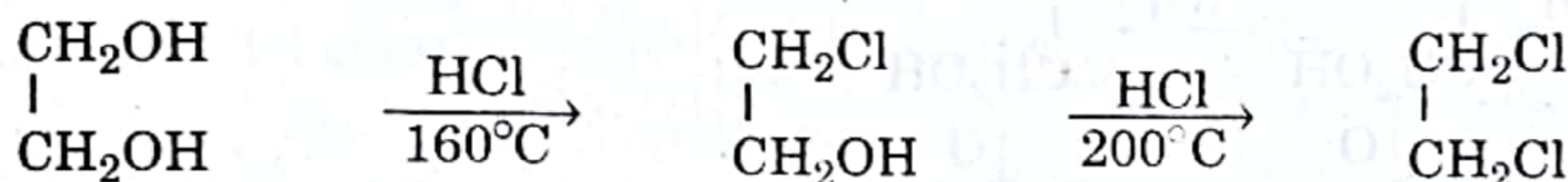
Properties

Physical Properties: Ethylene glycol is a colourless viscous liquid, b.p. 197°C , and has a sweet taste. It is miscible with water and ethanol in all proportions but is insoluble in ether. The high boiling point and high solubility of glycol in water is due to intermolecular hydrogen bonding involving both hydroxy groups.

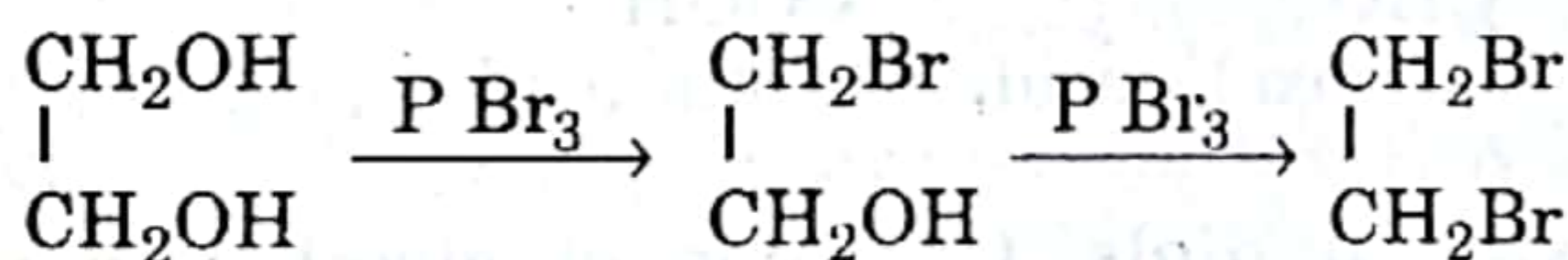
Chemical properties. Glycol contains two primary $-\text{OH}$ groups. Its chemical reactions are, therefore, those of monohydric primary alcohols twice over. Generally one $-\text{OH}$ group is completely attacked before the other reacts. More vigorous conditions are sometimes needed for the reactions of the second of the two $-\text{OH}$ groups. For example, glycol reacts with sodium at 50°C to form monoalkoxide, and dialkoxide when temperature is raised to 160°C .



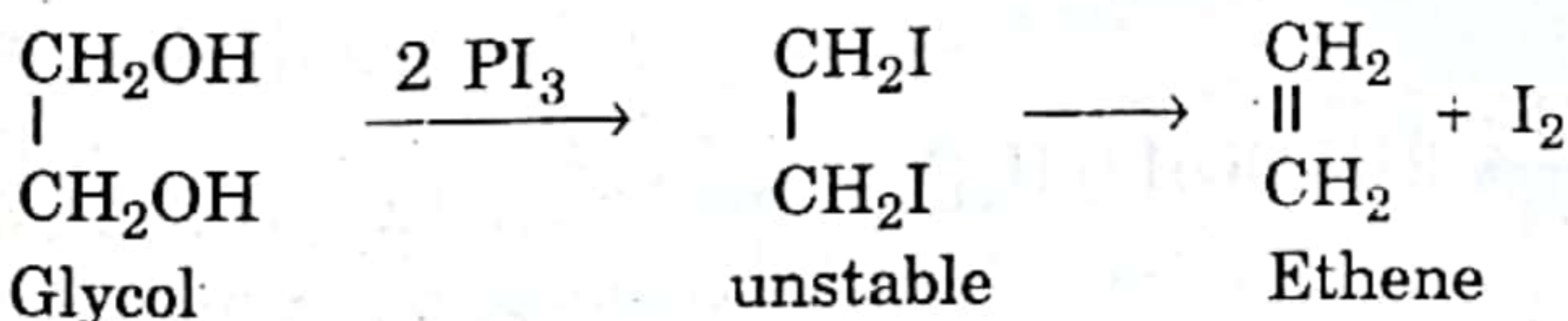
2. Reaction with HCl. Similarly glycol reacts with HCl to form ethylene chlorohydrin at 160°C and ethylene dichloride (1, 2 - dichloroethane) at 200°C .



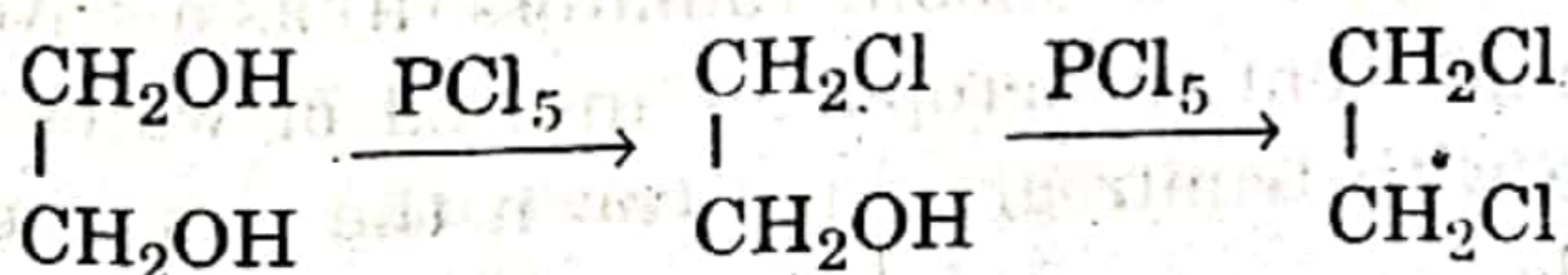
3. Reaction with Phosphorus halides. Glycol reacts with PCl_3 or PBr_3 to form the corresponding dihalides.



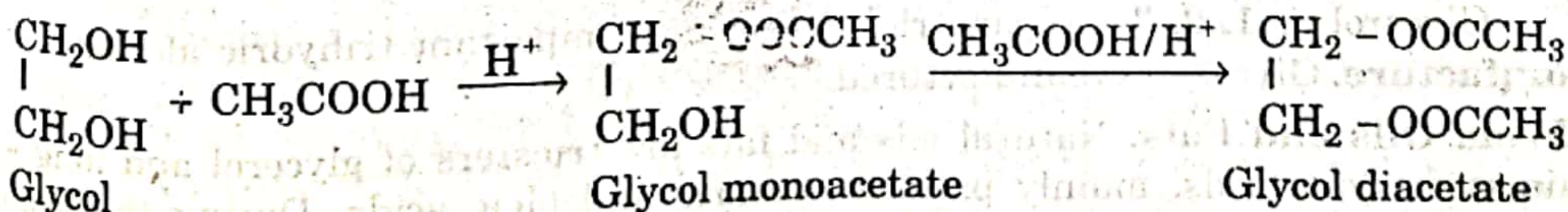
Ethylene glycol reacts with Phosphorus triiodide to form 1, 2- diiodoethane which is unstable and decomposes to give ethylene.



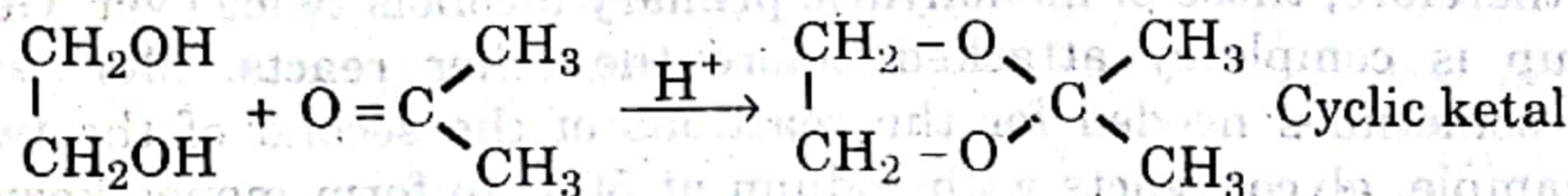
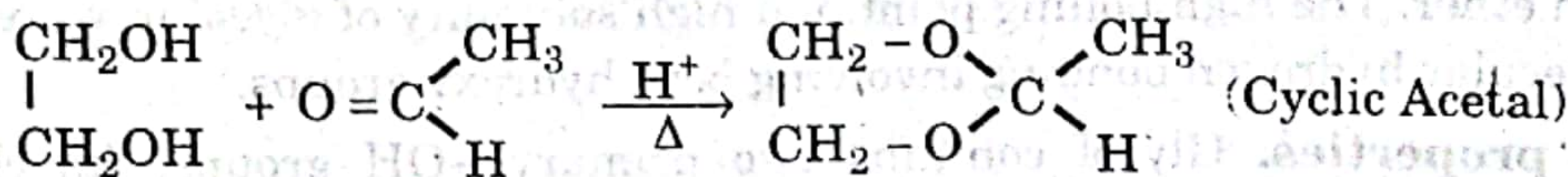
4. Reaction with Phosphorus Pentahalides. Ethylene glycol reacts with PCl_5 first to form ethylene chlorohydrin and then 1, 2- dichloroethane. PBr_3 reacts similarly.



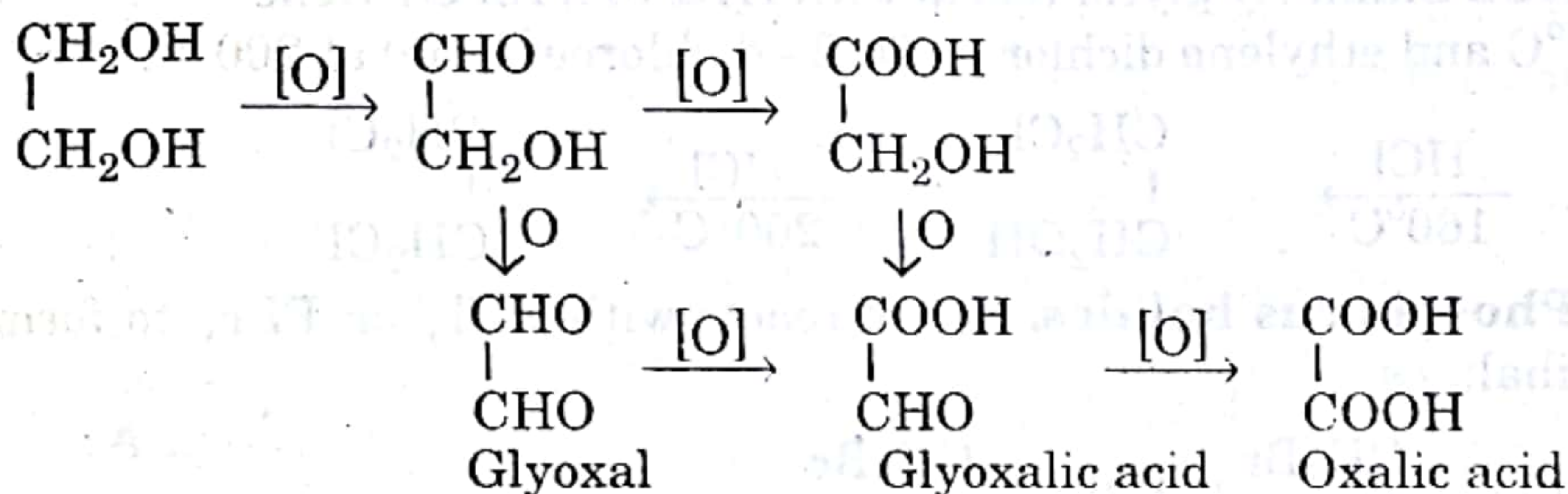
5. Reaction with carboxylic acids. Glycol reacts with carboxylic acids in the presence of mineral acid to form the corresponding esters or diesters.



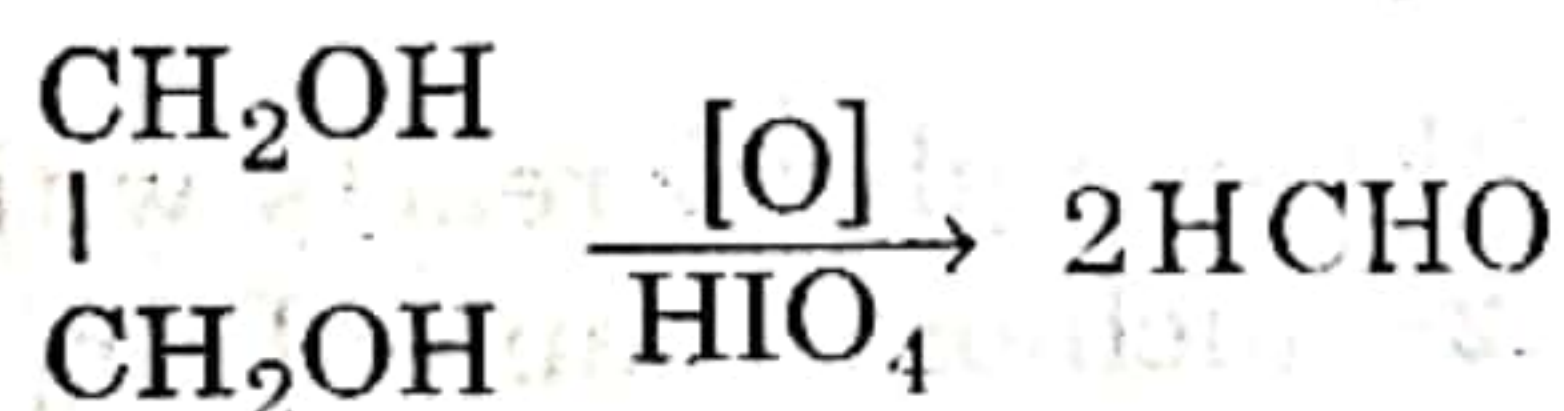
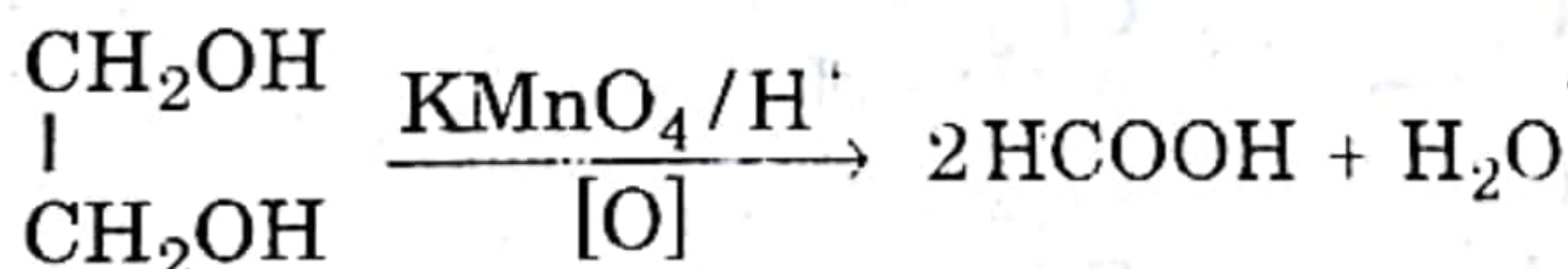
6. Reaction with carbonyl compounds. Glycol condenses with aldehydes or ketones in the presence of mineral acid to yield **Cyclic Acetals** or **Cyclic Ketals** respectively:



7. Oxidation. (a) The oxidation of glycol with nitric acid yields a number of substances as one or both the primary -OH groups may be oxidized first to aldehyde and then carboxylic acid. The final product of oxidation is oxalic acid.



(b) **Oxidation cleavage of vicinal diols.** Oxidation of glycol with acidified KMnO_4 , acidified $\text{K}_2\text{Cr}_2\text{O}_7$, lead tetracetate $\text{Pb}(\text{CH}_3\text{COO})_4$ or periodic acid (HIO_4), results in the cleavage of the C-C bond.



Uses. Glycol is used (i) as an antifreeze in automobile radiators (ii) as a solvent and as a preservative (iii) as a cooling agent in aeroplanes instead of water (iv) Its dinitrate is used as an explosive with trinitroglycerine (v) in the manufacture of dacron, dioxane and ethylene oxide.

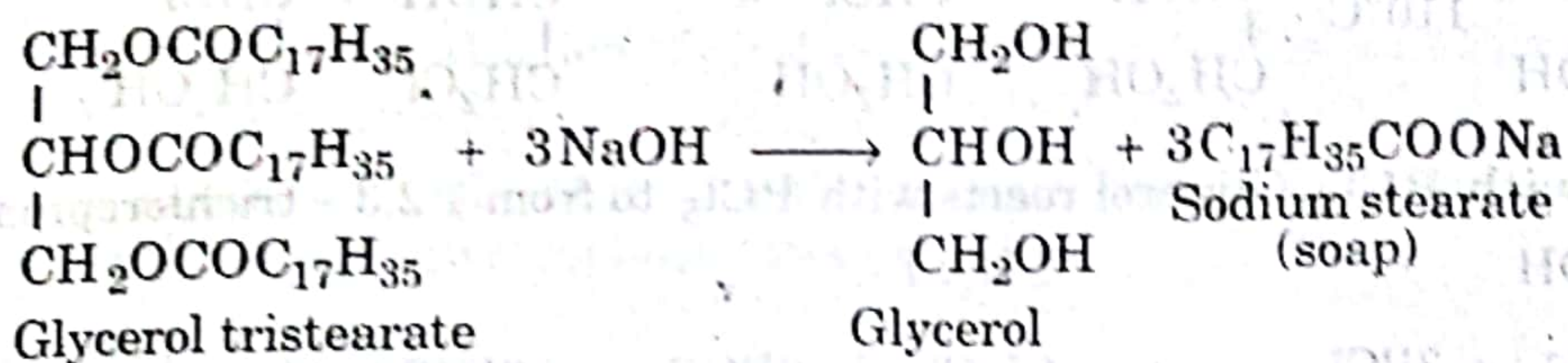
9.8 Trihydric alcohols: Glycerol (Propane -1,2,3-triol)

Glycerol or 1, 2, 3- propanetriol is the most important trihydric alcohol.

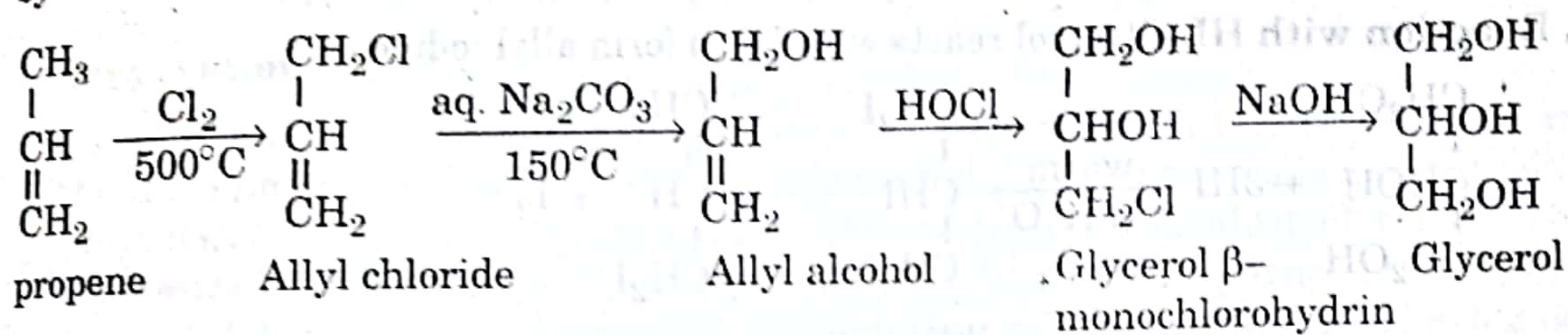
Manufacture. Glycerol is manufactured:

1. From Oils and Fats. Natural oils and fats are triesters of glycerol and long-chain carboxylic acids, mainly palmitic, stearic and oleic acids. During the soap

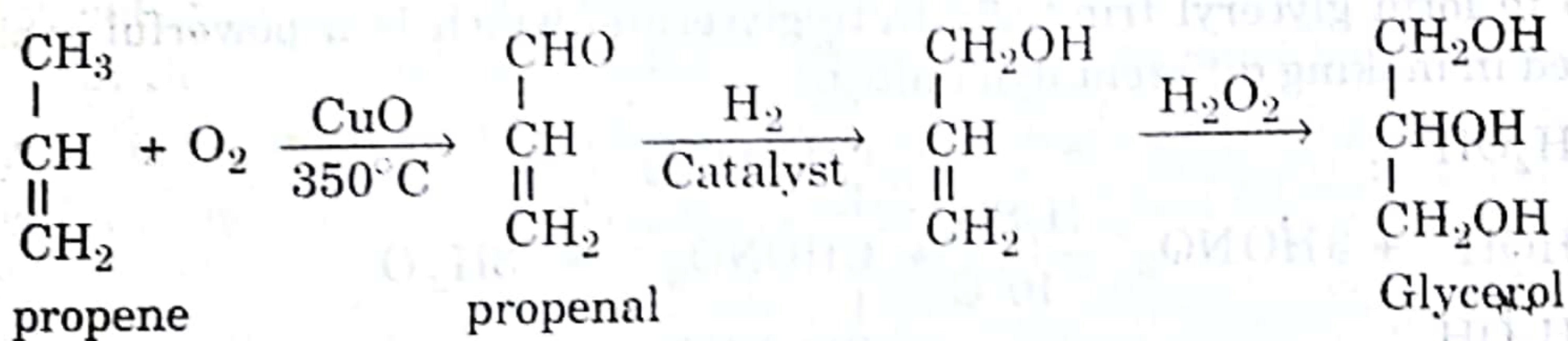
manufacture, oils and fats are hydrolyzed with alkali to form sodium salts of fatty acids, called soaps and glycerol is obtained as a by-product and this process is known as saponification.



2. From Propene. Today much of glycerol is manufactured from propene obtained by the catalytic cracking of petroleum as follows:



Alternative method for synthesis of glycerol from propene



9.9 Properties

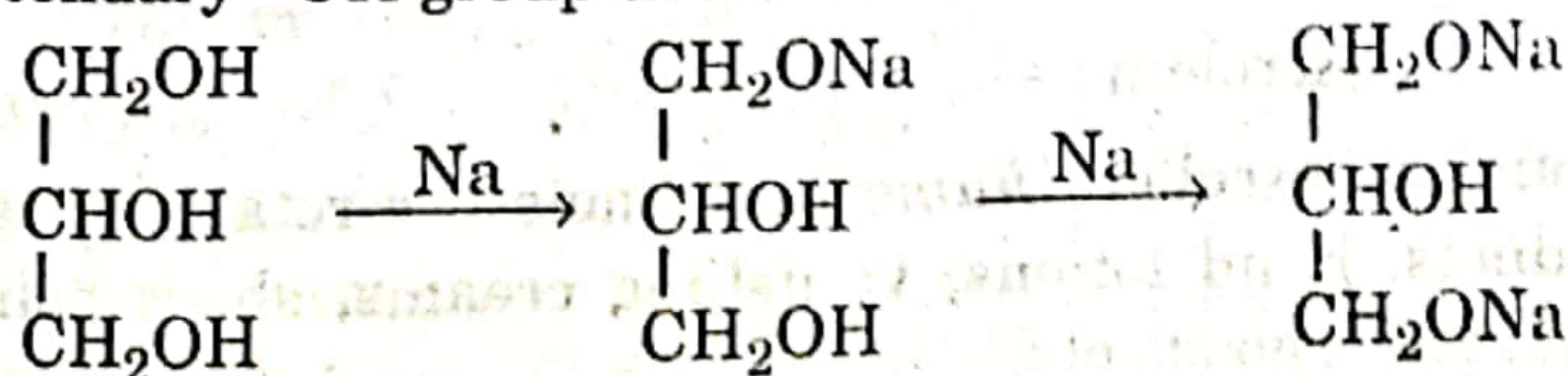
Glycerol is a colourless, odourless, and viscous hygroscopic liquid, b.p. 290°C . It is soluble in water and ethanol, but insoluble in ether.

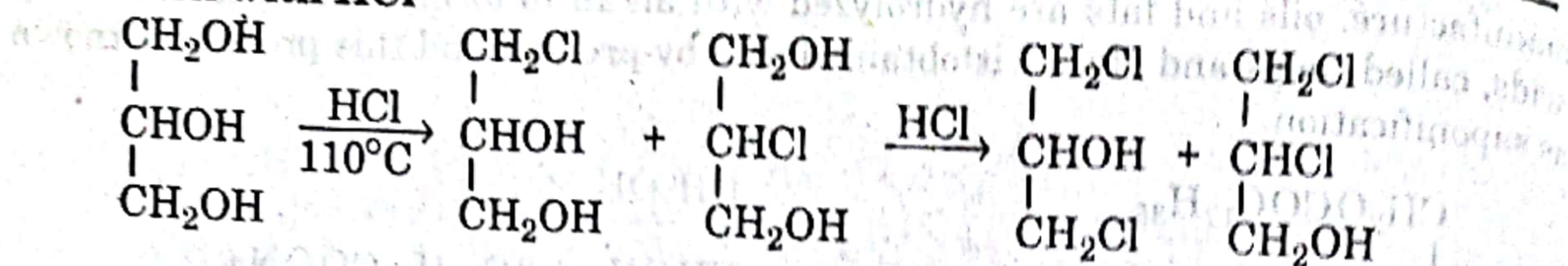
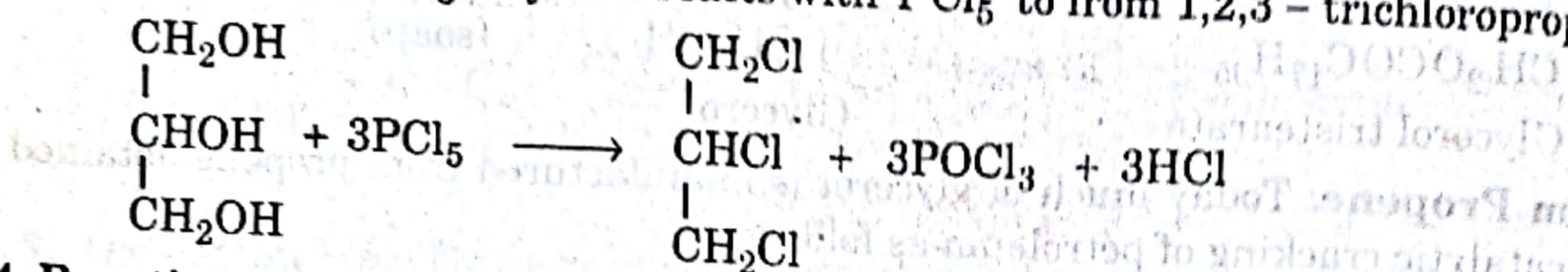
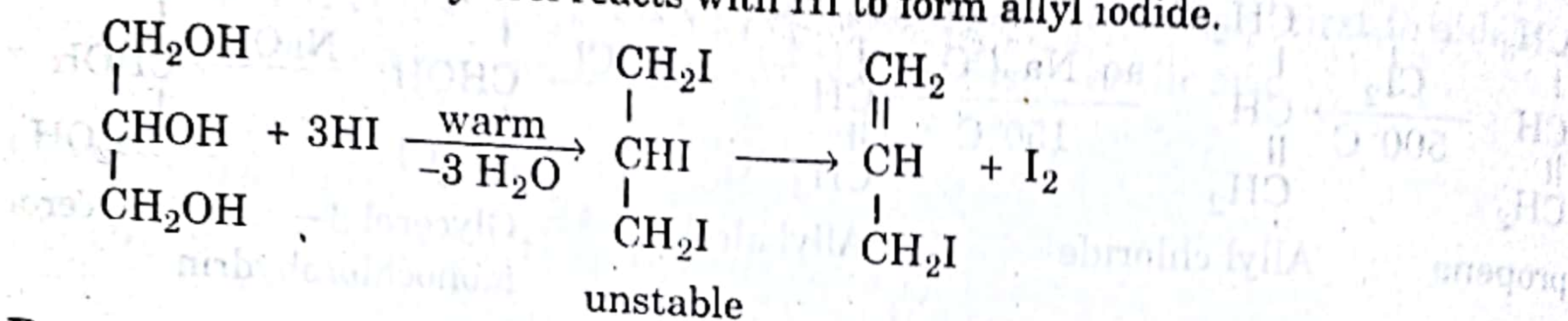
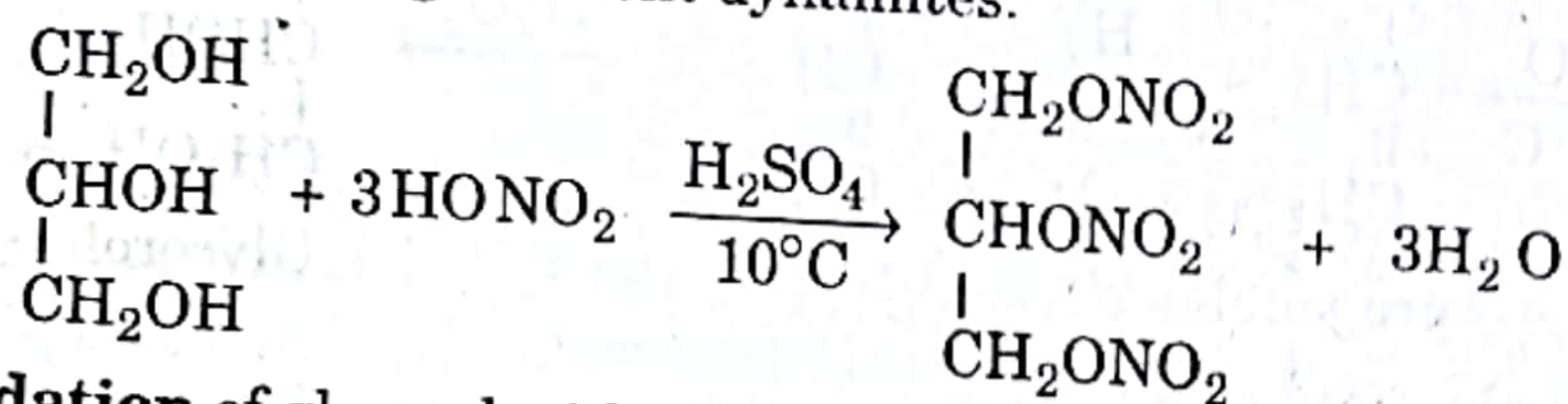
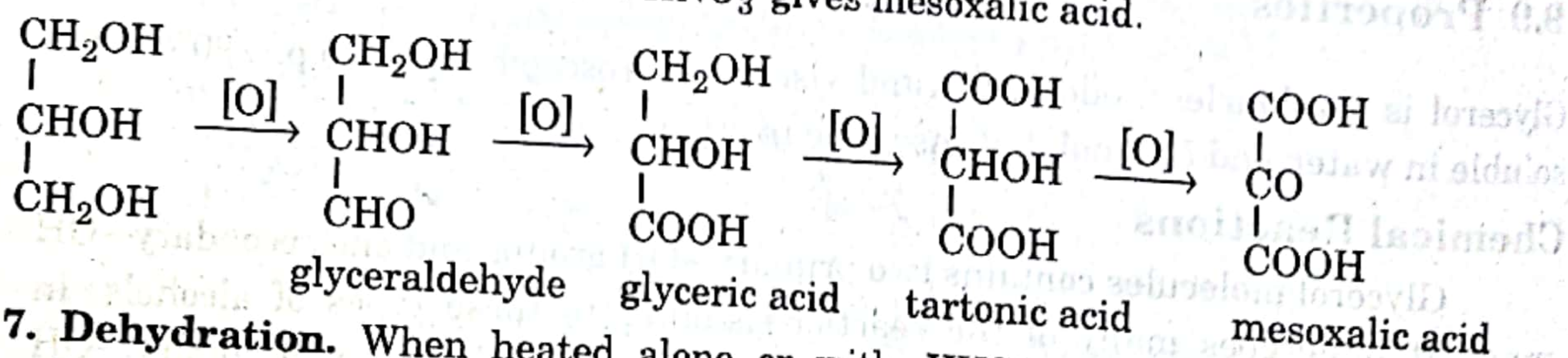
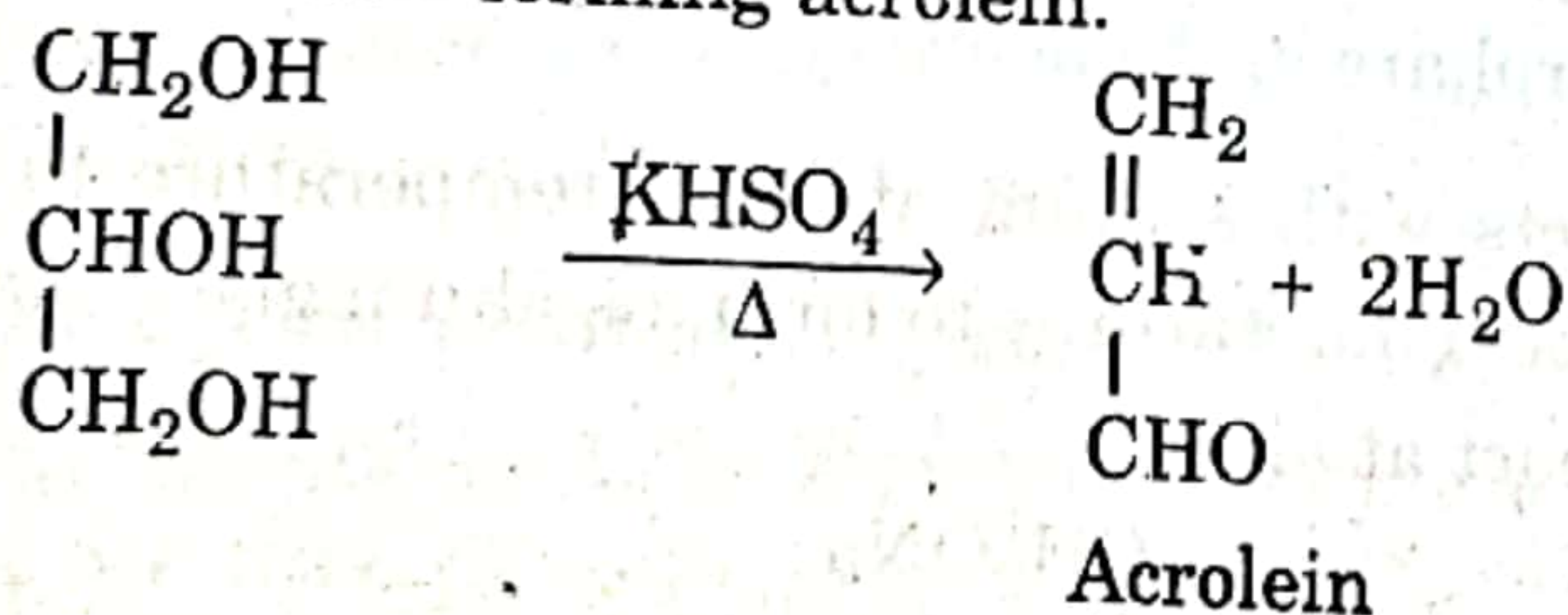
Chemical Reactions

Glycerol molecules contains two primary -OH groups and one secondary -OH group. It undergoes many of the reactions similar to these types of alcohols. In general, the two primary -OH groups are more reactive than the secondary -OH groups. Some of the reactions of glycerol are given below:

1. Reaction with Na. Glycerol reacts with sodium at room temperature to form monosodium glycerolate, and at higher temperatures to form disodium glycerolate:

The secondary -OH group does not react at all.



2. Reaction with HCl**3. Reaction with PCl₅.** Glycerol reacts with PCl₅ to form 1,2,3-trichloropropane.**4. Reaction with HI.** Glycerol reacts with HI to form allyl iodide.**5. Reaction with HNO₃.** Glycerol reacts with nitric acid in the presence of H₂SO₄ (catalyst) to form glyceryl trinitrate (nitroglycerine) which is a powerful explosive and is used in making different dynamites.**6. Oxidation of glycerol with dil. HNO₃** gives mesoxalic acid.**7. Dehydration.** When heated alone or with KHSO₄, glycerol eliminates two molecules of water forming acrolein.

Uses: Glycerol is nontoxic and an excellent *humectant* (moisture retaining agent).
 (i) It is used in bakery products, hand lotions, vanishing creams, shoes polishes, printing inks, shaving soaps, leather goods etc.

- (ii) It is used in the manufacture of explosives such as nitroglycerine.
- (iii) It is used in the manufacture of cosmetics and transparent soaps.
- (iv) It is used as a sweetening agent in confectionery and beverages.
- (v) It is used in production of plastics, synthetic fibers and surface coatings.
- (vi) Used as a lubricant for watches and clocks.
- (vii) It is used in medicine, externally, for smoothing inflammation and internally in the form of glycerophosphates (a tonic)

9.10 PHENOLS

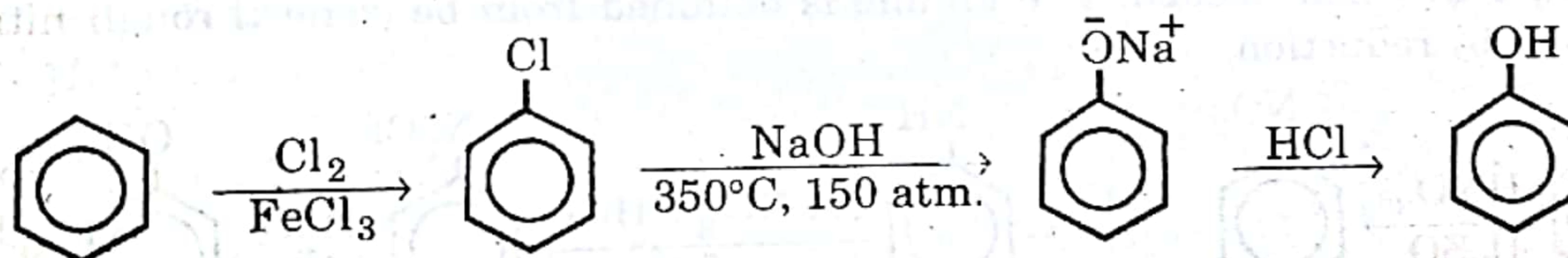
Phenols are the compounds in which one or more $-OH$ groups are directly attached to an aromatic ring including the polycyclic aromatic system.

Preparation of phenols

Phenols, cresols and xlenols are obtained from coal tar. However, to meet the large demand of phenol as the raw material for a large number of commercial products, several methods are used to synthesize phenol. Most of the phenol is synthesized from benzene. Direct oxidation of benzene to phenol is not usually successful because phenol is more readily oxidized than benzene. The following methods are used for industrial synthesis of phenols.

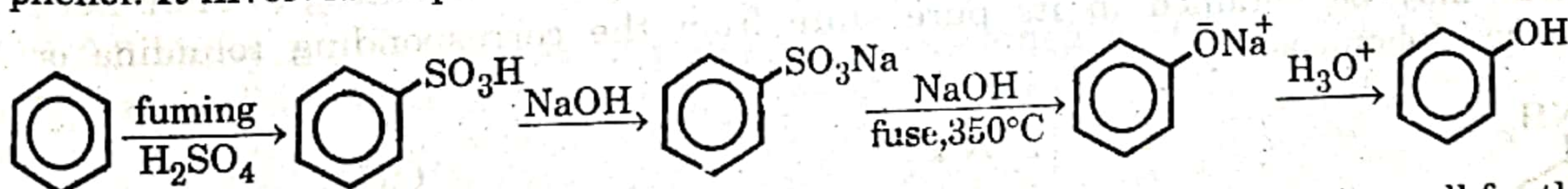
1. Hydrolysis of Chlorobenzene (Dow Process)

In this process, chlorobenzene which can be obtained by the chlorination of benzene, is heated at 350°C under high pressure with aqueous sodium hydroxide to get sodium phenoxide, which on acidification yields phenol.

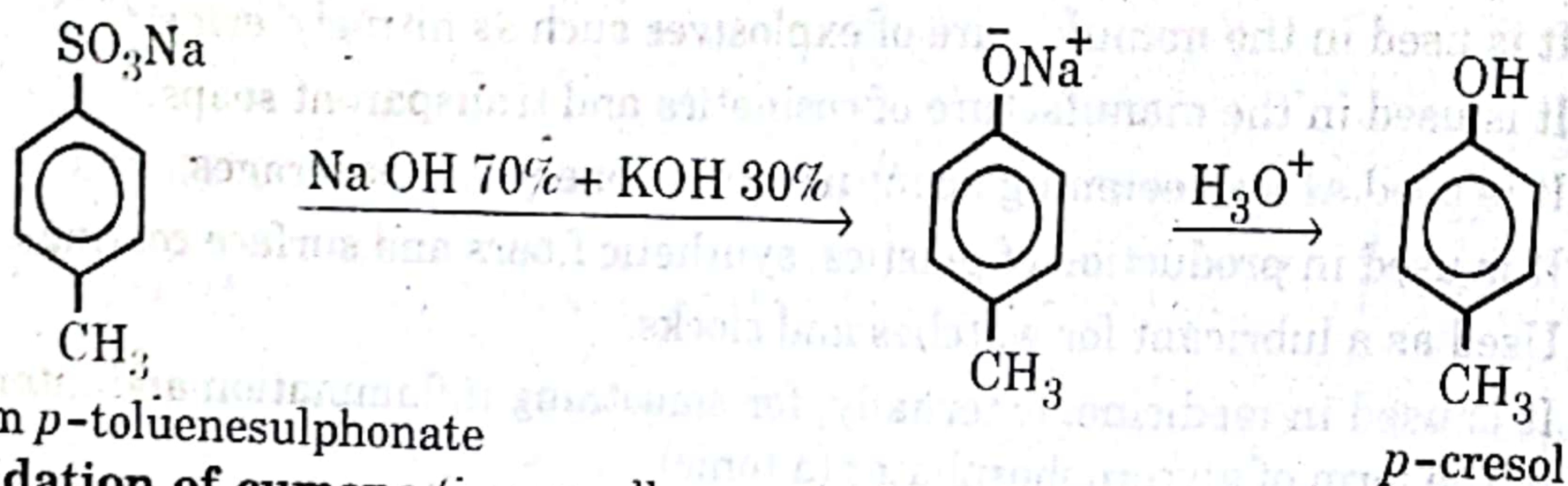


2. Alkali fusion of Sodium Benzenesulphonate

This, the first commercial process for industrial synthesizing phenol, was developed in Germany in 1890. Sodium benzenesulphonate is melted (fused) with sodium hydroxide at 350°C to produce sodium phenoxide, which on acidification yields phenol. It involves sulphonation of benzene.

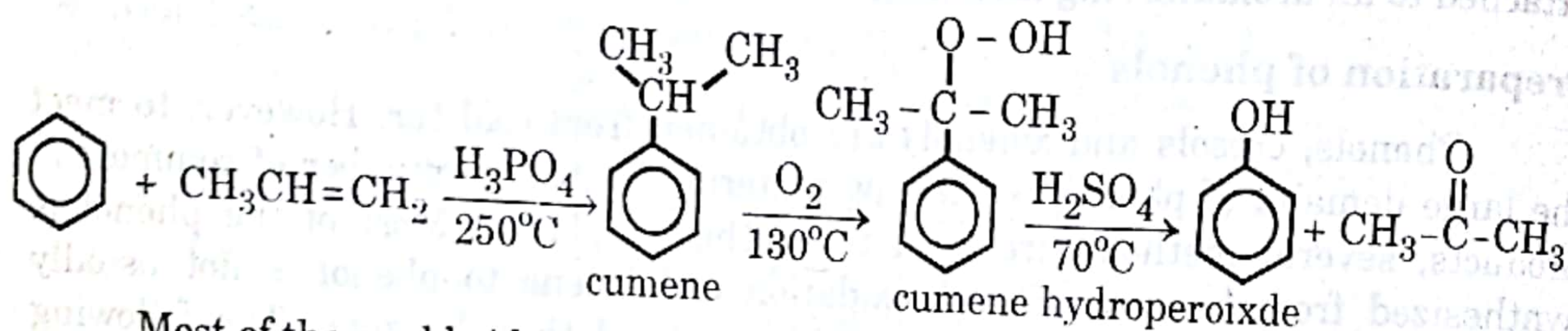


This procedure can also be used in the laboratory and works quite well for the preparation of *p*-cresol. In the laboratory, a mixture of sodium and potassium hydroxide is used which permits the reaction to occur at lower temperature. However, the conditions required to bring about the reaction are so vigorous that its use in the preparation of many phenols is limited.



Sodium *p*-toluenesulphonate

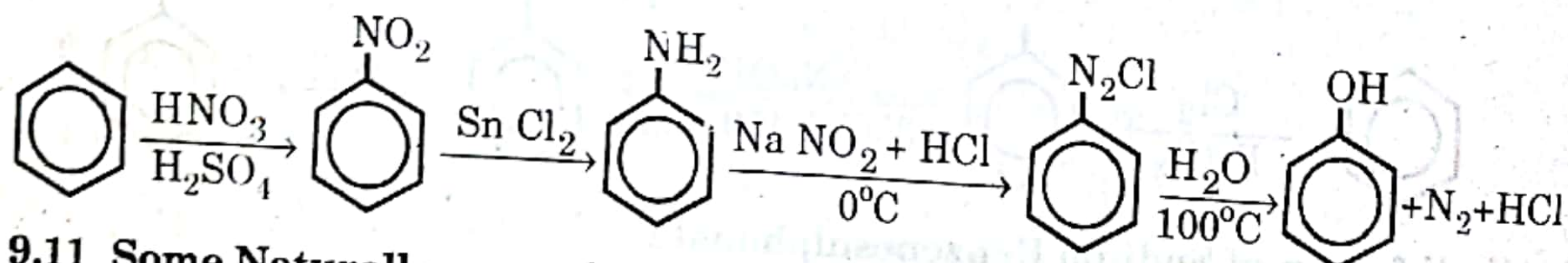
3. Oxidation of cumene (isopropylbenzene). Benzene is alkylated with propene to produce cumene, which is oxidized with air to produce cumene hydroperoxide, which on treatment with 10% H_2SO_4 undergoes a hydrolytic rearrangement to yield phenol and acetone, (a valuable by-product).



Most of the worldwide production of phenol is now based on this method.

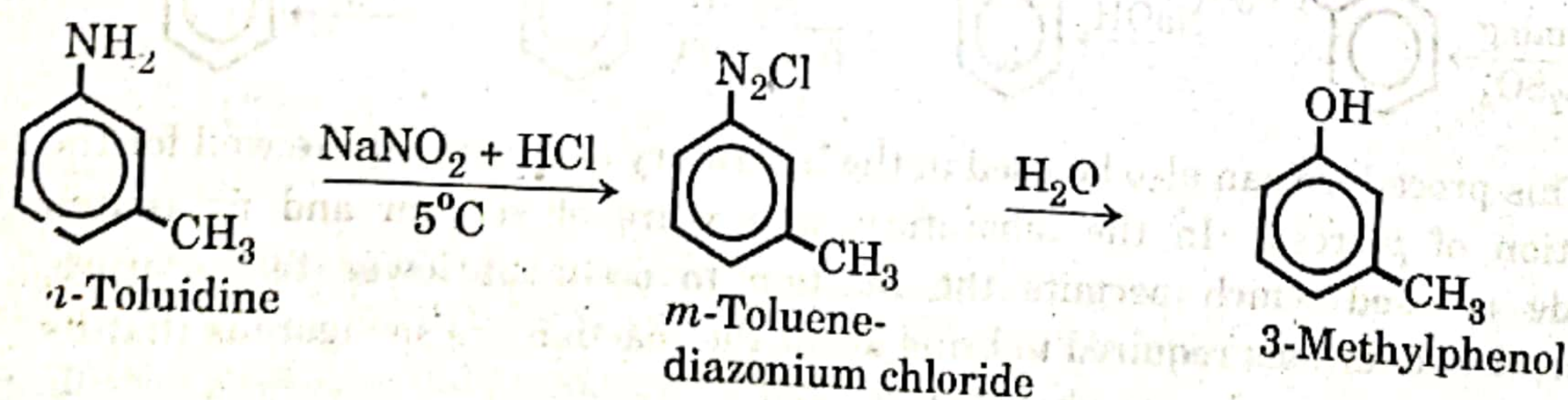
4. Hydrolysis of Benzenediazonium salts

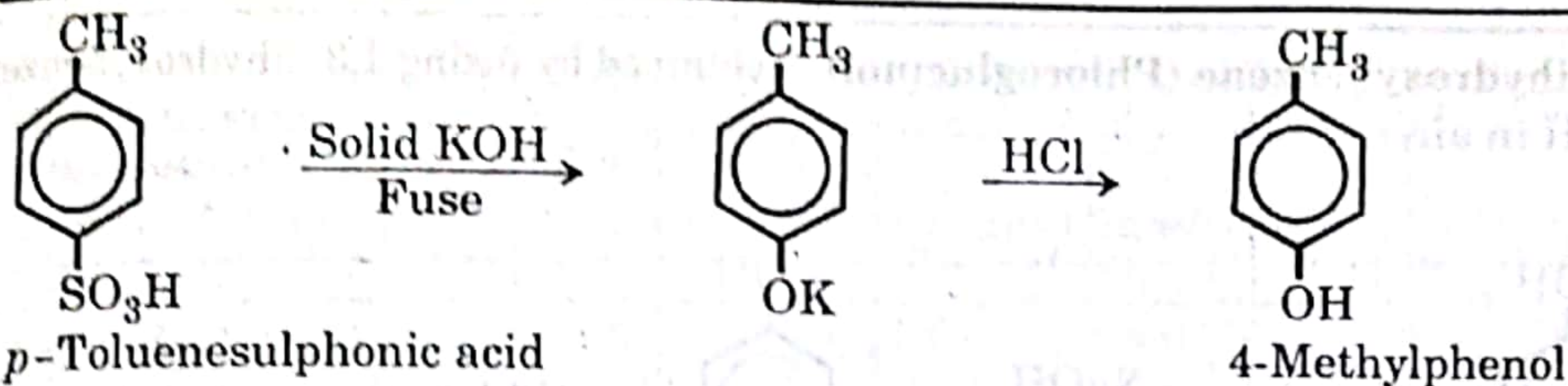
Aqueous solution of benzene diazonium salt, obtained by the reaction of aniline with nitrous acid at 0°C , on boiling with water loses nitrogen to produce phenol. Nitrous acid, being unstable, is generated by the reaction of NaNO_2 with HCl at 0°C , when needed. The aniline is obtained from benzene through nitration followed by reduction.



9.11 Some Naturally occurring Phenols

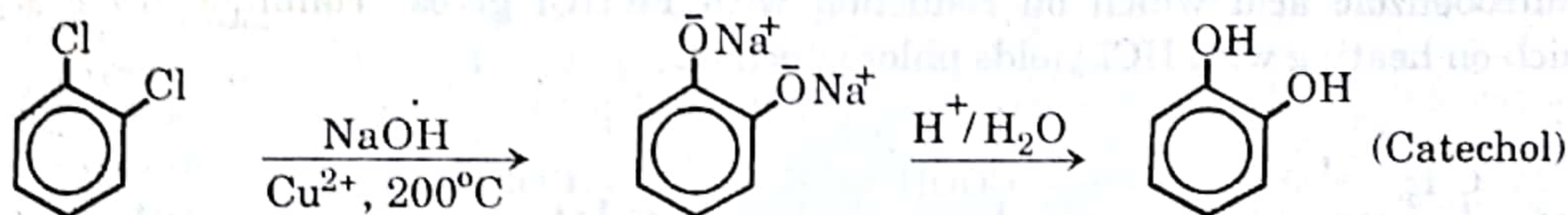
1. Methyl phenols (Cresols), $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$, occur in the middle oil and heavy oil fractions of coal-tar. *o*-isomer (b.p. 191°C) is separated from the *m*- (b.p. 201°C) and *p*-isomer (b.p. 225.5°C) by fractional distillation using a fractionating column. Each isomer may be obtained in its pure state from the corresponding toluidine or toluenesulphonic acid.



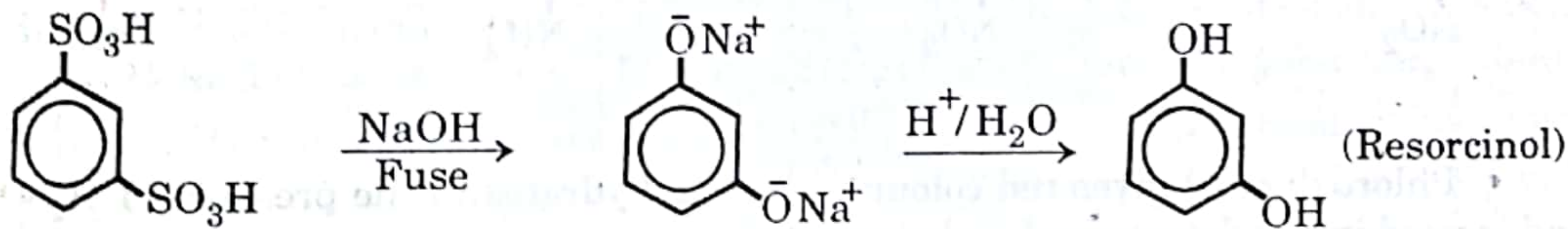


Dihydric Phenols: They are obtained by methods similar to those used for phenols.

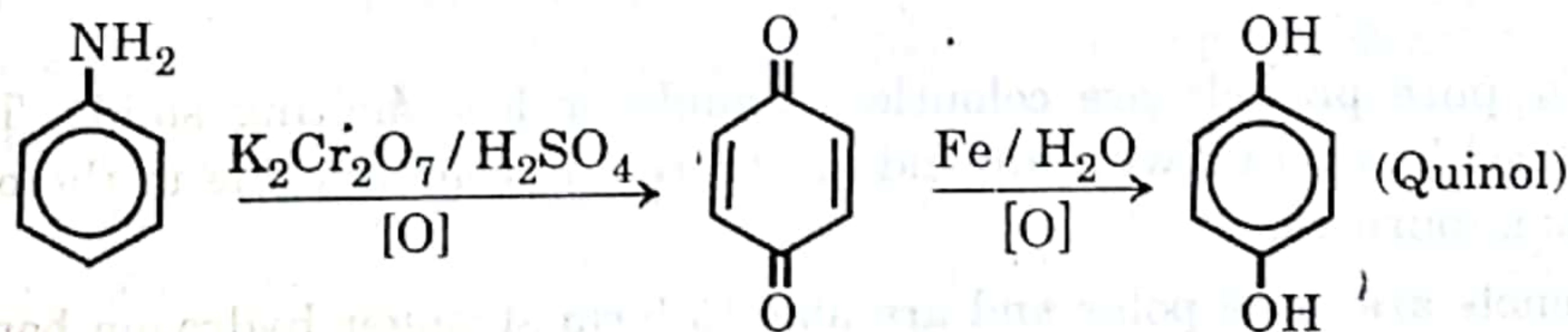
2. 1,2-Dihydroxybenzene (Catechol) occurs in certain plants. Commercially catechol is obtained by hydrolysis of *o*-dichlorobenzene with dilute NaOH solution at 200°C and in the presence of CuSO₄ solution.



3. 1,3-Dihydroxybenzene (Resorcinol) is obtained by alkalies fusion of *m*-benzenedisulphonic acid (commercial method).



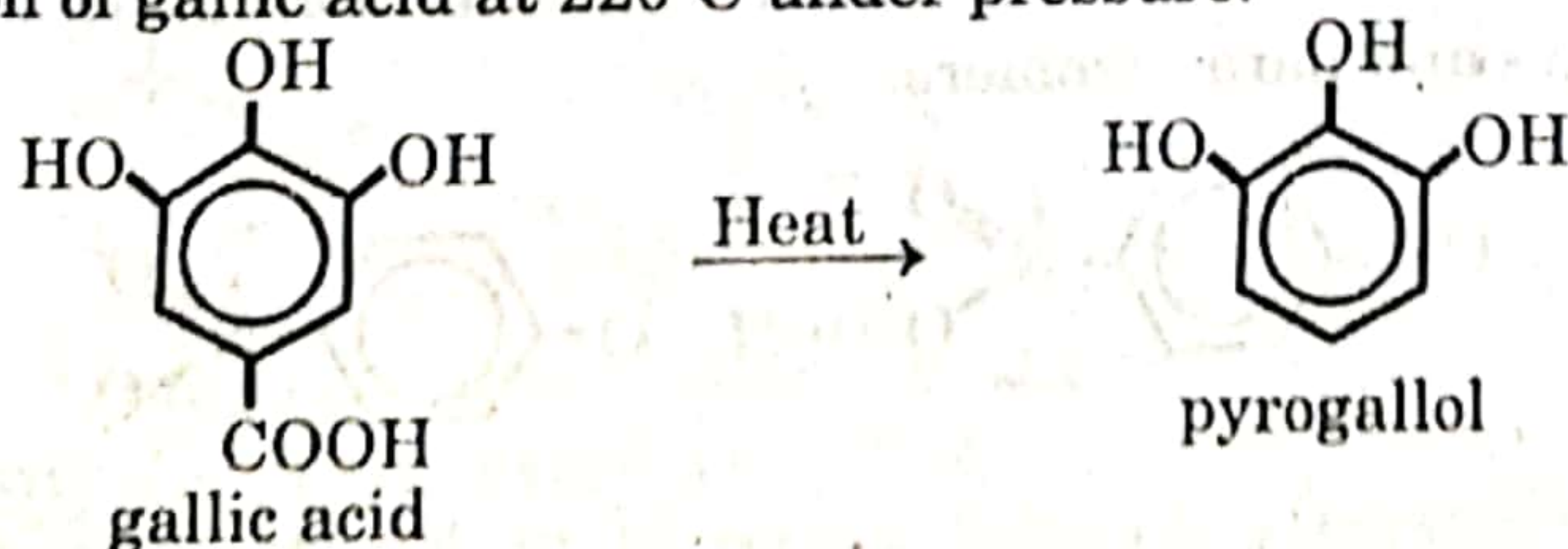
4. Quinol (Hydroquinone) is obtained by reduction of *p*-benzoquinone with iron in the presence of water. *p*-Benzoquinone is prepared by oxidation of aniline.



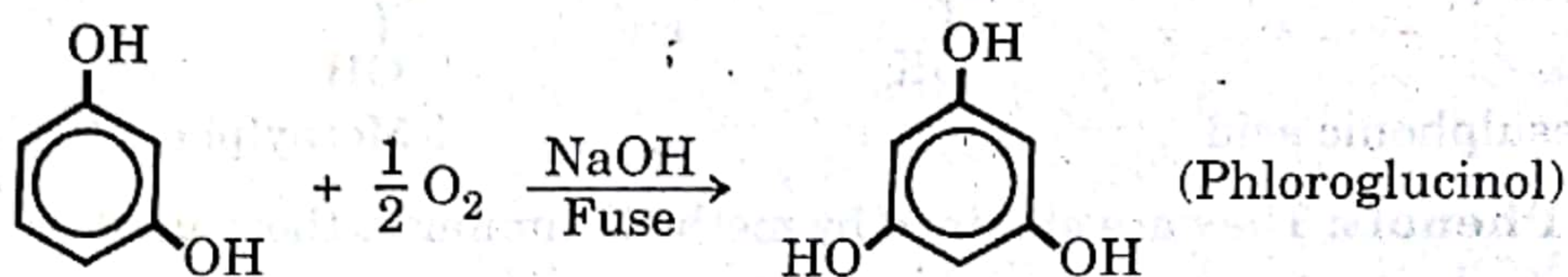
Dihydric phenols are colourless solids having melting points; Catechol 104°C; Resorcinol 110°C; Quinol (Hydroquinone) 173°C. Their reactions are similar to phenol.

Trihydric Phenols. Pyrogallol and phloroglucinol are important trihydric phenols.

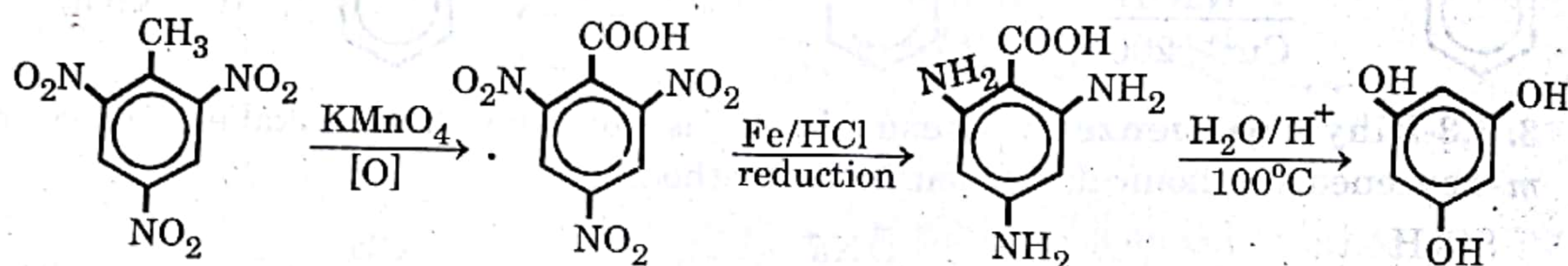
1. 1,2,3-Trihydroxybenzene (Pyrogallol) is obtained by heating an aqueous solution of gallic acid at 220°C under pressure.



2. 1,3,5-Trihydroxybenzene (Phloroglucinol) is obtained by fusing 1,3-dihydroxybenzene with NaOH in air.



(ii) It can be obtained from 2,4,6-trinitrotoluene (TNT). TNT on oxidation gives trinitrobenzoic acid which on reduction with Fe/HCl gives triaminobenzoic acid which on heating with HCl yields phloroglucinol.



Phloroglucinol gives red colour with carbohydrates in the presence of H₂SO₄ and is used in the detection of carbohydrates.

9.12 Physical Properties of Phenols

Most pure phenols are colourless liquids or low melting solids. They are easily oxidized by contact with air and are therefore, coloured due to the oxidation products as impurities.

Phenols are more polar and are able to form stronger hydrogen bonds than the corresponding aliphatic alcohols. Thus the phenols have higher melting and boiling points and higher water solubility than the corresponding alcohols.

Among the isomeric chloro - and nitrophenols, the ortho isomers have lower melting and boiling points, water solubilities and are weaker acids, than the corresponding meta- and para- isomers. These are due to *intramolecular hydrogen bonding* in the case of ortho isomers and *intermolecular hydrogen bonding* in the case of meta - and para - isomers.

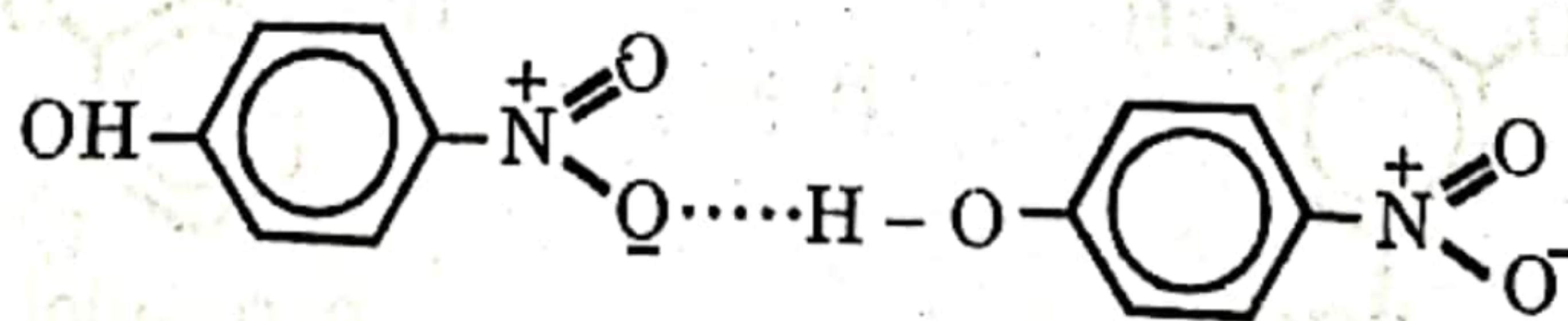
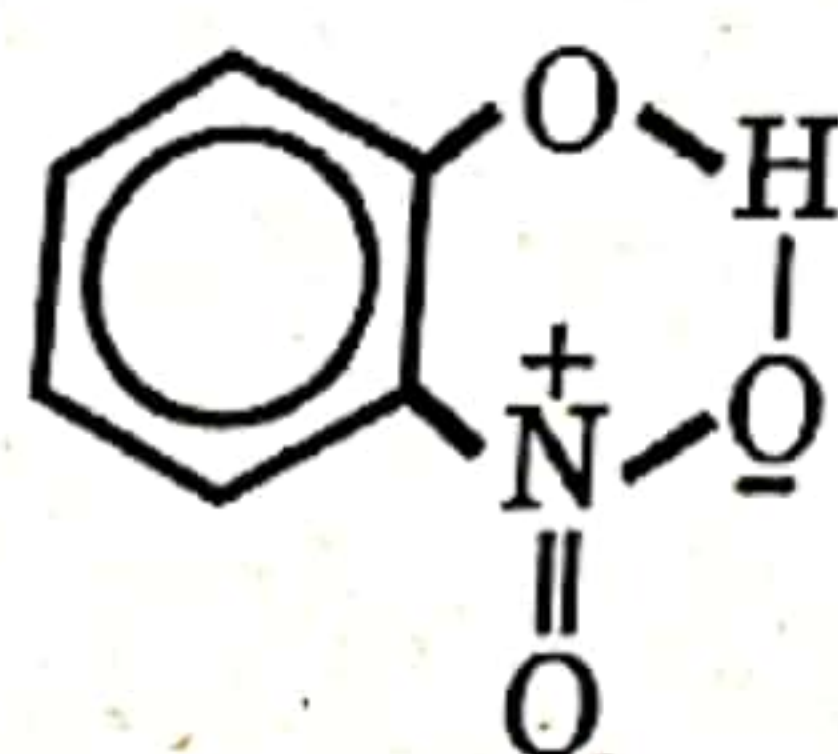


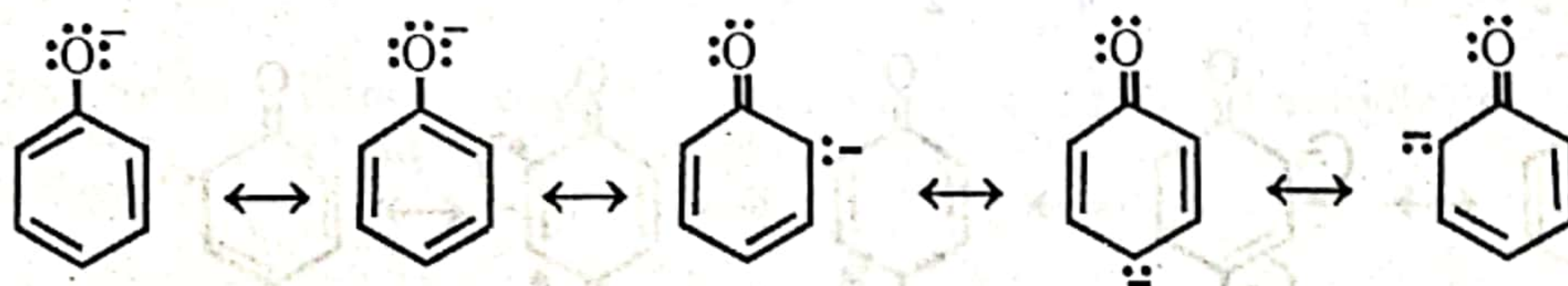
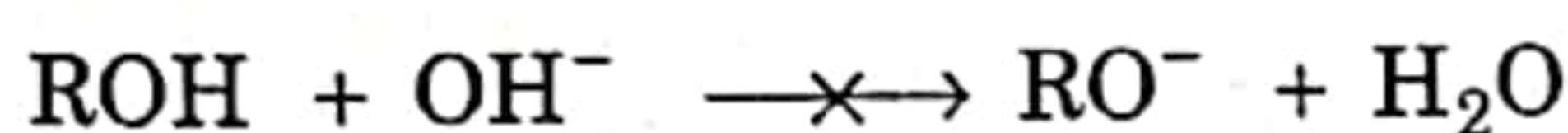
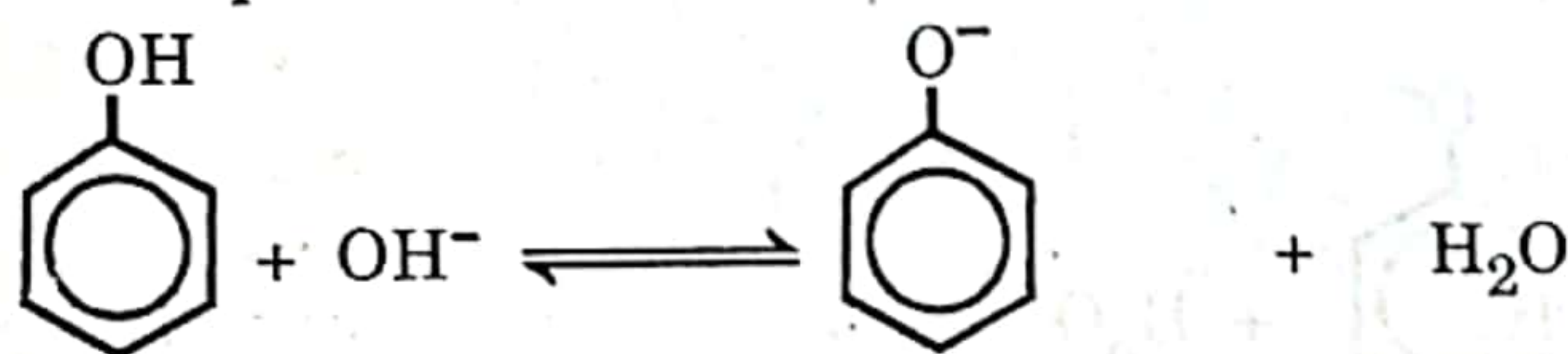
Table 9.2 Physical constants of Phenols

Compound	m.p. (°C)	b.p. (°C)	Solubility (g/100g of H ₂ O)	pK _a
Phenol	41	182	9.3	10.00
<i>o</i> -cresol	31	191	2.6	10.29
<i>m</i> -cresol	11	202	2.6	10.09
<i>p</i> -cresol	35	202	2.3	10.14
<i>o</i> -chlorophenol	9	173	2.8	8.48
<i>m</i> -chlorophenol	33	214	2.6	9.02
<i>p</i> -chlorophenol	43	219	2.7	9.38
<i>o</i> -nitrophenol	45	217	0.2	7.23
<i>m</i> -nitrophenol	96		1.4	8.35
<i>p</i> -nitrophenol	114	279	1.7	7.15
Resorcinol	110	277	123	9.7
Hydroquinone	173	286	8	9.96

9.13 Nature of the -OH group in Alcohols and phenols -Acidity of Phenols

As the -OH group of both alcohols and phenols contains lone pair of electrons, they are expected to behave as bases. It is seen that both types of compounds behave as weak acids because the -OH bond in alcohols and phenols is polar and allows the release of the hydrogen atom as proton (H⁺). However, phenols are much more acidic than alcohols but considerably weaker acids than carboxylic acids. The pK_a values of alcohols, phenols and carboxylic acids are in the vicinity of 18, 10 and 5, respectively. The greater acidity of phenols relative to alcohols is attributed to the formation of stable phenoxide ions when phenols are treated with aqueous alkali whereas alcohols do not react under these conditions because the position of equilibrium acid - base reaction will favour hydroxide ion and alcohol molecules.

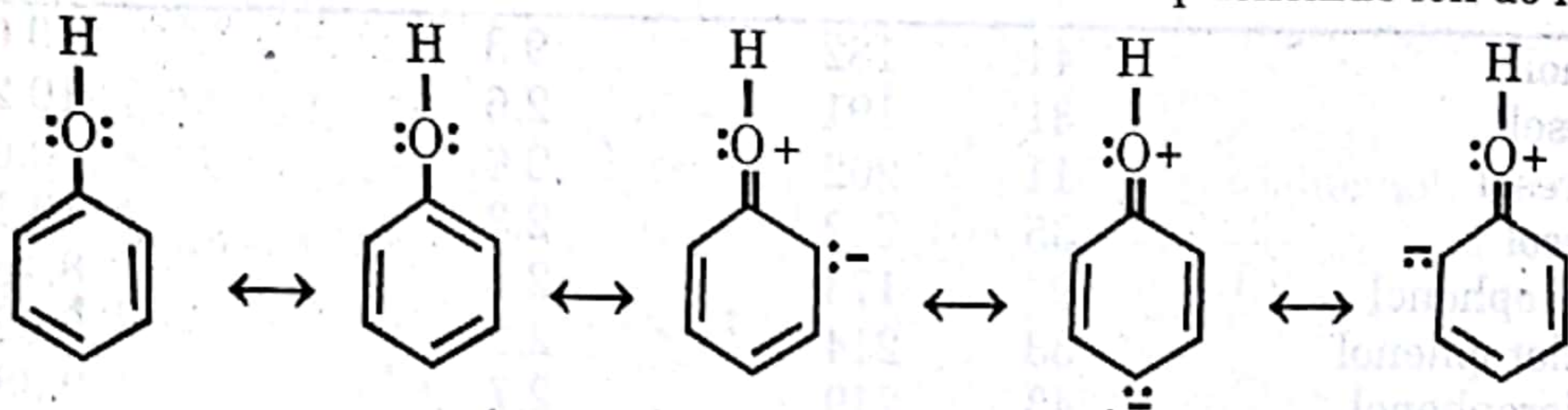
The phenoxide ion is stable due to resonance, while no analogous resonance structures are possible for alcohols and alkoxide ions (RO⁻) derived from alcohol.



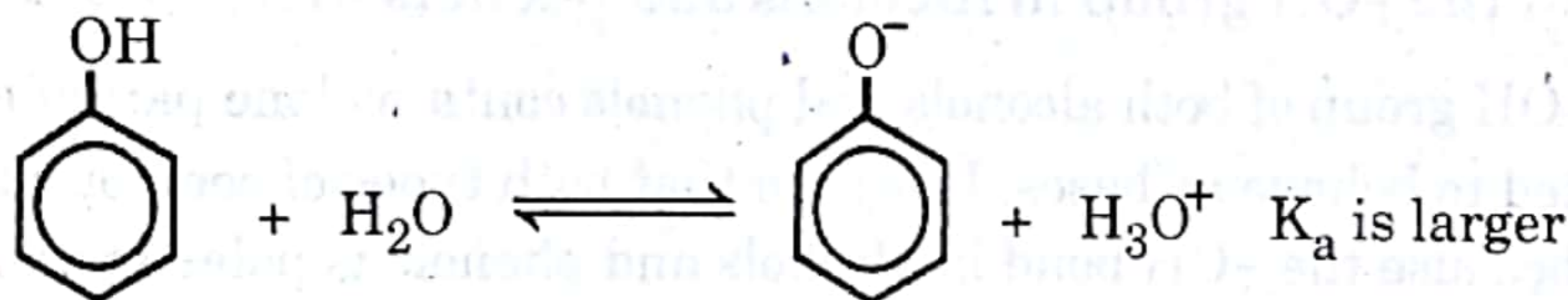
Resonance stabilization of the phenoxide ion is particularly important because the negative charge is **delocalized** over the benzene ring, while the negative charge is localized on a single oxygen atom in alkoxide ion (RO⁻).

Consequently phenols are much stronger acid than alcohols.

Further, resonance stabilizes the phenoxide ion more than it does the phenol, because the resonance structures for phenol require energy to separate opposite charges while the corresponding resonance structure for the phenoxide ion do not.



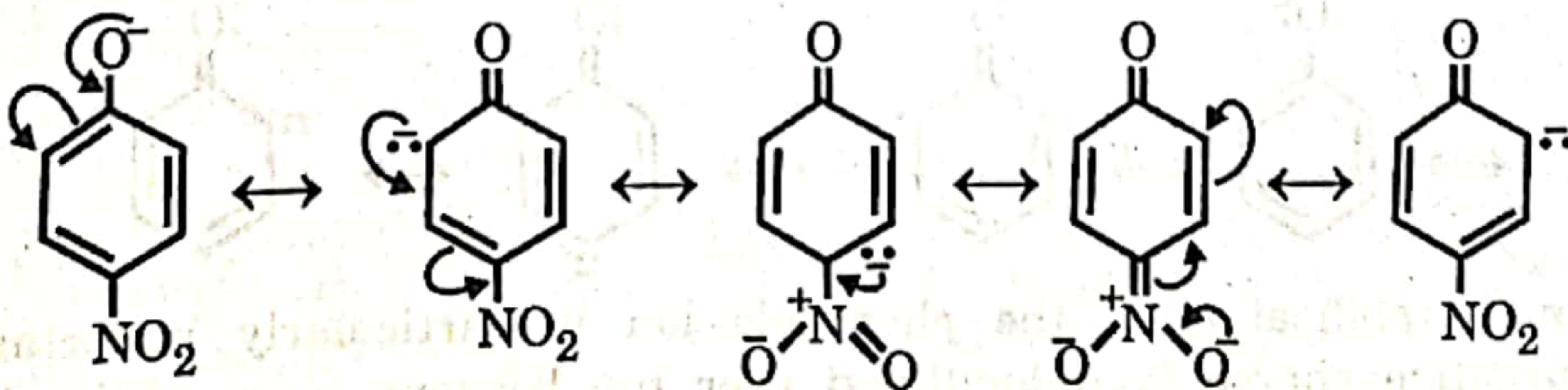
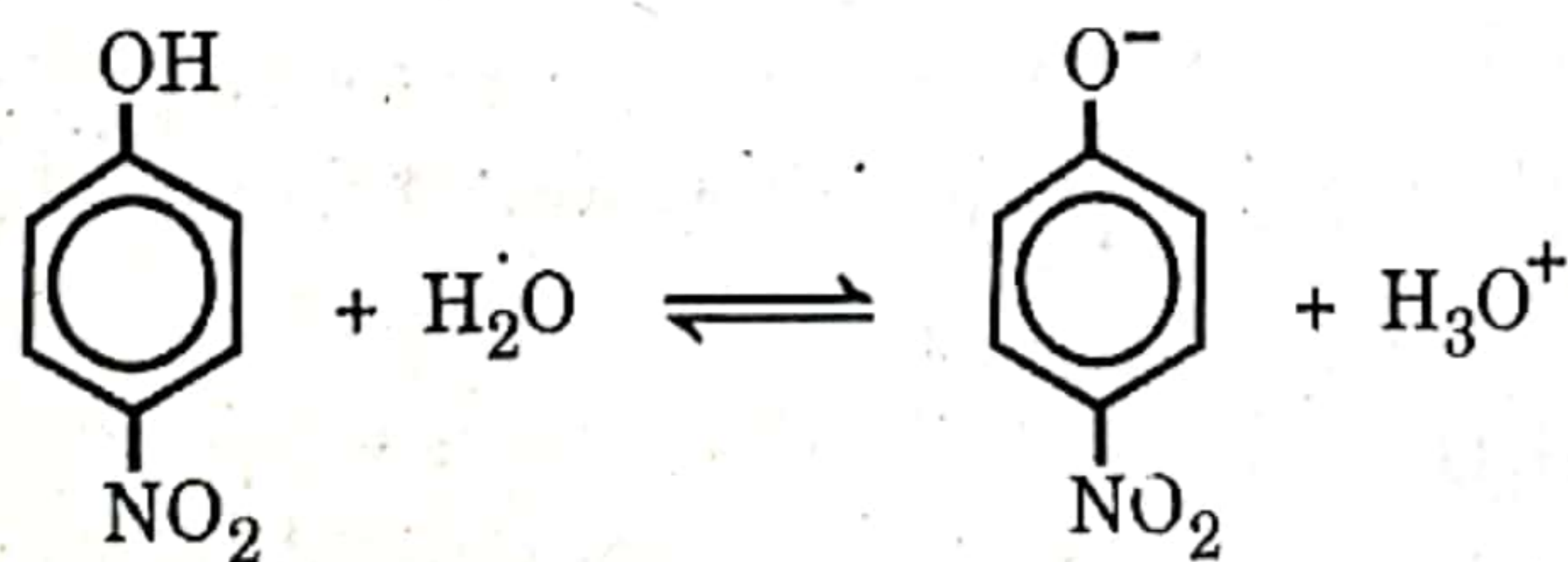
Since resonance stabilizes the phenoxide ion more than it does phenol itself. In, the ionization of alcohol and phenol the equilibrium between phenol and its phenoxide ion will, as a consequence, favour the formation of phenoxide ion and the hydronium ion to a greater extent than the corresponding equilibrium involving alcohol (where neither the alcohol nor the alkoxide ion is resonance stabilized). Both phenols and alcohols are acidic but, of the two, phenol is the stronger.



Effect of Substituents on the Acidity of Phenols

(i) **Effect of electron-withdrawing substituents.** An electron withdrawing group (e.g., $-\text{NO}_2$, $-\text{Cl}$, $-\text{CN}$, $-\text{CHO}$, $-\text{COOH}$) on the aromatic ring is acid-strengthening.

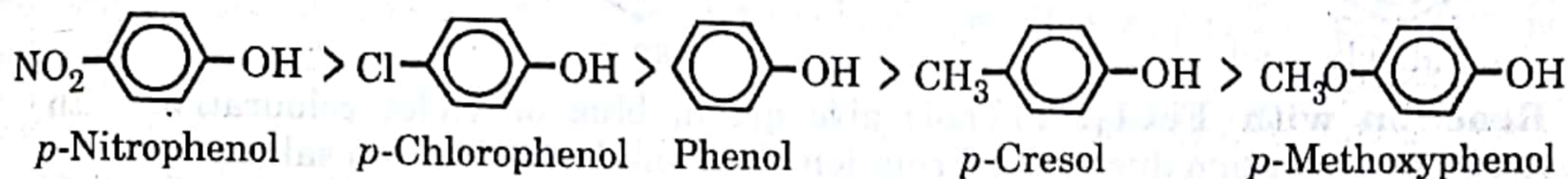
Phenols having electron-withdrawing groups attached to the benzene ring are more acidic than phenol itself, since they enable the ring to withdraw more electrons from the phenoxy oxygen. This stabilizes the phenoxide ion by its resonance and inductive effects which results in a stronger acid. For example, *p*-nitrophenol is more acidic than phenol.



Resonance forms of *p*-nitrophenol ion.

(ii) **Effect of electron-releasing substituents.** An electron-releasing group (e.g., CH_3 , OCH_3 , $-\text{NH}_2$) on the aromatic is acid-weakening. Phenols having electron-releasing groups attached to the benzene ring are less acidic than phenols, since they strengthen the negative charge on phenoxy oxygen and inhibit the charge delocalization due to resonance. This destabilizes the phenoxide ion by its inductive effect and results in weaker acid. For example, *p*-cresol is less acidic than phenol.

The relative strengths of some phenols as acids are as follows:



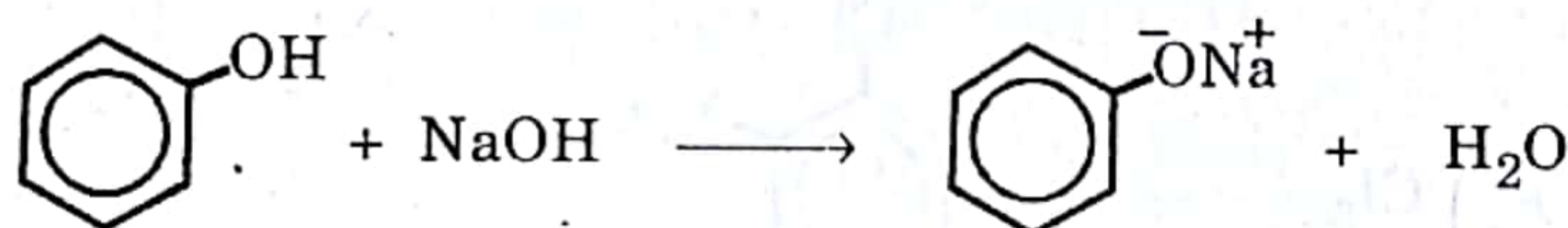
9.14 Reactions of phenols

Phenols generally give two types of reactions:

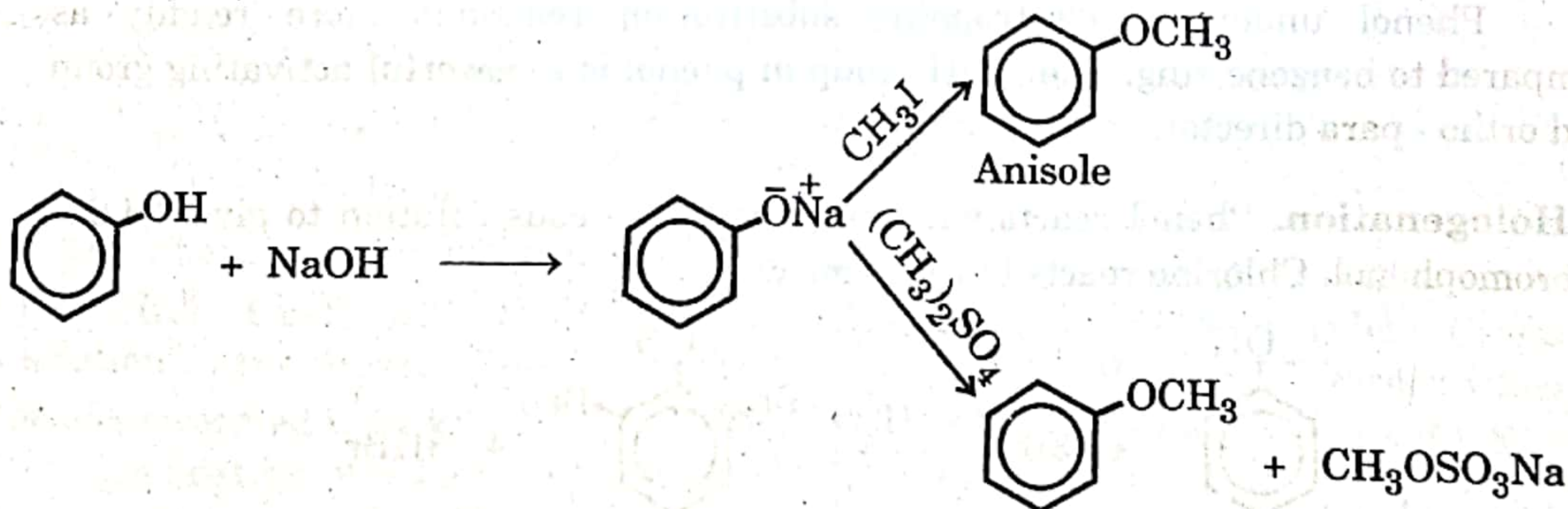
(i) Reactions due to the $-\text{OH}$ group, and (ii) the reactions due to the benzene ring

A. Reactions due to $-\text{OH}$ group

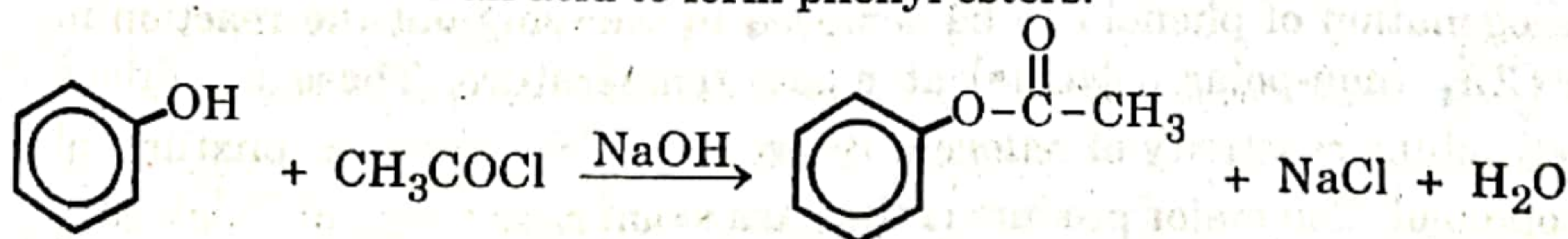
1. Salt Formation. Since phenols are more acidic than water, they react with aqueous solution of sodium or potassium hydroxide to form water soluble sodium or potassium phenoxides.

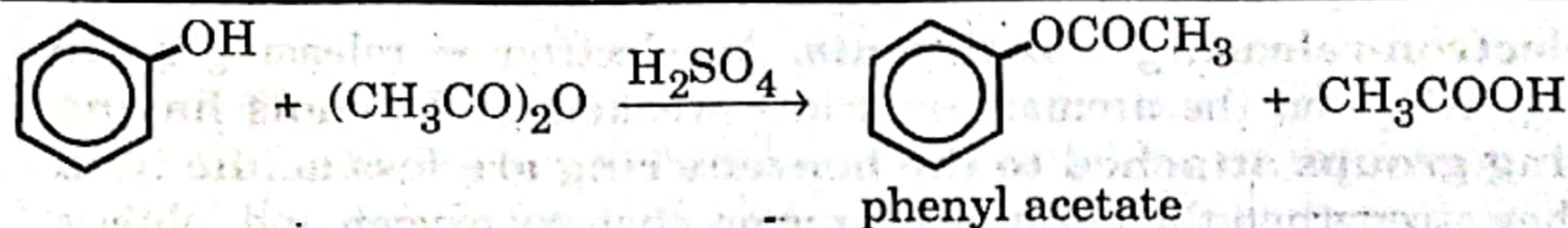


2. Ether Formation. Phenol reacts with alkyl halides and dialkyl sulphates in alkali solution to form phenyl ethers. The alkali first forms the phenoxide ion which then reacts with alkyl halides and dialkyl sulphates. The reaction is known as **Williamson ether synthesis**.

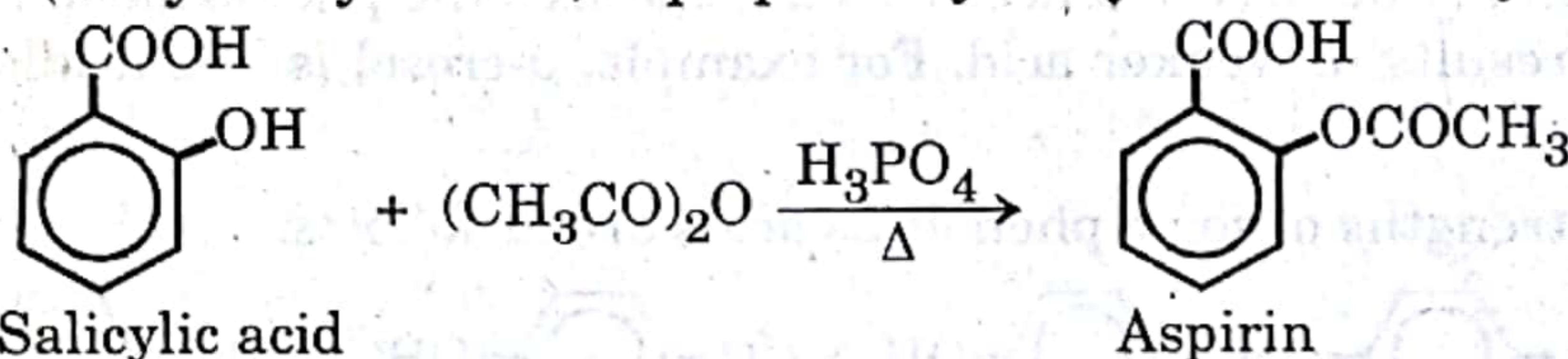


3. Ester Formation. Phenols react with acid chlorides and acid anhydrides in the presence of a base or an acid to form phenyl esters.



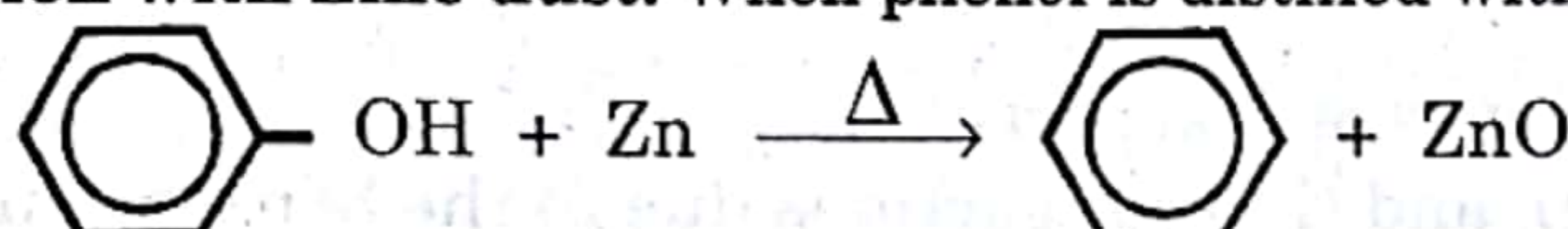


Aspirin (acetylsalicylic acid) is prepared by acetylation of salicylic acid.

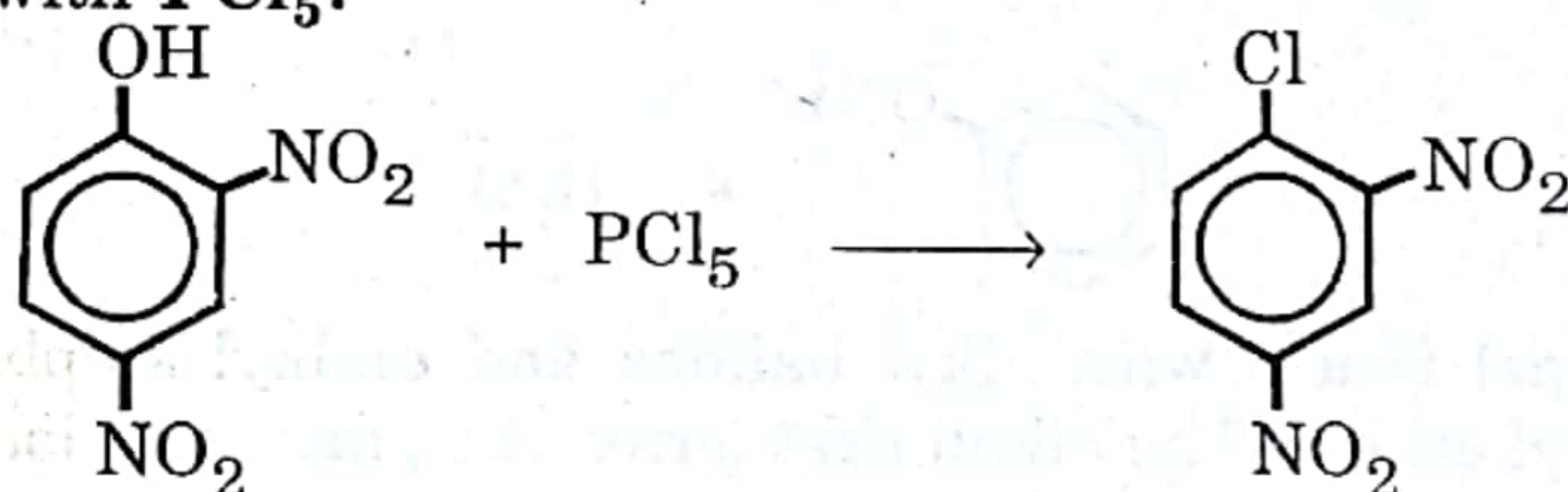


4. Reaction with FeCl_3 . Phenols give green, blue or violet colouration with neutral FeCl_3 solution due to the formation of coloured complex iron salt.

5. Reaction with Zinc dust. When phenol is distilled with zinc dust, benzene is obtained.



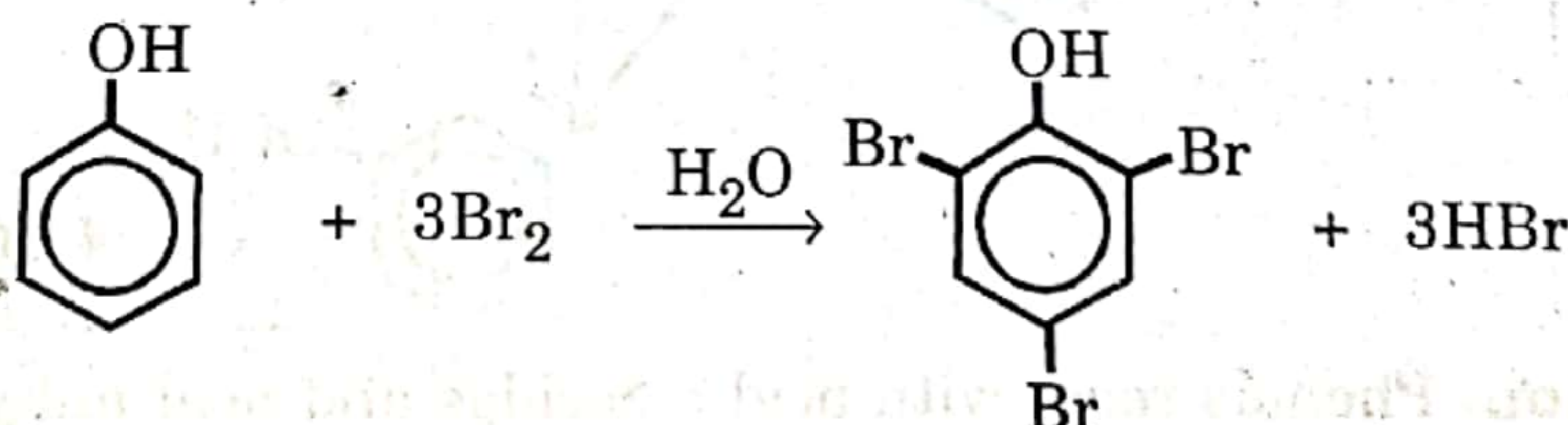
6. Conversion of phenol to Aryl Halides. It is very difficult to convert phenol to aryl halide because it involves the breaking of carbon - oxygen bond. The reaction is possible only if hydroxy group is activated by *electron - withdrawing group at o - and p - position*. For example, 2,4-dinitrophenol is readily converted to 2,4-dinitrochloro benzene with PCl_5 .



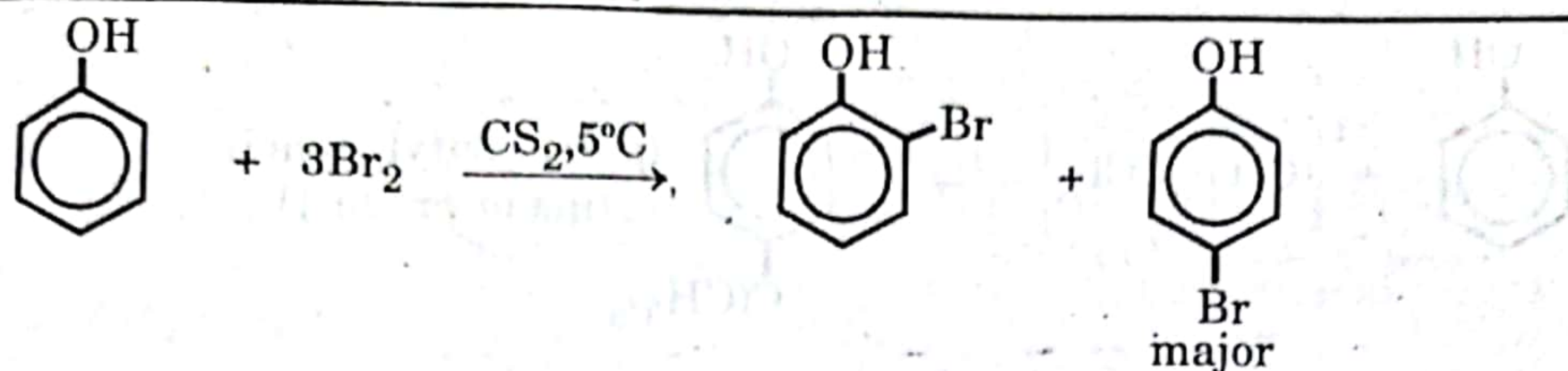
B. Reaction of Benzene Ring: (Electrophilic substitution Reactions)

Phenol undergoes electrophilic substitution reactions more readily as compared to benzene ring. The -OH group in phenol is a powerful activating group and ortho - para director.

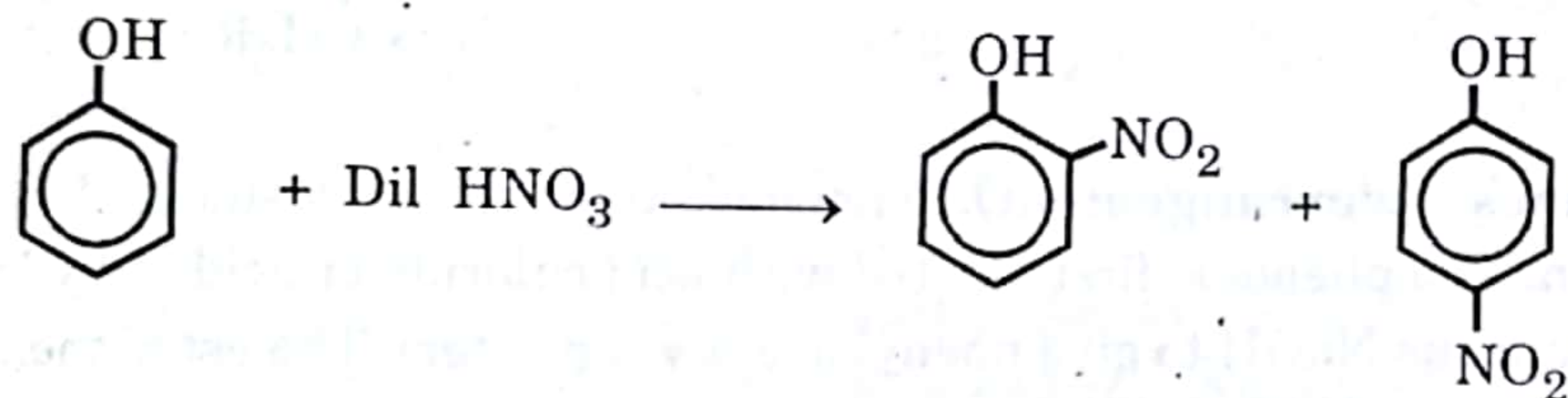
7. Halogenation. Phenol reacts with bromine in aqueous solution to give 2,4,6-tribromophenol. Chlorine reacts in the same way.



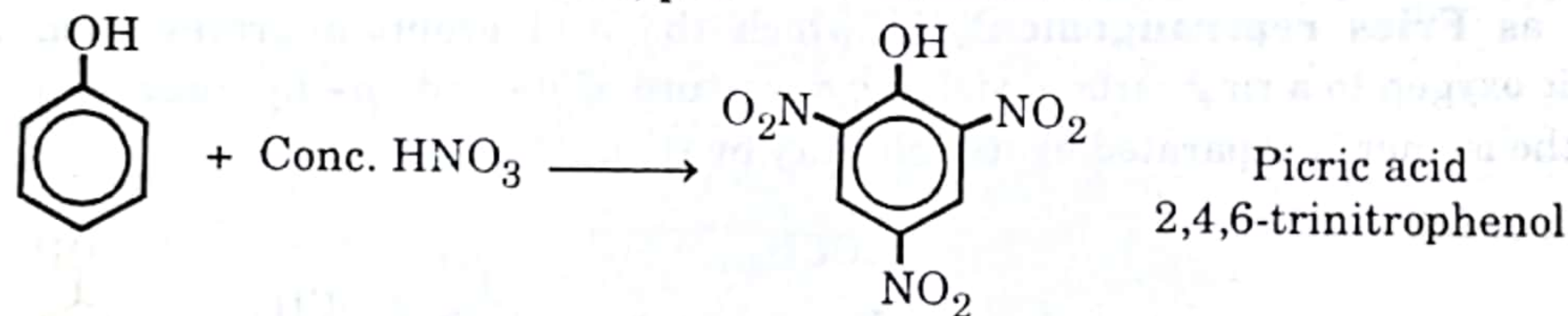
Monohalogenation of phenol can be achieved by carrying out the reaction in CS_2 , CHCl_3 or CCl_4 (non-polar solvents) at a low temperature. These conditions reduce the electrophilic reactivity of halogen. Bromine in CS_2 gives a mixture of *o*- and *p*- bromophenol. The major product is the para isomer.



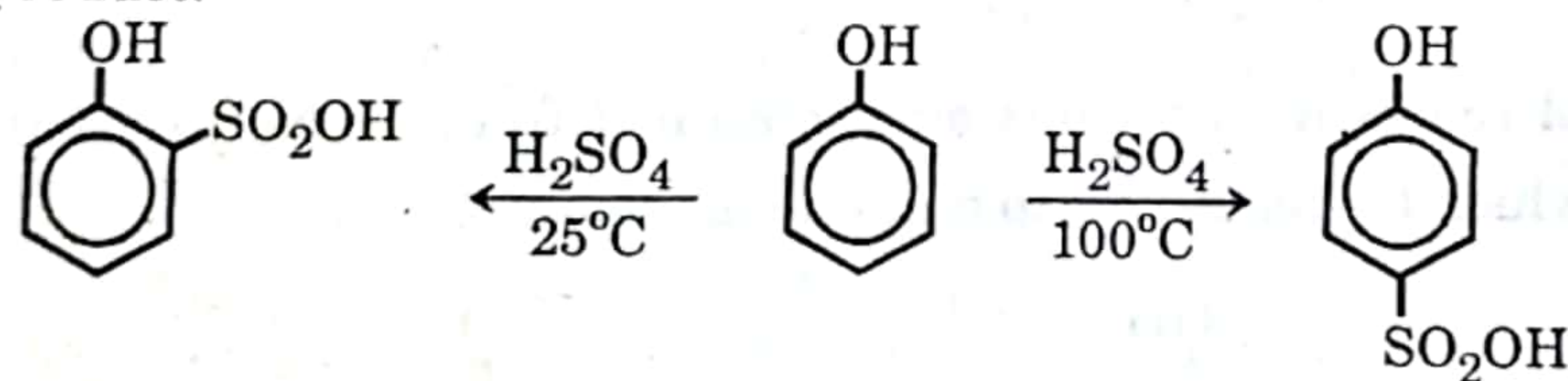
8. Nitration. Phenol reacts with dilute nitric acid to give a mixture of *o*- and *p*-nitrophenol. The ortho and para isomers can be separated by steam distillation. *o*-Nitrophenol is more volatile isomer because its hydrogen bonding is intramolecular. Thus *o*-nitrophenol passes over with the steam leaving behind *p*-nitrophenol.



With concentrated nitric acid, picric acid is formed.



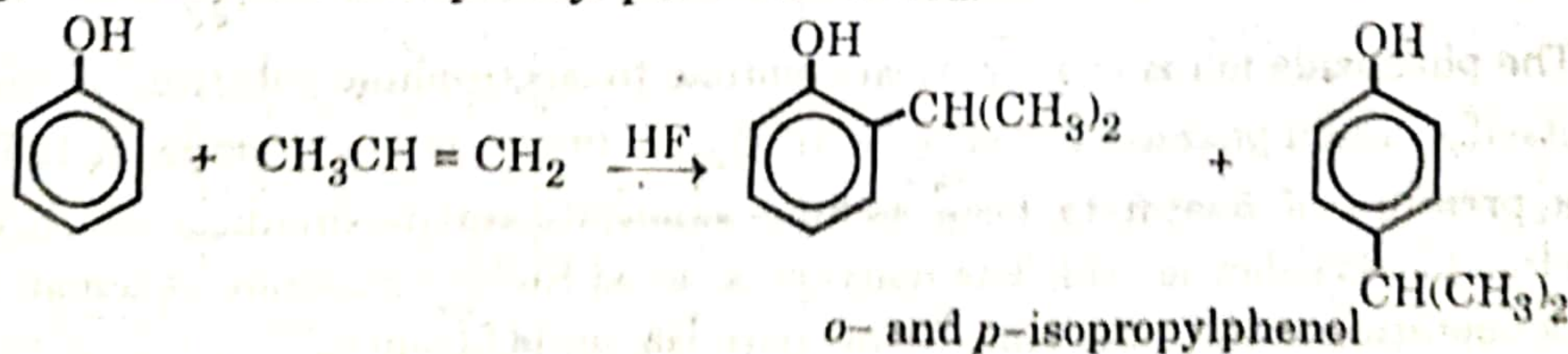
9. Sulphonation. When phenol is treated with concentrated H_2SO_4 at 25°C , *o*-phenolsulphonic acid is the main product. At 100°C , *p*-phenolsulphonic acid is the main product.

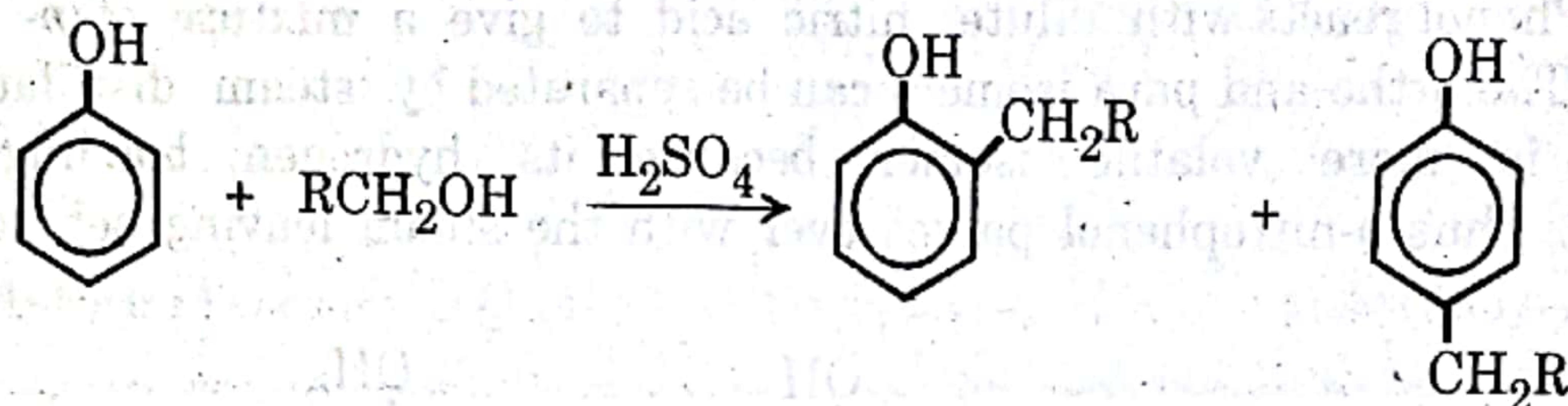
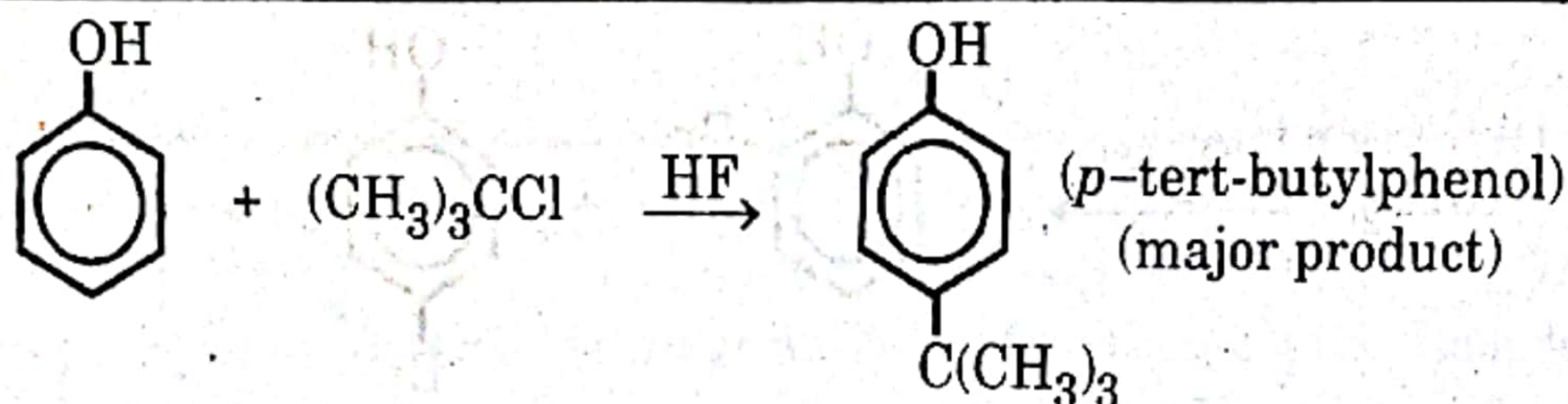


o-hydroxy benzenesulphonic acid

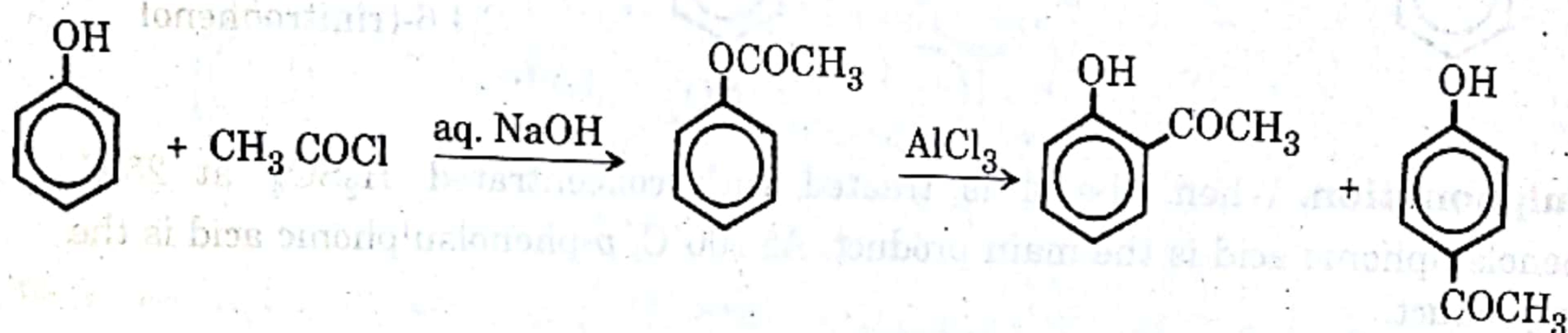
p-hydroxy benzenesulphonic acid

10. Friedel - Crafts alkylation. Alkylphenols can be prepared by Friedel - Crafts alkylation in the presence of AlCl_3 , but the yields are often, poor. However, when phenol is warmed with an alkene or alcohol or alkyl halide in the presence of HF or H_2SO_4 , a mixture of *o*- and *p*-alkyl phenol is formed.

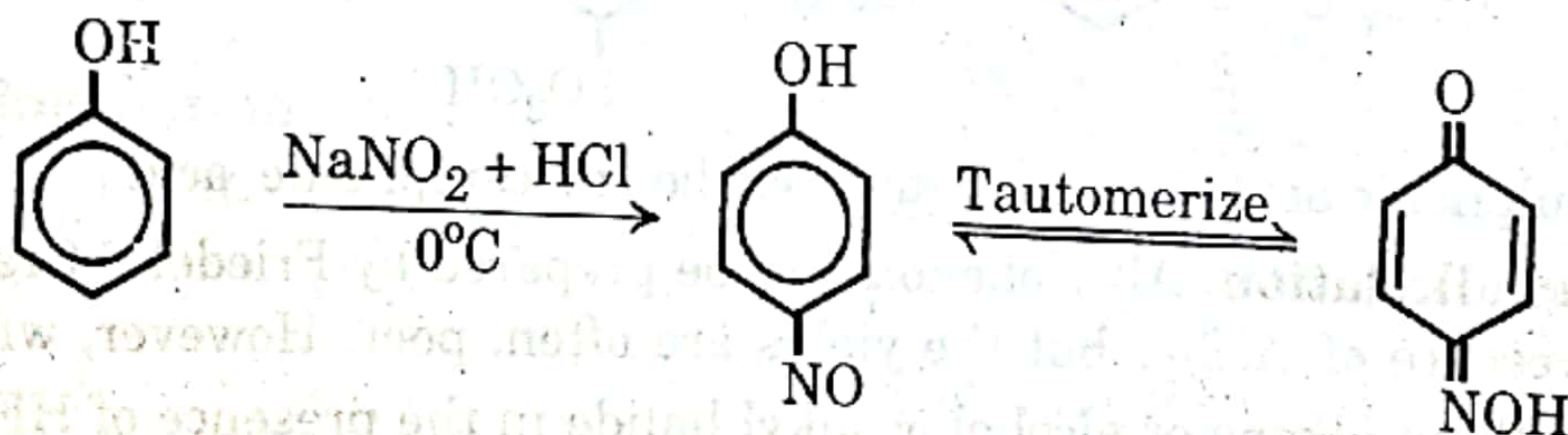




11. Acylation (Fries Rearrangement). Phenolic ketones are usually formed through O-acylation. The phenol is first treated with acid chloride or acid anhydride in the presence of aqueous NaOH to give phenyl acetate (an ester). The ester then on treatment with anhydrous $AlCl_3$ in nitrobenzene or CS_2 undergo a rearrangement, known as **Fries rearrangement**, in which the acyl group migrates from the phenolic oxygen to a ring carbon, yielding a mixture of *o*- and *p*-hydroxy ketones. The ortho isomer is separated by its volatility by steam.

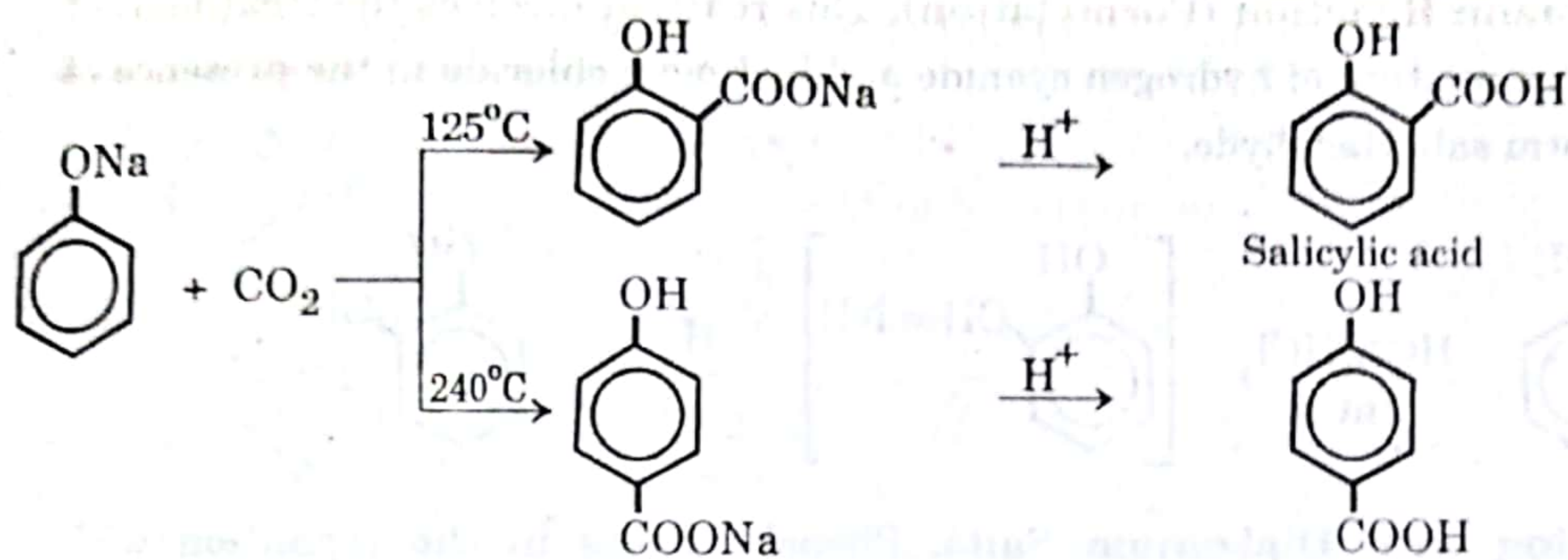


12. Nitrosation. Phenol reacts with nitrous acid (obtained from $NaNO_2 + HCl$) to form *p*-nitrosophenol which tautomerizes to quinone monoxime.



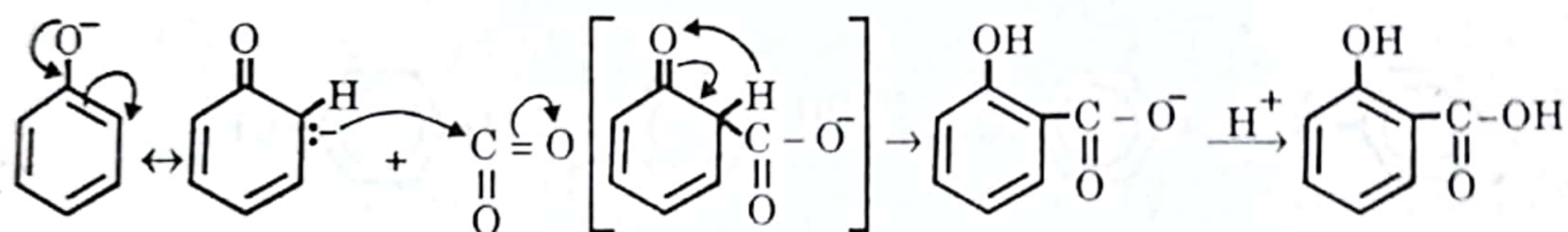
13. Carbonation or Carboxylation (Kolbe-Schmidt reaction)

The phenoxide ion is even more susceptible to electrophilic substitution than phenol itself. Sodium phenoxide reacts with CO_2 , acting as an electrophile, at $125^\circ C$ under a pressure of 5 atm to form sodium salicylate (ortho product) which on acidification yields salicylic acid. The reaction is called Kolbe - Schmidt reaction. At higher temperature ($240^\circ C$) the more stable para isomer is favoured.



The probable mechanism of the reaction is as follows:

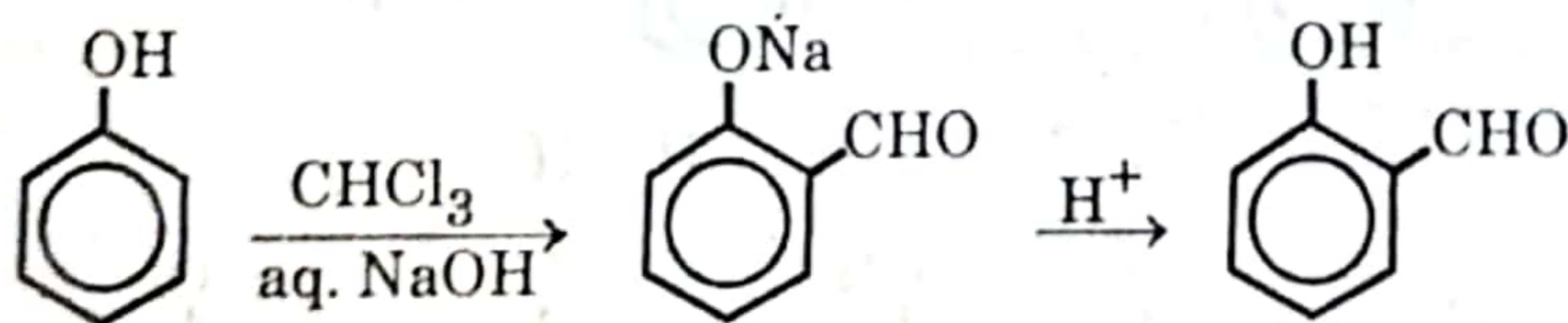
(i) Phenoxide carbanion adds at the electrophilic carbon of CO_2 .



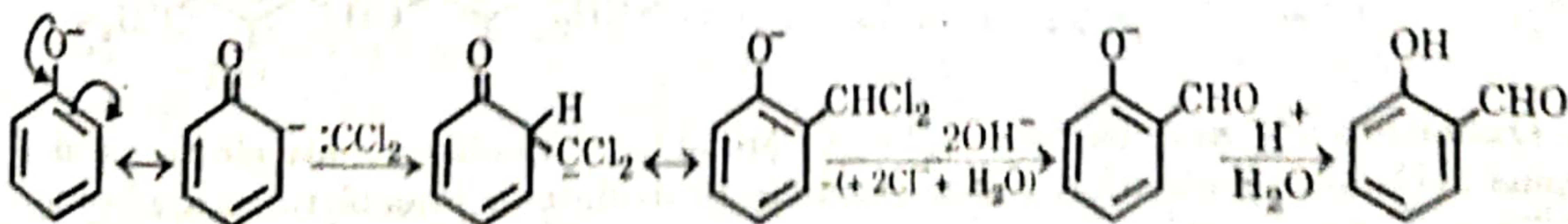
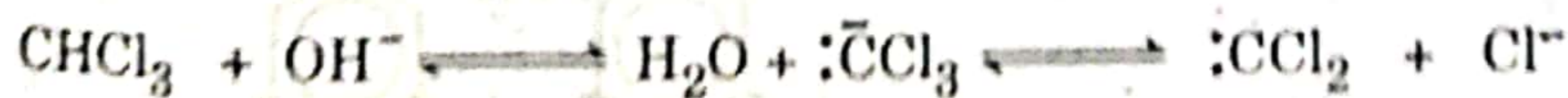
The conjugated ketonic diene tautomerizes to reform the more stable benzenoid ring.

This reaction is widely used for the production of salicylic acid because a number of salicylic acid derivatives are important medicinally. Aspirin is one such derivative.

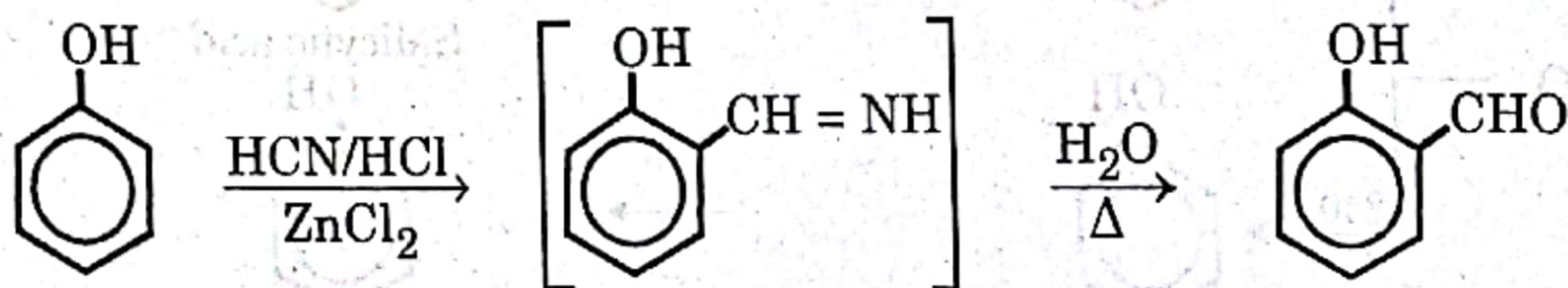
14. Reimer-Tiemann Reaction. The Reimer-Tiemann reaction is the reaction of a phenol with chloroform in aqueous NaOH to give sodium salt of salicylaldehyde which on acidification gives Salicylaldehyde (*o*-hydroxy benzaldehyde). An aldehyde group is introduced in the *o*-position to OH group.



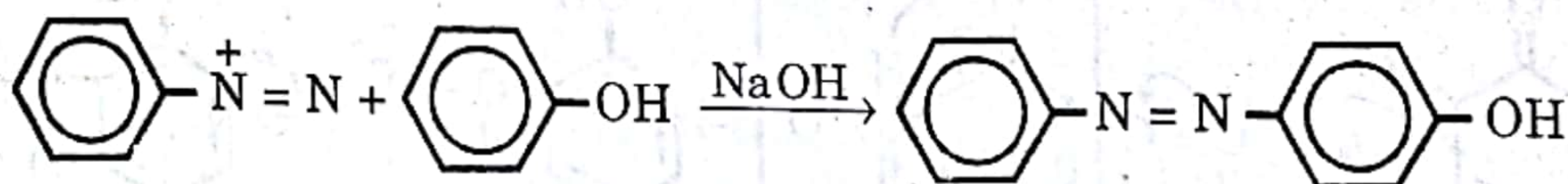
Mechanism: Chloroform first reacts with NaOH to produce dichlorocarbene, (CCl_2). The electron-deficient dichloro carbene (an electrophile) then reacts with sodium phenoxide to form a dihalide which is then hydrolysed to give an aldehyde. Acidification yields the hydroxy aldehyde.



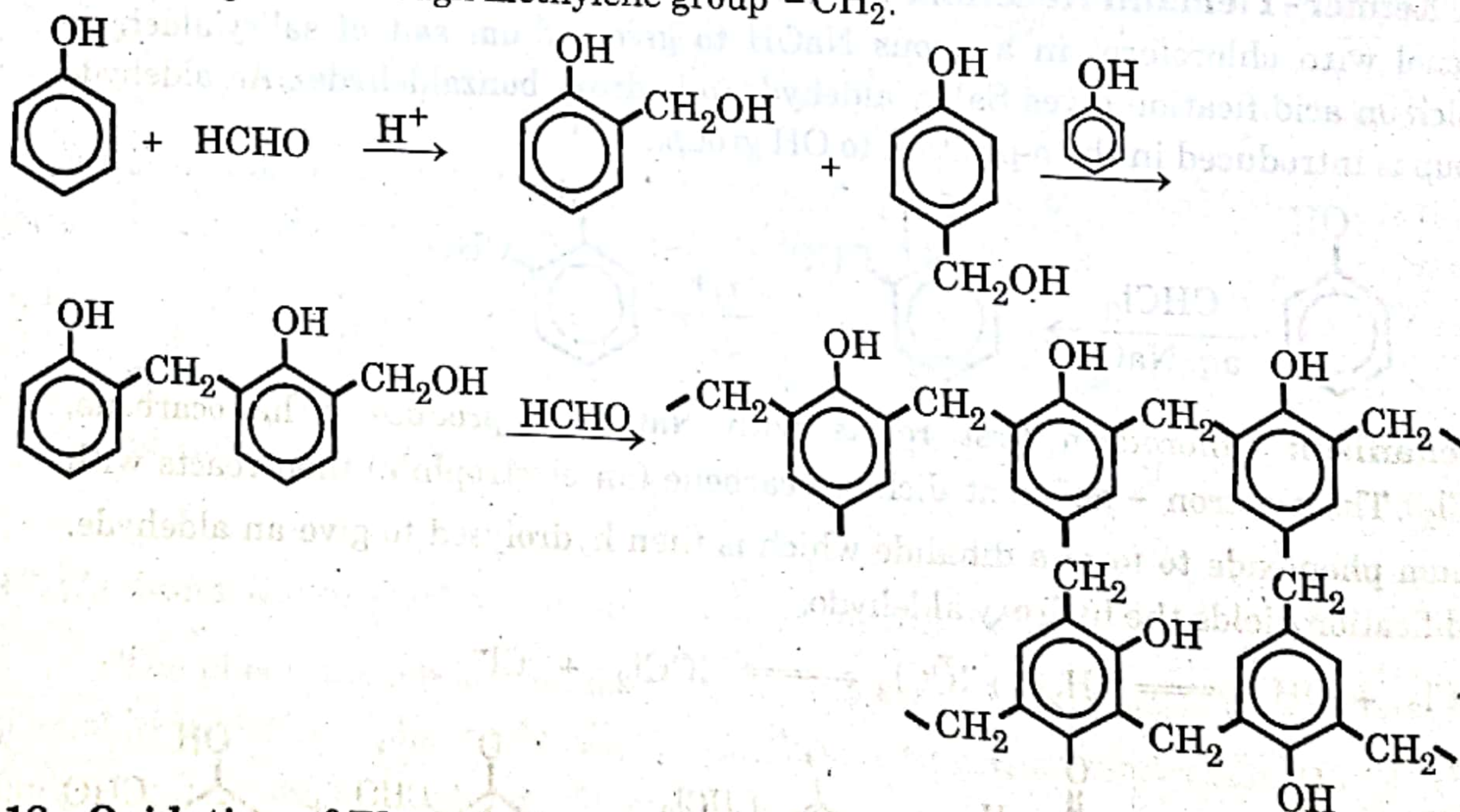
15. Gattermann Reaction (Formylation). This reaction involves the treatment of phenol with a mixture of hydrogen cyanide and hydrogen chloride in the presence of ZnCl_2 to form salicylaldehyde.



16. Coupling with Diazonium Salts. Phenol couples in the μ -position with diazonium ion, ArN_2^+ , a weak electrophile, in a basic solution to form arylazophenols, which are intensely coloured compounds and constitute an important class of azo dyes.

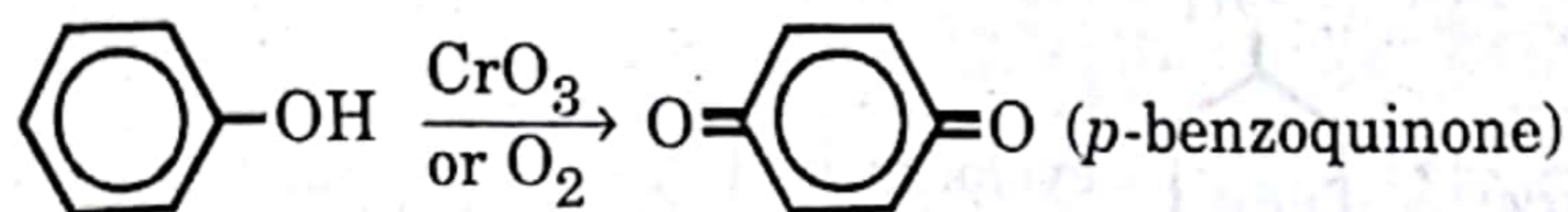


17. Reaction with Formaldehyde. Phenol reacts with formaldehyde in the presence of dilute alkali (or an acid) to give a mixture of o- and p-hydroxybenzyl alcohol. The reaction is difficult to control because of further condensations, and gives phenol - formaldehyde resin called **bakelite**, which contains many phenol rings held together through methylene group $-\text{CH}_2$.

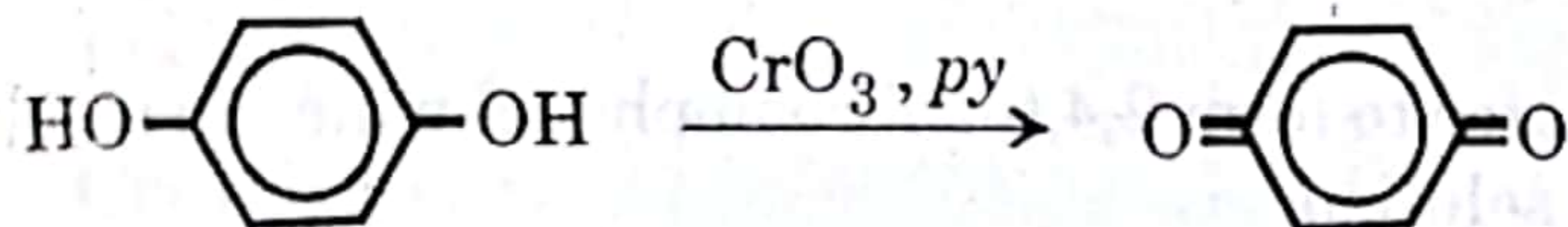


18. Oxidation of Phenols. As the phenols are able to readily donate electrons to various oxidizing agents, they are susceptible to oxidation. Phenol turns pink on

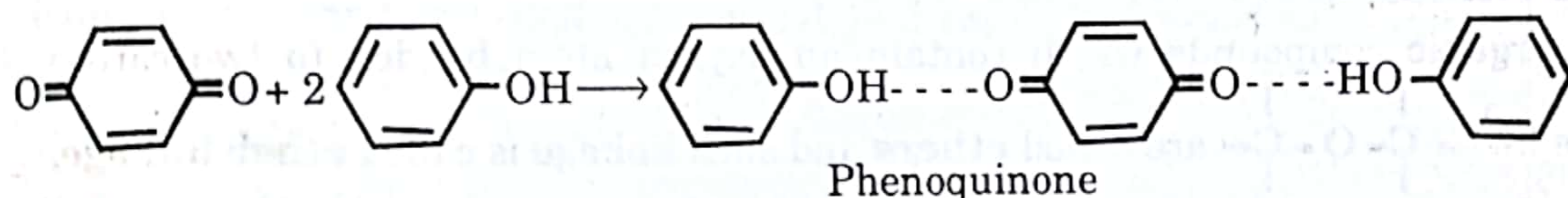
exposure to air and light due to slow oxidation. Phenol undergoes oxidation with air or chromic acid to form *p*-benzoquinone.



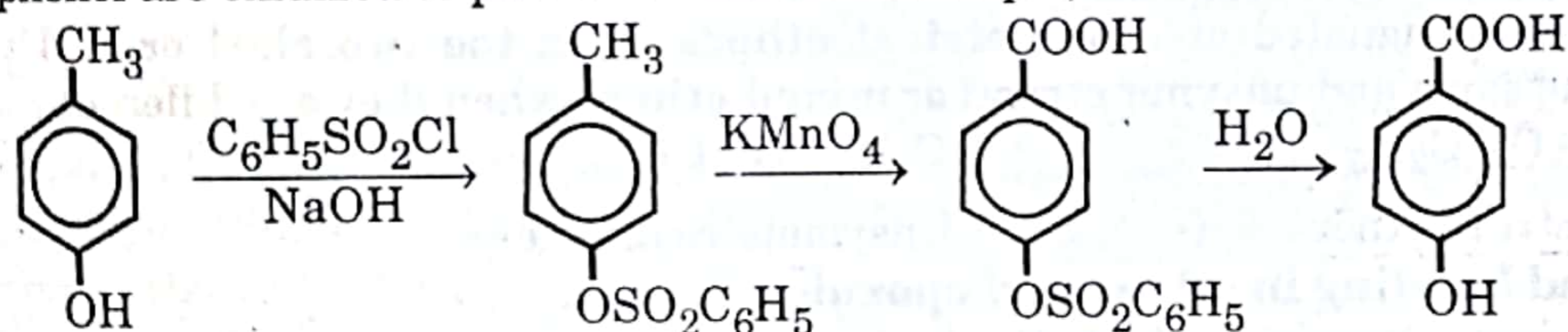
Hydroquinone is oxidized to the yellow coloured *p*-benzoquinone.



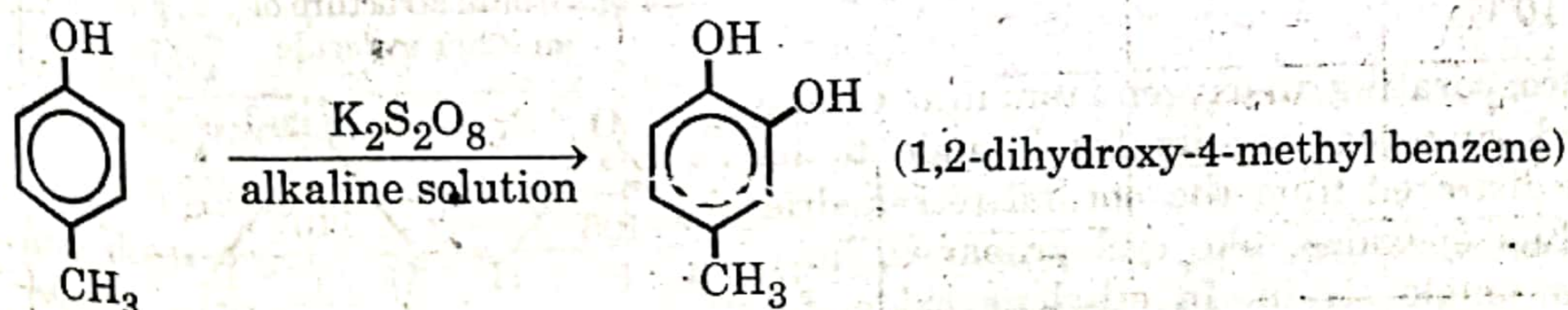
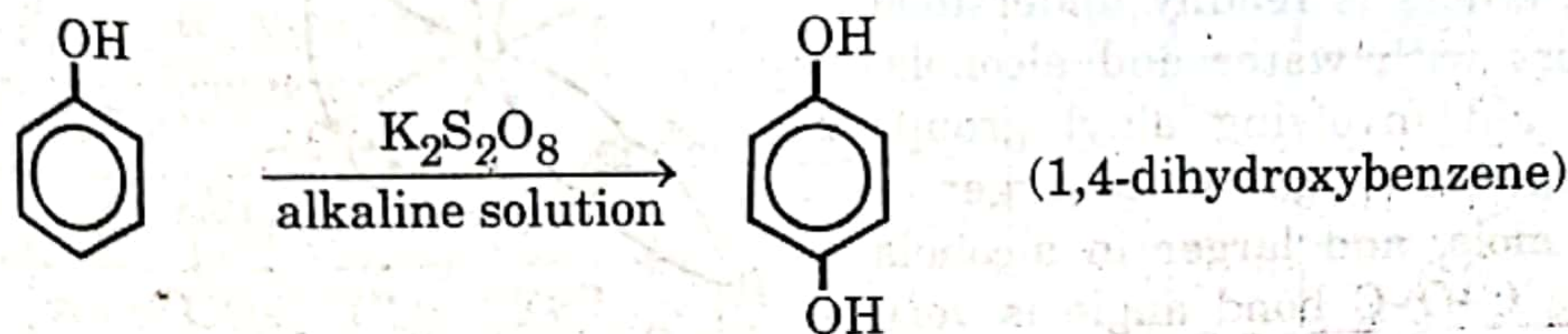
Complex mixture of products are formed on oxidation by air or other oxidising agents. One of the oxidation products in air is quinone which forms a red addition phenol known as phenoquinone, in which two phenol molecules are joined to one molecule of quinone through hydrogen bonds.



On oxidizing Phenol (or its homologues, with KMnO_4 the ring breaks. If, however, the phenolic group is prevented by alkylation or acylation, homologues of phenol are oxidized to phenolic acids. For example,

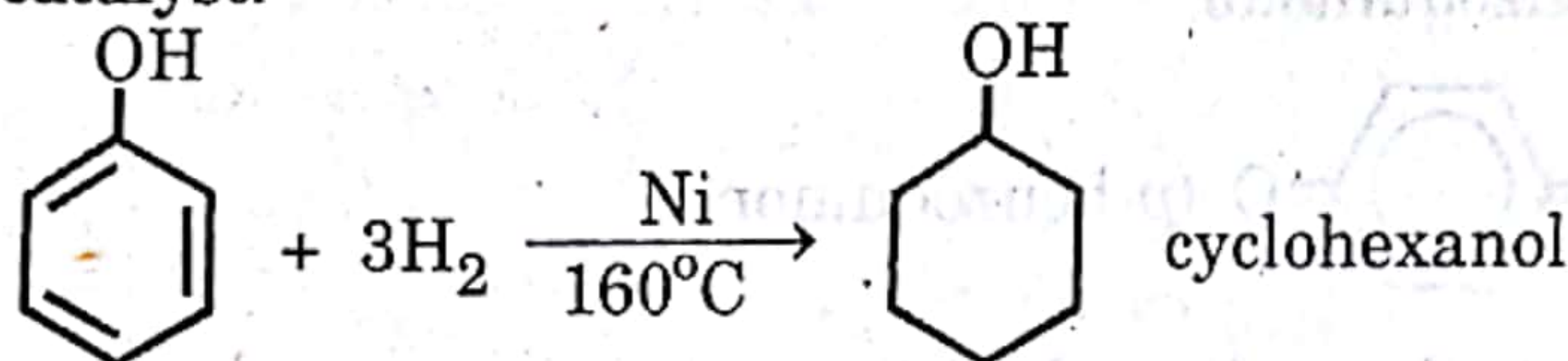


Monohydric phenols on oxidation with potassium persulphate in alkaline solution yield dihydric phenols. The newly-entering $-\text{OH}$ group enters the para position to the $-\text{OH}$ group. In case para position is not free (blocked), the new group enters the position ortho to the hydroxyl group. This is known as **Elbs persulphate oxidation**.



19. **Catalytic Hydrogenation (Reduction).** Phenols can be reduced into

corresponding cyclohexanols. Generally reduction is carried out with hydrogen over nickel catalyst.



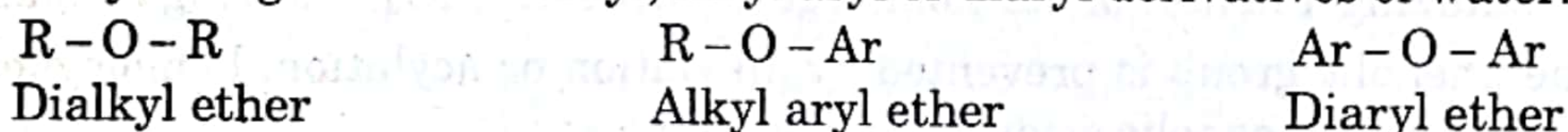
Chemical tests for phenols

1. Phenol reacts with bromine water to form 2,4,6-tribromophenol which is insoluble in water and gives turbidity in a solution.
2. Almost all phenols in water or alcohol give a characteristic colour ranging from violet through blue and green to red with neutral FeCl_3 solution. The colour develops due to the formation of ferric phenoxide salts. Phenol itself gives a violet colouration and cresols give a blue colour.

9.15 ETHERS

Organic compounds which contain an oxygen atom bonded to two carbon atoms like $\begin{array}{c} | \\ -\text{C}-\text{O}-\text{C}- \\ | \end{array}$ are called **ethers** and such linkage is called **ether linkage**.

Ethers may be regarded as dialkyl, alkyl aryl or diaryl derivatives of water.



They are designated as **Symmetrical ethers** when the two alkyl or aryl groups are the same and **unsymmetrical** or **mixed ethers** when they are different.



Structure and bonding in ethers and epoxides

In ethers and epoxides both the carbon and oxygen atoms are sp^3 hybridized. The two C-O σ bonds are formed by sp^3-sp^3 overlap. The two unshared pairs of electrons on oxygen occupy sp^3 hybrid orbitals.

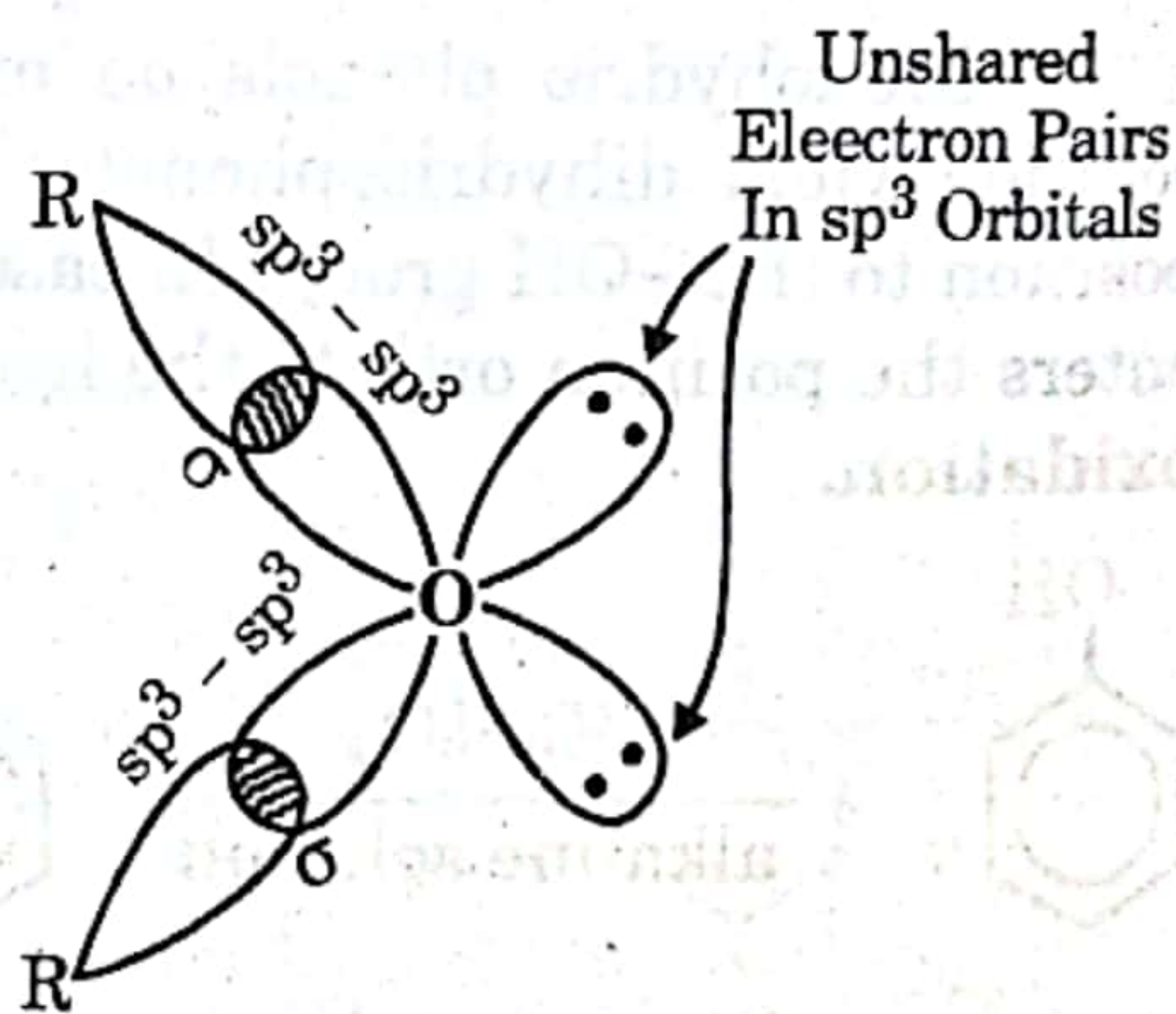
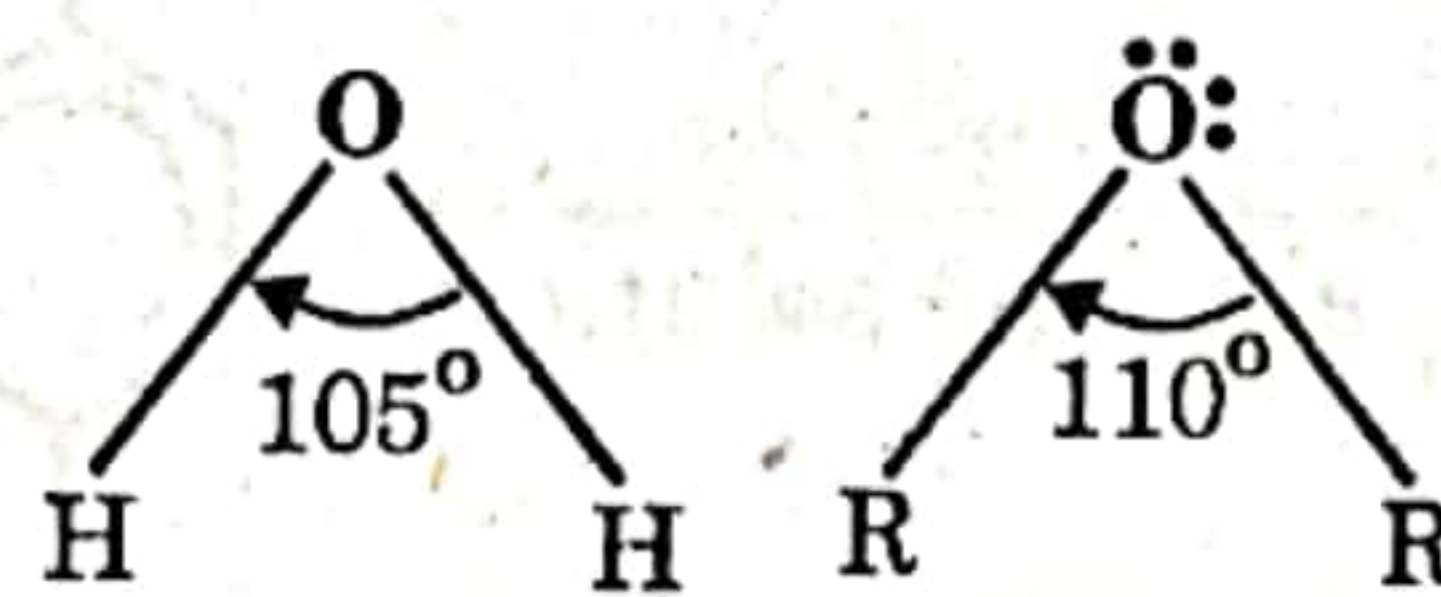


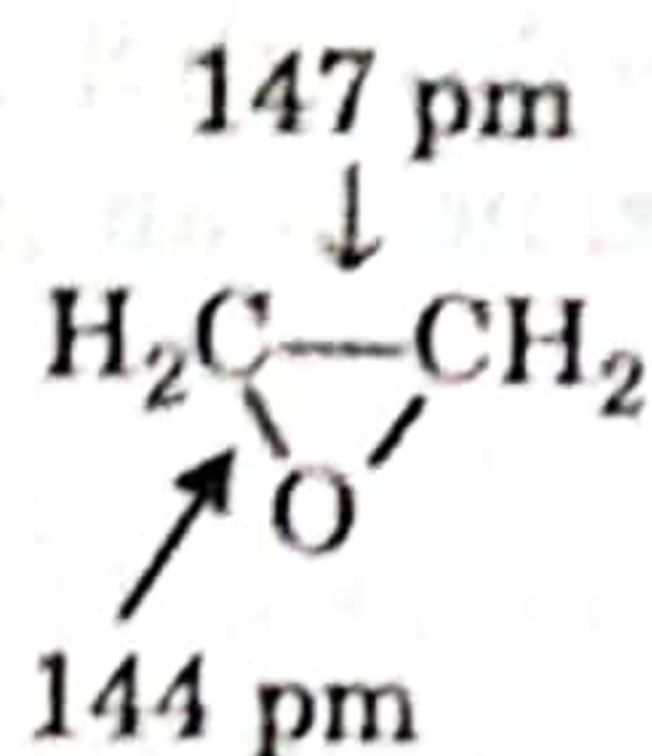
Fig. Orbital structure of an ether molecule

Bonding in ethers is readily understood by comparing ethers with water and alcohols. van der Waals strain involving alkyl groups causes the bond angle at oxygen to be larger in ethers than in alcohols, and larger in alcohols than in water. The C-O-C bond angle is very close to 110° .

Incorporating an oxygen atom into a three membered ring requires its bond angle to be seriously distorted from the normal tetrahedral value. Thus epoxides, like cyclopropanes, have significant angle strain. In ethylene oxide, for example, the bond angle at oxygen is 61.5° . They tend to undergo reactions that open



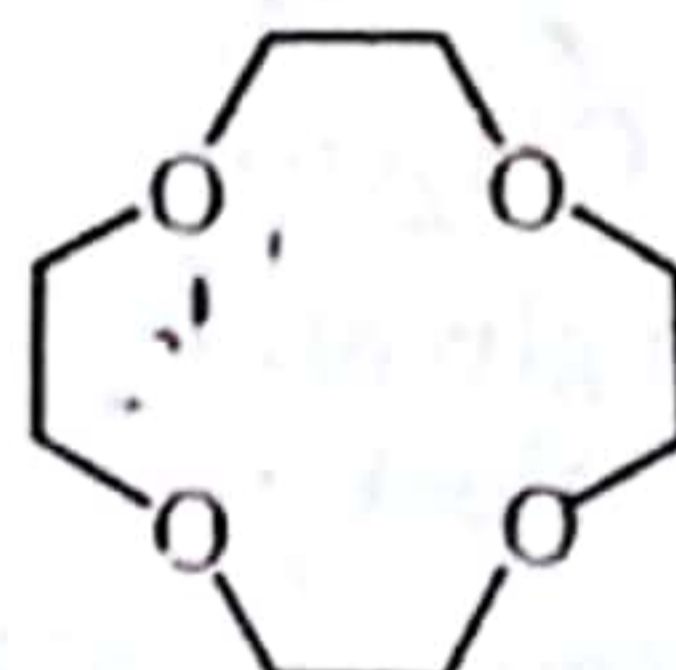
the three - membered ring by cleaving one of the carbon - oxygen bonds.



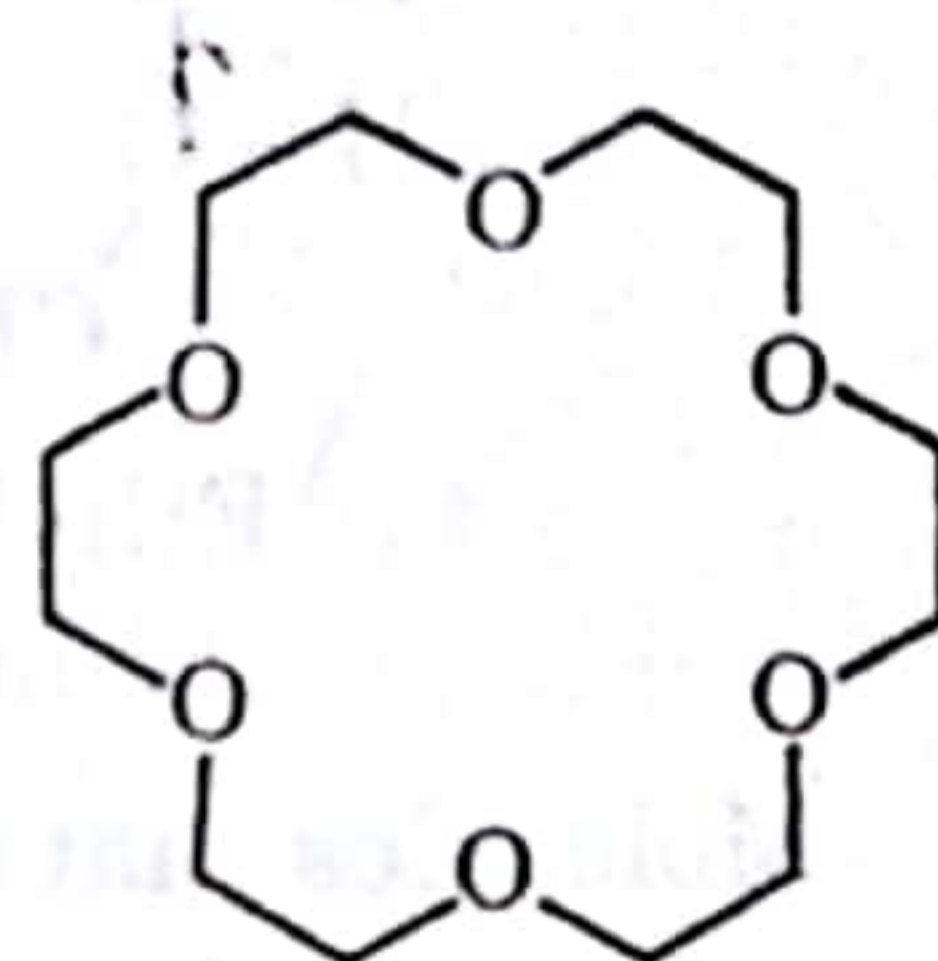
C - O - C angle 61.5°

C - C - O angle 59.2°

9.16 Crown ethers. Crown ethers are cyclic polyethers having four or more oxygens in a ring of 12 or more atoms. These compounds are called **crown ethers**, because their molecular models resemble crown. The first number in their names indicates the ring size and the second number indicates the number of oxygen atoms.



12-Crown-4

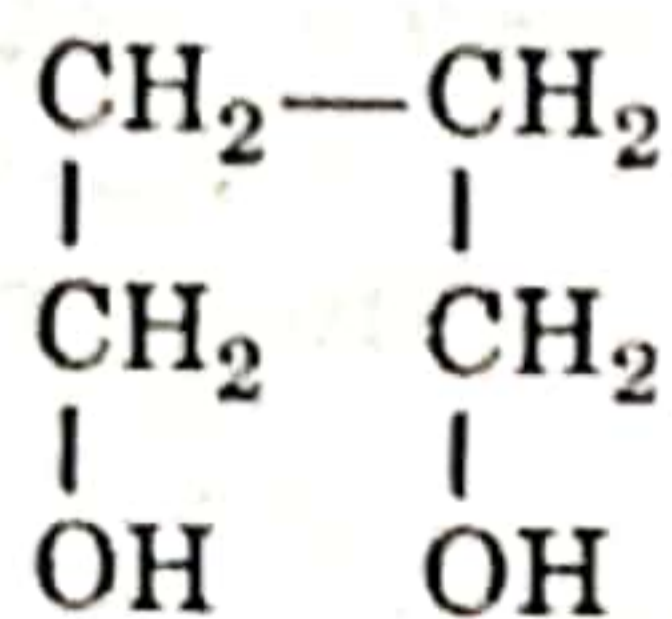


18-Crown-6

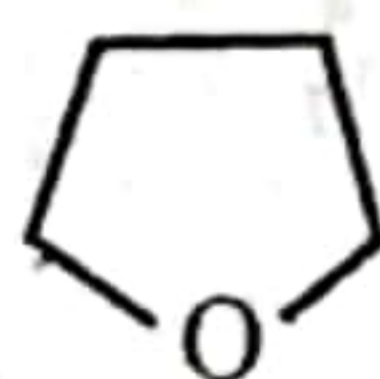
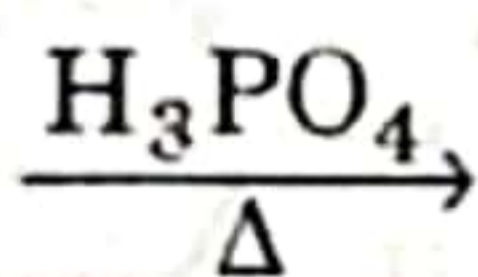
12-Crown-4 and 18-Crown-6 are a cyclic tetramer and hexamer, respectively of repeating $-\text{OCH}_2\text{CH}_2-$ units; they are polyethers based on ethylene glycol ($\text{HOCH}_2-\text{CH}_2\text{OH}$) as the parent alcohol. The cavity of a crown ether is a polar region, and the unshared pair of electrons on the ether oxygen can solvate alkali metal ions. The outer surface of a crown ether is non-polar and hydrocarbon like. Crown ethers are valuable for their ability to cause ionic compounds to dissolve in non-polar organic solvents. For examples, potassium fluoride (KF) is ionic and practically insoluble in benzene alone, but dissolves in it when 18-crown-6 is present. When KF is added to a solution of 18-crown-6 in benzene, K^+ ion interacts with the oxygen of the crown ether to form a Lewis acid-Lewis base complex. The metal-ion complexing properties of crown ethers are clearly evident in their effects on the solubility and reactivity on ionic compounds in non polar media.

9.17 Tetrahydrofuran (THF). Tetrahydrofuran is a saturated cyclic ether and is commonly designated as THF.

1. It may be obtained by catalytic hydrogenation of furan.
2. It may be obtained by acid catalysed dehydration of 1,4-butanediol (commercial)



1, 4-butanediol

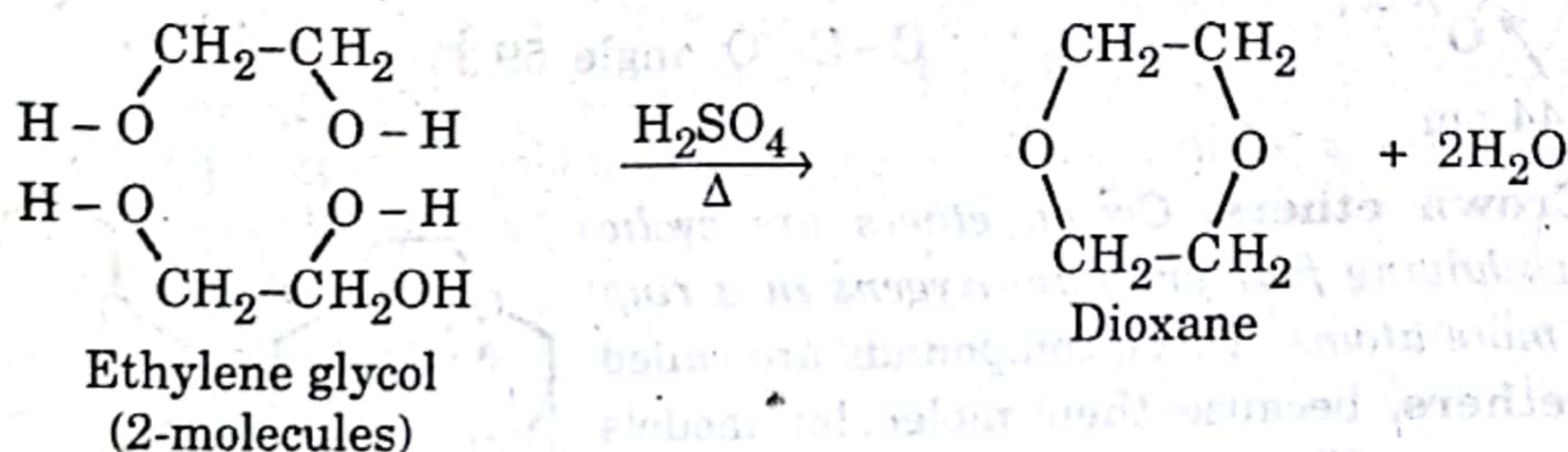


Tetrahydrofuran (THF).

THF is a poisonous volatile liquid, b.p. 66°C . It is miscible with both water and most organic solvents. (i) It is used as a solvent in the preparation of organic reagents and its reactions and (ii) in the manufacture of nylon 6-6 and 1,3-butadiene.

9.18 Dioxane. Cyclic ether that has two ether groups are called

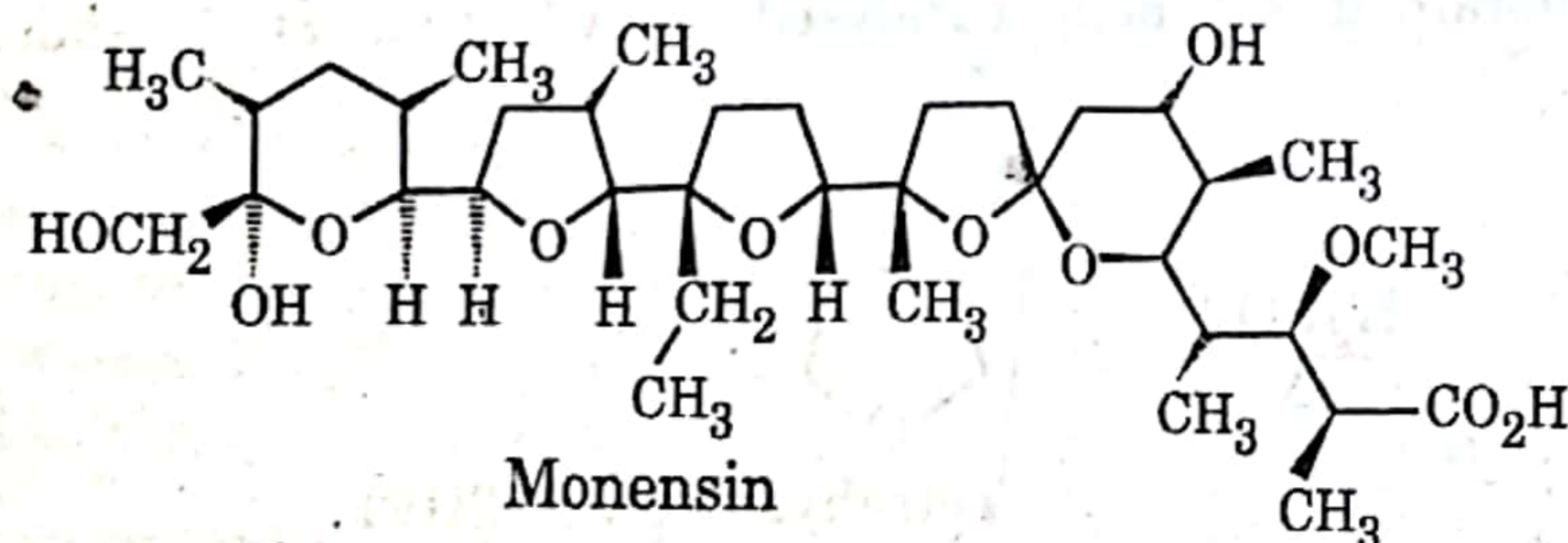
dioxane. 1,4-dioxane has two ether groups, requiring dehydration between two pairs of OH groups. The alcohol must be diol and the alcohol used is ethylene glycol, $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$ and the dehydration is intermolecular. Dioxane is an important industrial solvent.



Molecules that contain several ether functions are referred to as **polyethers**.

9.19 Polyethers as antibiotics. Antibiotics are, by definition, toxic (*anti* = "against"; *bios* = "life") and the goal is to find substances that are more toxic to infectious organisms than to their human hosts.

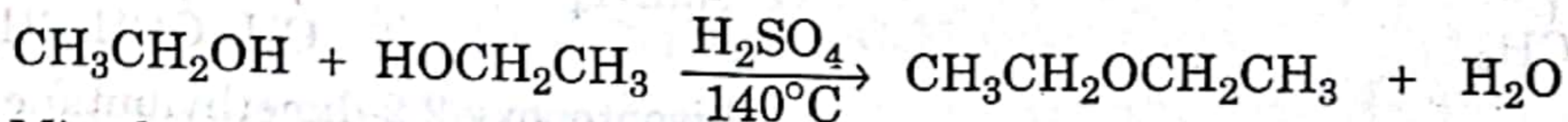
Since 1950, a number of polyether antibiotics have been discovered using fermentation technology. They are characterized by the presence of several cyclic ether structural units, e.g., monensin (See Fig.). Monensin and other naturally occurring polyethers are similar to crown ethers in their ability to form stable complexes with metal ions. The structural of the sodium salt of monensin has four ether oxygens and two hydroxyl groups surround a sodium ion. The alkyl groups are oriented toward the outside of the complex, and the polar oxygens and the metal ion are on the inside. The hydrocarbon-like surface of the complex permits it to carry its Na^+ ion through the hydrocarbon-like interior of a cell membrane. This disrupts the normal balance of Na^+ ions within the cell and interferes with important processes of cellular respiration. Small amounts of monensin are added to poultry feed to kill parasites that live in the intestines of chickens. Compounds such as monensin and the crown ethers that effect metal ion transport are referred to as ionophores.



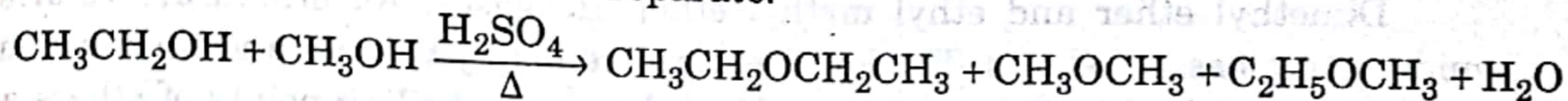
9.20 Preparation of Ethers

1. dehydration of alcohols. Symmetrical ethers are prepared by heating an excess of alcohol with conc. H_2SO_4 at 140°C . Dehydration to ethers rather than to alkenes is controlled by the choice of reaction conditions. Dehydration of an alcohol to an alkene takes place at a higher temperature than the dehydration to an ether. For

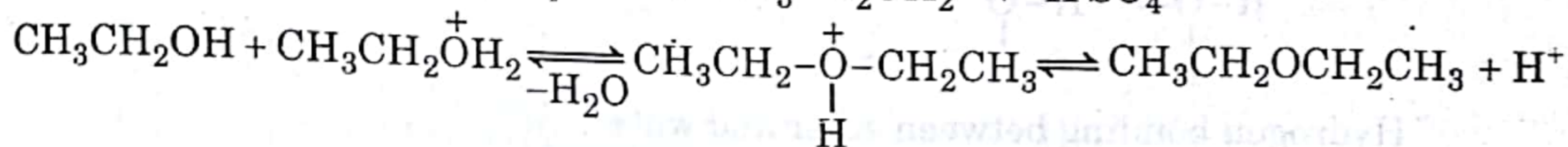
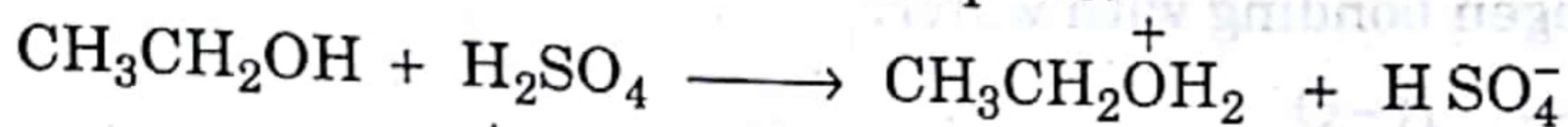
example, dehydration of ethanol with conc. H_2SO_4 at 180°C , mainly yields ethene, whereas at 140°C , mainly yields diethyl ether.



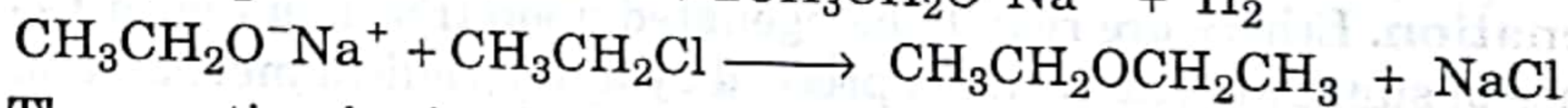
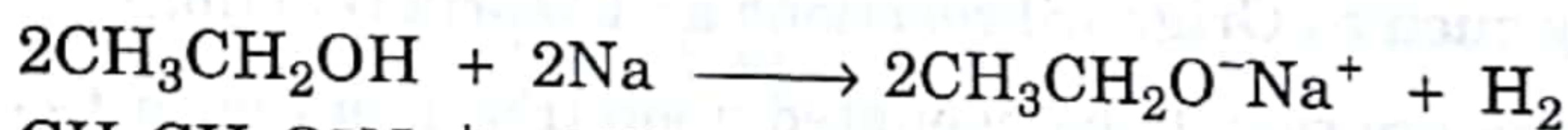
Mixed ethers cannot be prepared by this method because we obtain a mixture of ethers which is too difficult to separate.



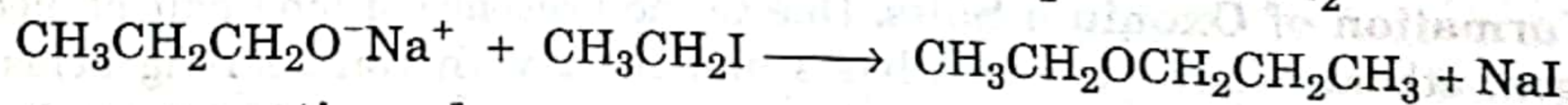
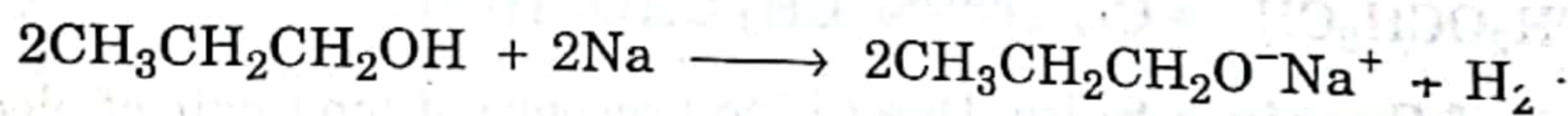
The formation of ether probably involves an $\text{S}_{\text{N}}2$ mechanism in which one molecule of the alcohol in the protonated form acts as the substrate and another molecule of the alcohol acts as the nucleophile.



2. Williamson's Synthesis (Conversion of alcohols to ethers). In this synthesis an alkoxide or a phenoxide is made to react with alkyl halide, alkyl sulphate or alkyl sulphonate to form ether. Sodium alkoxides are obtained by treating alcohols with sodium metal. Both symmetrical and unsymmetrical ethers can be prepared by this method.

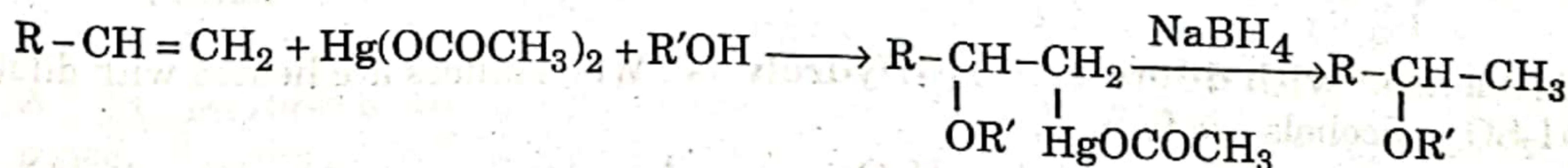


The reaction is simple $\text{S}_{\text{N}}2$ displacement of halide ion from an alkyl halide by an alkoxide or a phenoxide ion. For the synthesis of a mixed ether, the alkoxide may be derived from a primary, secondary or tertiary alcohol, but the alkyl halide, sulphonate or sulphate must be primary (or methyl) to minimize the competing elimination reaction.

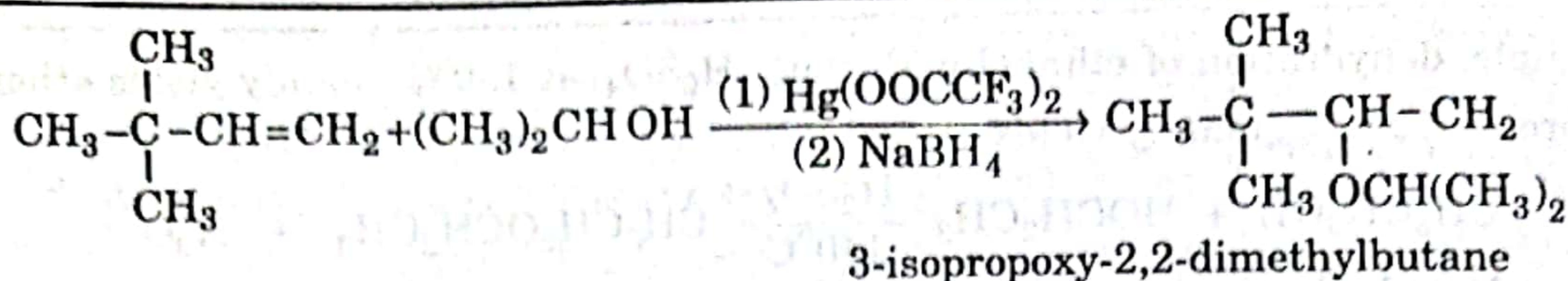


3. Alkoxymercuration - demercuration of alkenes

Alkenes react with mercuric acetate in the presence of an alcohol to give alkoxymercurial compound which on reduction with NaBH_4 gives ether.

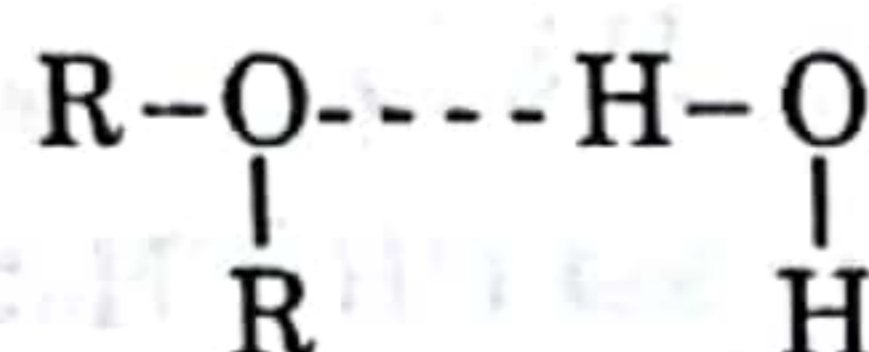


This method has advantage over the Williamson's synthesis because there is no competing elimination reaction and can be used for the synthesis of *nearly every kind* of ethers. However, with a bulky alcohol (secondary or tertiary), mercuric trifluoroacetate gives a better yield.



9.21 Physical Properties

Dimethyl ether and ethyl methyl ether are gases. All others are colourless liquids with pleasant odours. The lower ethers are highly volatile and their vapours are highly inflammable. Ethers are weakly polar so the boiling points of ethers are slightly higher than hydrocarbons having comparable molecular masses, but have lower boiling points than isomeric alcohols. Ethers are slightly soluble in water and thus can form hydrogen bonding with water.

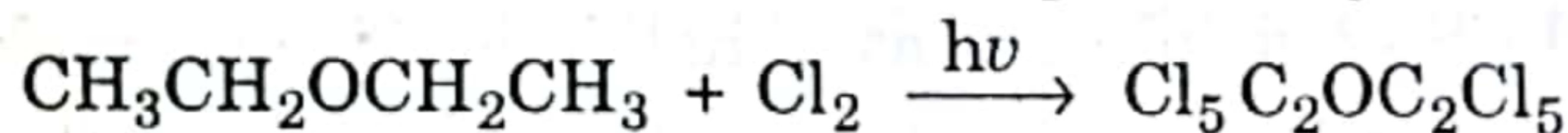


Hydrogen bonding between ether and water.

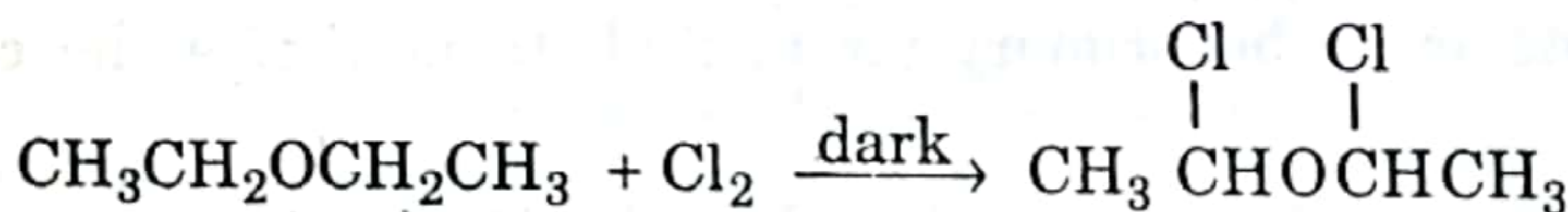
9.22 Reaction of Ethers

Ethers are quite stable compounds. They do not react with bases, oxidizing and reducing agents and active metals. Since the C - O bond of ethers does not cleave readily, they are relatively inert to most reagents and are used as solvents in many organic reactions such as Grignard reactions and Wurtz reactions.

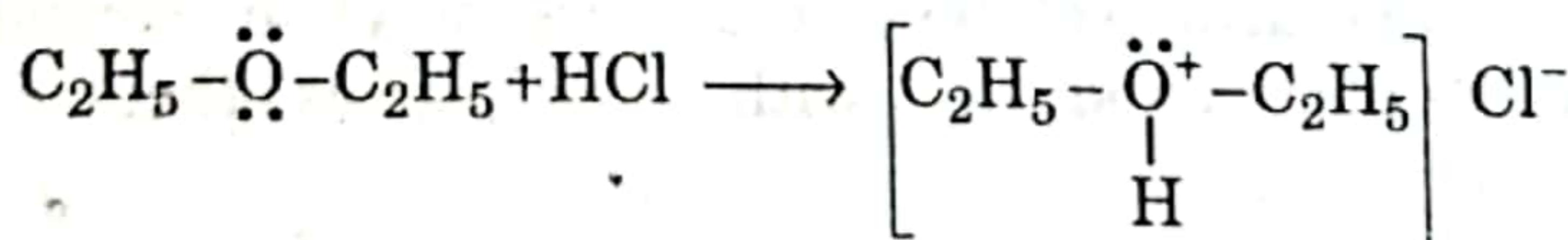
1. Halogenation. Ethers are readily halogenated upon treatment with Cl_2 or Br_2 in the presence of sunlight. The reaction proceeds by a free radical mechanism.



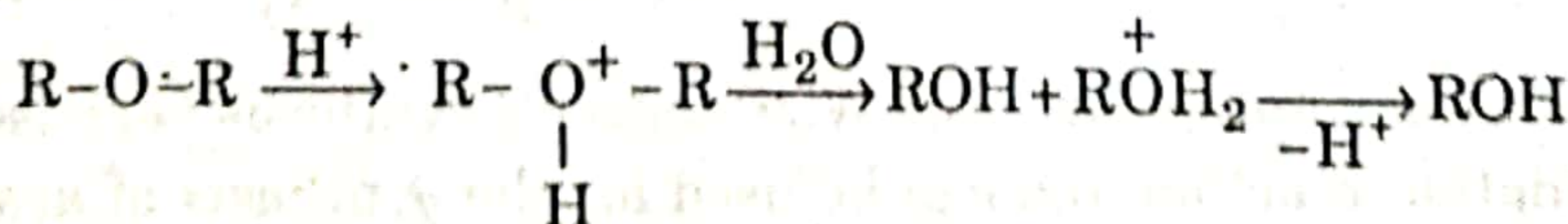
However, in the dark, halogenation takes place only at α -carbon atom.



2. Formation of Oxonium Salts. Due to the presence of lone pair of electrons on oxygen, ethers behave as weak bases and react with conc. strong acids (HCl or H_2SO_4) to form oxonium salts which are unstable and are readily cleaved.



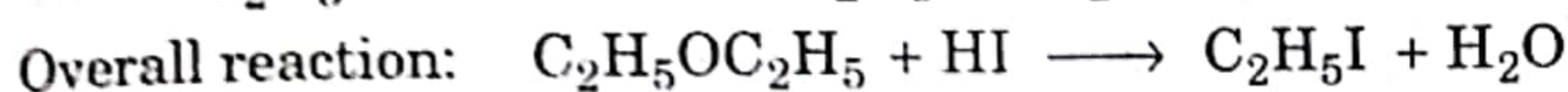
3. Reaction with dilute H_2SO_4 (Hydrolysis). When ethers are heated with dilute H_2SO_4 , alcohols are formed.



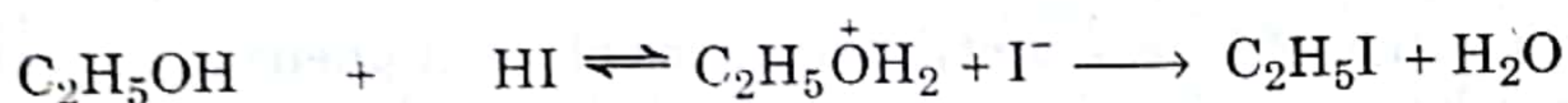
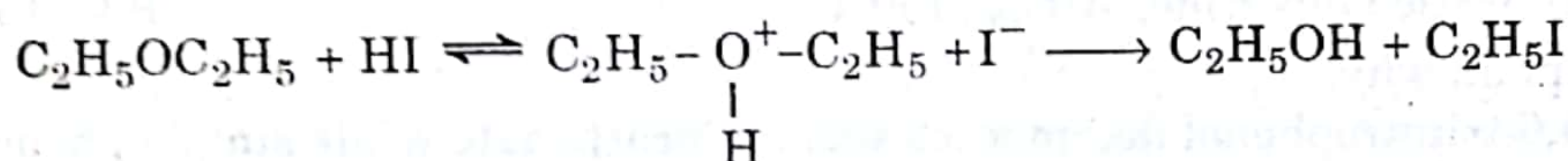
4. **Reaction with halogen acids.** Ethers react with halogen acids at high temperature to form alkyl halides and alcohols. HI is the most effective and reacts at room temperature



In the presence of excess of halogen acid (HI), the alcohols thus formed, reacts with HI to form alkyl halide.



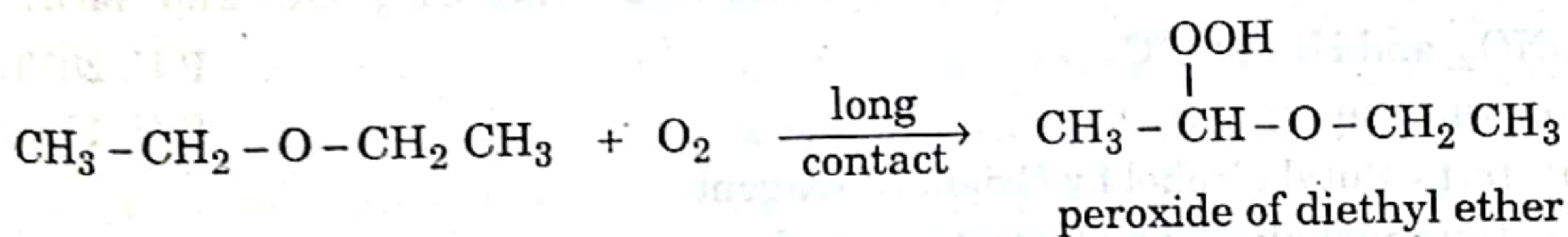
The mechanism of the reaction involves the following steps.



With mixed ethers, the smaller alkyl group (methyl) is preferentially removed as alkyl halide (CH_3I), since the nucleophile halide would attack the less hindered alkyl (methyl) group.

5. Autoxidation

A slow oxidation of compounds in the presence of atmospheric oxygen is known as **autoxidation**. On prolonged contact with air, aliphatic ethers form peroxides by a free radical mechanism.



9.23 Spectroscopic Identification

IR Spectrum of Alcohols. Alcohols, if not associated as a result of hydrogen bonding, give characteristic absorption (O-H) stretching in the region $3580\text{-}3650\text{ cm}^{-1}$. Inter molecular hydrogen bonding if present in alcohols shows broad absorption band in the region $3230\text{-}3550\text{ cm}^{-1}$ whereas in the case of intermolecular hydrogen bonding absorption appears in the region $3420\text{-}3590\text{ cm}^{-1}$.

Primary alcohols show C-O stretching vibrations at $\sim 1050\text{ cm}^{-1}$, secondary alcohols absorb at $\sim 1100\text{ cm}^{-1}$ and tertiary alcohols absorb at $\sim 1150\text{ cm}^{-1}$.

Ethers show a strong, broad band due to C-O stretching in the $1050\text{-}1400\text{ cm}^{-1}$ range.

Infrared stretching bands of phenols are $3200\text{-}3600\text{ cm}^{-1}$ for the O-H (like alcohols), but 1230 cm^{-1} for the C-O in phenols (alcohols: $1050\text{-}1150\text{ cm}^{-1}$) and $1300\text{-}1400\text{ cm}^{-1}$ for O-H bending.

Questions

1. (a) Give one method in each case for the preparation of primary, secondary and tertiary alcohols.
 (b) Give end products and names when phenol is made to react with the following reagents.
 (i) NaOH, CO₂, 150°C (ii) NaNO₂, HCl, 0°C
 (iii) Acetic anhydride, AlCl₃, 150°C (P.U. 1999)
2. Explain why:
 (i) 2,4,6-trinitrophenol decomposes sodium bicarbonate while simple phenol does not.
 (ii) In the preparation of aspirin acetylation takes place at phenolic group rather than carboxylic group. Starting material is salicylic acid.
 (iii) Phenol is more acidic than cyclohexanol.
 (iv) Benzoic acid is a stronger acid than phenol. P.U. 1999
3. How will you distinguish between ethanol, isopropyl alcohol and tertiary butyl alcohol?
4. What happens when phenol is treated with:
 (i) C₂H₅Br and NaOH (ii) CHCl₃ and NaOH (iii) HCHO and H₃O⁺
 (iv) Bromine water (v) Br₂ and CS₂ at 5°C (vi) Conc. H₂SO₄
 (vii) Dil HNO₃ (viii) Acetic anhydride and H₃O⁺ (ix) CH₃COCl and NaOH
 (x) NaNO₂ and HCl at 0°C. P.U. 2003
5. (a) How will you prepare: P.U. 1992
 (i) tert - Butyl alcohol by Grignard reagent.
 (ii) Isopropyl alcohol by hydration of alkene.
 (iii) Isopropyl methyl ether by Williamson's method.
6. How will you distinguish between primary, secondary and tertiary alcohols. P.U. 1994
7. How will you affect the following organic conversions?
 (i) Phenol to tribromophenol (ii) Benzene to phenol
 (iii) Glycerol to Nitroglycerine (iv) Phenol to anisol P.U. 1995
8. (a) Give an account of four different methods for the commercial synthesis of phenol. P.U. 1991
 (b) How does phenol react with the following:-
 (i) Conc. nitric acid (ii) Bromine water
 (iii) Carbon dioxide under pressure (iv) Phthalic anhydride
 (v) Benzene diazonium chloride (vi) Chloroform and NaOH
9. (a) Give three methods to prepare phenol. P.U. 2002
 (b) Give reactions of phenol with: (i) Zn (ii) CH₃COCl
 (iii) HNO₃ (iv) NaOH + CH₃I (iv) Formaldehyde

- (c) What is Reimer - Tiemann Reaction? P.U. 1985
10. Phenols are acidic, where as alcohols are neutral. Explain. P.U. 1977.
11. Phenols are more acidic than alcohol. B.Z. U. 1988,89, 94.
12. How is diethyl ether prepared. Give its reactions with
 (i) dilute H_2SO_4 (ii) Cl_2 in the presence of light
 (iii) O_2 ; long contact (iv) HI
13. Write the structural formulas and give IUPAC names for all isomeric alcohols of the molecular formula $C_4H_{10}O$.
14. How does ethyl alcohol react with
 (i) Na (ii) $K_2Cr_2O_7 + H_2SO_4$ (iii) $SOCl_2$
 (iv) Conc. HBr (v) PCl_5 (vi) conc. H_2SO_4 at $170^\circ C$
15. Explain why alcohols have higher boiling points than alkanes of comparable molecular masses.
16. How will you distinguish between phenol and ethanol?

SHORT QUESTIONS

1. Explain why propanol boils at a higher temperature than the corresponding hydrocarbon.

Ans. Propanol boils at a higher temperature, due to association of molecules through hydrogen bonding, than the corresponding hydrocarbon which cannot hydrogen bond intermolecularly. $C_3H_7 - \underset{\text{H}}{\text{O}} \cdots \text{H} - \text{O} - C_3H_7$.

2. Explain why propanol, unlike propane or butane is soluble in H_2O .

Ans. Propanol can form hydrogen bond with H_2O , therefore, it is soluble in water, while propane or butane cannot H-bond. $C_3H_7 - \underset{\text{H}}{\text{O}} \cdots \text{H} - \text{O} - \text{H}$.

3. Explain why hexanol is not soluble in water?

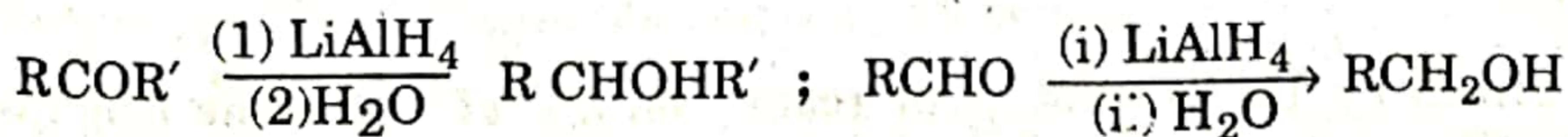
Ans. As the R group becomes larger, ROH resembles the hydrocarbon more closely. There is little H-bonding between H_2O and n-hexanol, therefore, hexanol is insoluble in H_2O .

4. Prepare 1-butanol from an alkene.

Ans. $6CH_3CH_2CH=CH_2 \xrightarrow[\text{THF}]{B_2H_6} (CH_3CH_2CH_2CH_2)_3B \xrightarrow{H_2O_2, OH^-} CH_3CH_2CH_2CH_2OH$

5. How do the alcohols from $LiAlH_4$ or catalytic reduction of ketones differ from those derived from aldehydes?

Ans. Ketones yield 2° (sec.) alcohols while aldehydes give 1° (prim) alcohols.

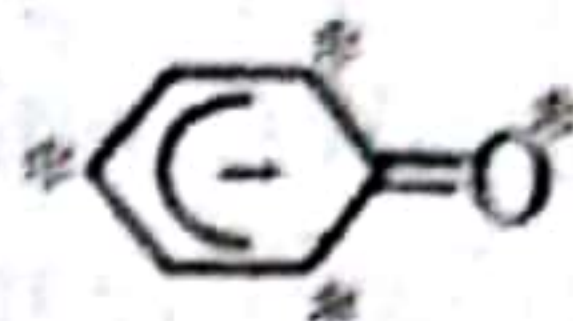


6. Explain the relative acidity of 1°, 2° and 3° alcohols.

Ans. The order of decreasing acidity of alcohols, $\text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ$, is attributed to electron-releasing alkyl (R) groups. These intensify the charge on the conjugate base, RO^- , and destabilize this ion, making the acid weaker.

7. Account for the considerable greater acid strength of $\text{C}_6\text{H}_5\text{OH}$ ($\text{pK}_a = 10$) than that of ROH ($\text{pK}_a = 18$).

Ans. The negative charge on the alkoxide anion, RO^- , cannot be delocalized, but on $\text{C}_6\text{H}_5\text{O}^-$ the negative charge is delocalized to the *ortho* and *para* ring positions as indicated by the starred sites in the resonance hybrid. $\text{C}_6\text{H}_5\text{O}^-$ is therefore, a weaker base than RO^- , and $\text{C}_6\text{H}_5\text{OH}$ is a stronger acid.



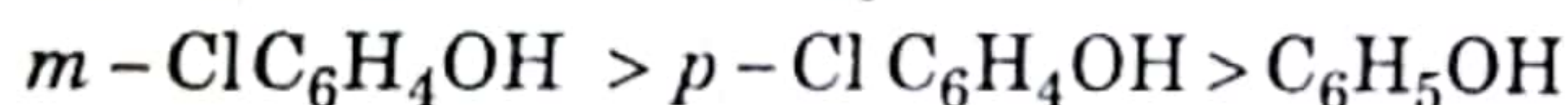
8. What is the effect of (a) electron-attracting and (b) electron-releasing substituents on the acid strength of phenols?

Ans. Electron attracting substituents disperse negative charges and therefore, stabilize $\text{C}_6\text{H}_5\text{O}^-$ and increase acidity of $\text{C}_6\text{H}_5\text{OH}$. (b) Electron releasing substituents concentrate the negative charge on O, destabilize $\text{C}_6\text{H}_5\text{O}^-$ and decrease acidity of $\text{C}_6\text{H}_5\text{OH}$.

9. In terms of resonance and inductive effects, account for the relative acidities. (a) $p\text{-O}_2\text{NC}_6\text{H}_4\text{OH} > m\text{-O}_2\text{NC}_6\text{H}_4\text{OH} > \text{C}_6\text{H}_5\text{OH}$.

Ans. The $-\text{NO}_2$ is electron-withdrawing and acid-strengthening. Its resonance effect, which occurs only from *para* and *ortho* positions, predominates over its inductive effect, which occurs also from the *meta* position. Other substituents in this category are: $\text{C}=\text{O}$, $-\text{CN}$, $-\text{COOR}$, $-\text{SO}_2\text{R}$.

10. Account for the following relative acidities:



Ans. Cl is electron-withdrawing by induction. This effect diminishes with increasing distance between Cl and OH. The *meta* is closer than the *para* position and *m*-Cl is more acid-strengthening than *p*-Cl. Other substituents in this category are F, Br, I, NR_3^+

11. Alkylation of $\text{C}_6\text{H}_5\text{O}^-$ with an active alkyl halide such as $\text{CH}_2=\text{CHCH}_2\text{Cl}$ gives, in addition to phenyl allyl ether, some *o*-allylphenol. Explain.

Ans. $\text{C}_6\text{H}_5\text{O}^-$ is an ambident anion with negative charge on both O and the *ortho* C atoms of the ring. Attack by O' gives the ether; attack by the *ortho* carbanion gives *o*-allylphenol.

12. Why does $\text{C}_6\text{H}_5\text{OR}$ cleave to give RI and $\text{C}_6\text{H}_5\text{OH}$ rather than $\text{C}_6\text{H}_5\text{I}$ and ROH?

Ans. $\text{S}_\text{N}2$ attack by I^- does not occur readily on a C of a benzene ring nor does

$C_6H_5^+$ form by an S_N1 reaction. Therefore, C_6H_5I cannot be product.

13. Explain why:

(i) 2,4,6-trinitrophenol decomposes sodium bicarbonate while simple phenol does not.

(ii) In the preparation of aspirin acetylation takes place at phenolic group rather than carboxylic group. Starting material is salicylic acid.

(iii) Phenol is more acidic than cyclohexanol.

(iv) Benzoic acid is a stronger acid than phenol.

P.U.

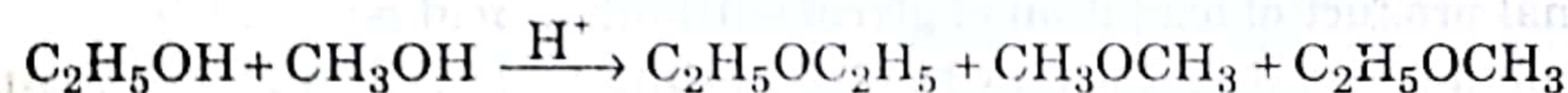
1999

Ans: See (i), (ii), (iii) and (iv) in chapter 16 Predicting Trends

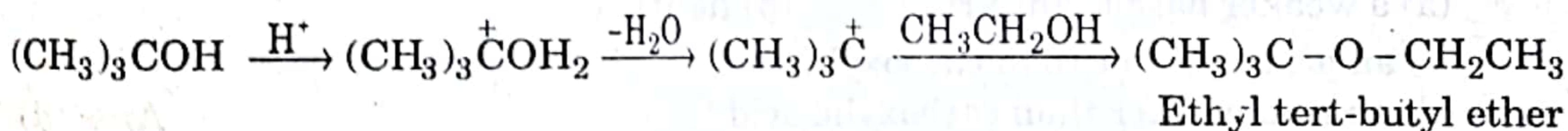
14. A mixture of ethanol and methanol on treatment with H_2SO_4 gives a mixture of three ethers, while a mixture of ethanol and tert-butanol under similar conditions gives a single ether. Explain.

Ans. Ethanol and methanol are 1° alcohols. For 1° alcohols, the mechanism is S_N2 with alcohol as the attacking nucleophile and H_2O as the leaving group.

These 1° alcohols react by S_N2 mechanism to give a mixture of three ethers: $C_2H_5OC_2H_5$ from $2 C_2H_5OH$, CH_3OCH_3 from $2CH_3OH$ and $C_2H_5OCH_3$ from C_2H_5OH and CH_3OH .



tert-butanol is 3° alcohol and mechanism for 3° alcohol is S_N1 .



Reaction between $(CH_3)_3C^+$ is sterically hindered and therefore it reacts with C_2H_5OH and thus, it gives only one ether, $(CH_3)_3C-O-CH_2CH_3$.

15. Explain the relative acidity $1^\circ, 2^\circ$ and 3° alcohols.

Ans. The order of decreasing acidity of alcohols, $CH_3OH > 1^\circ > 2^\circ > 3^\circ$ is attributed to electron releasing alkyl groups. These intensify the charge on the conjugate base, RO^- , and destabilizes this ion, making the acid weaker.

Multiple Choice Questions

1. A secondary alcohol is formed through oxymercuration-demercuration of which of the following?

(a) 2, 2-dimethyl-propene

(b) 1-hexanal

(c) 1-hexene

(d) hexane

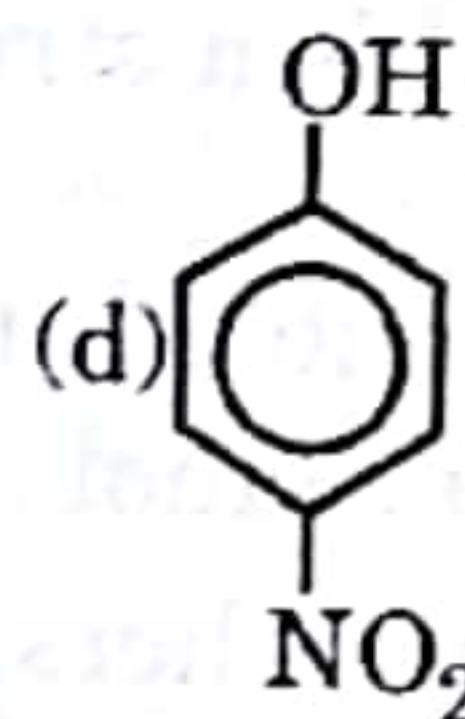
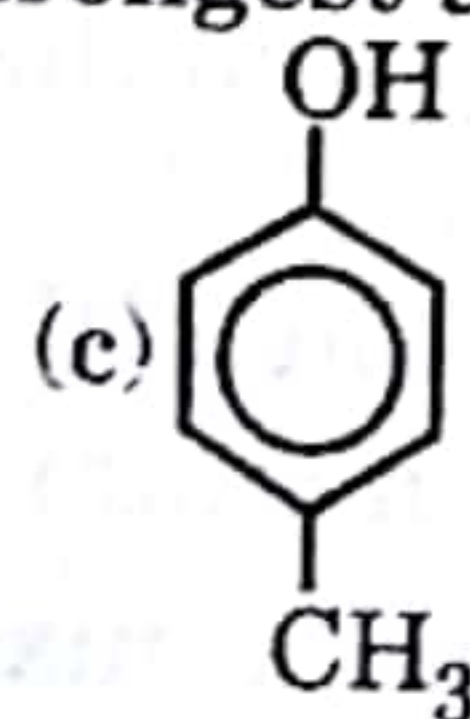
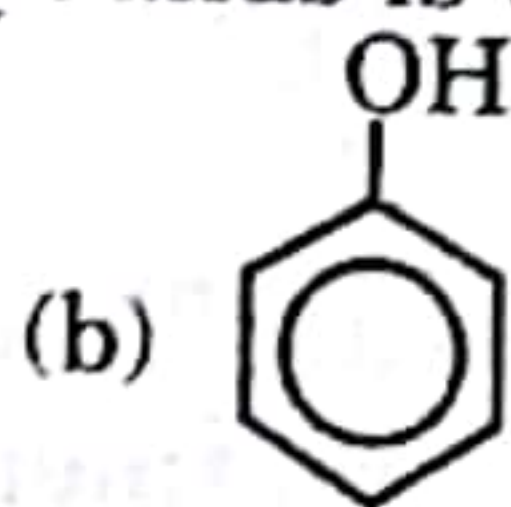
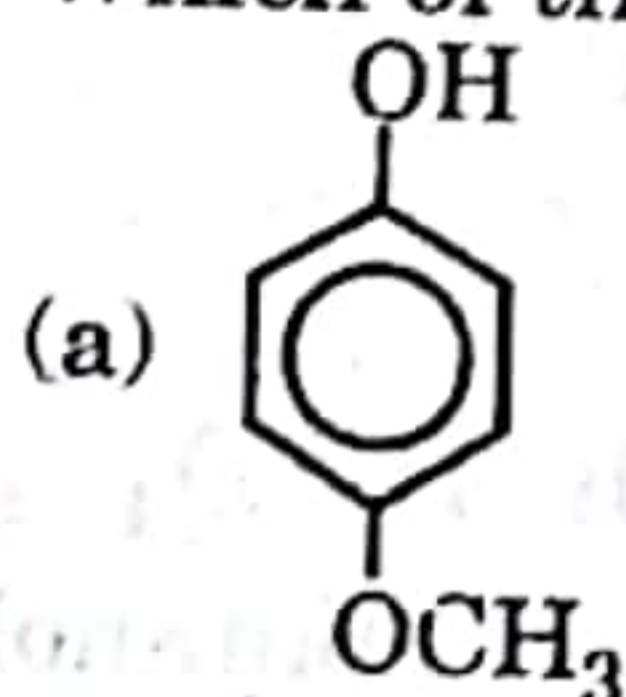
Ans: (c)

2. Which of the following has the highest boiling point?

(a) $CH_3CH_2(CH_3)_2COH$

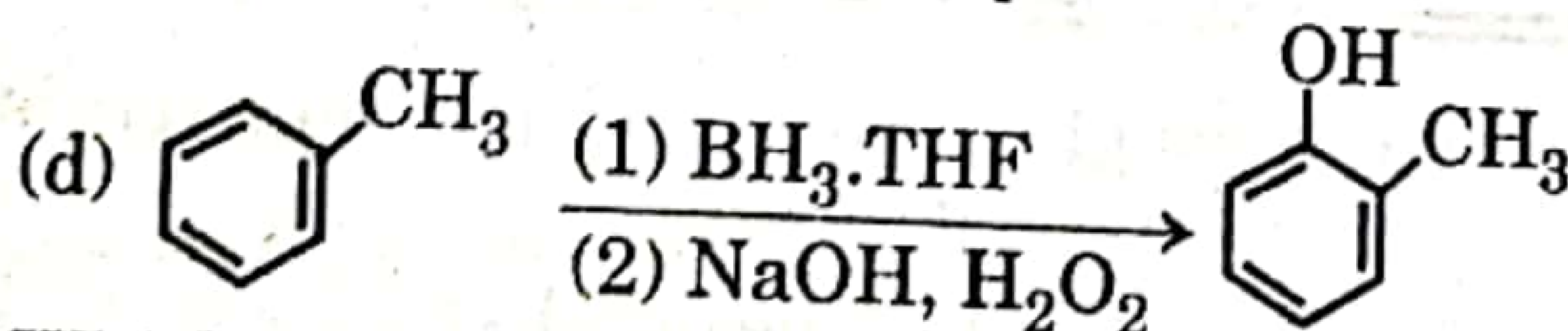
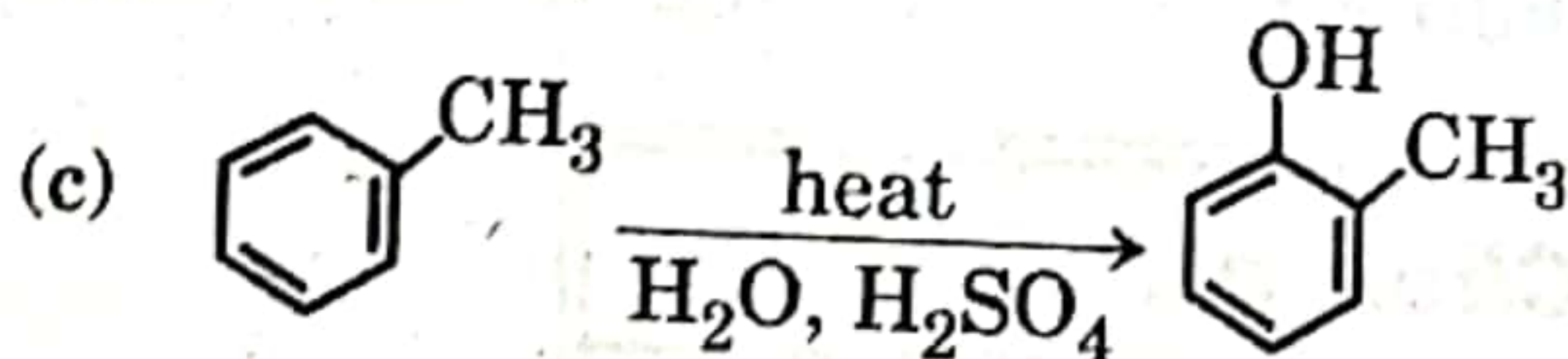
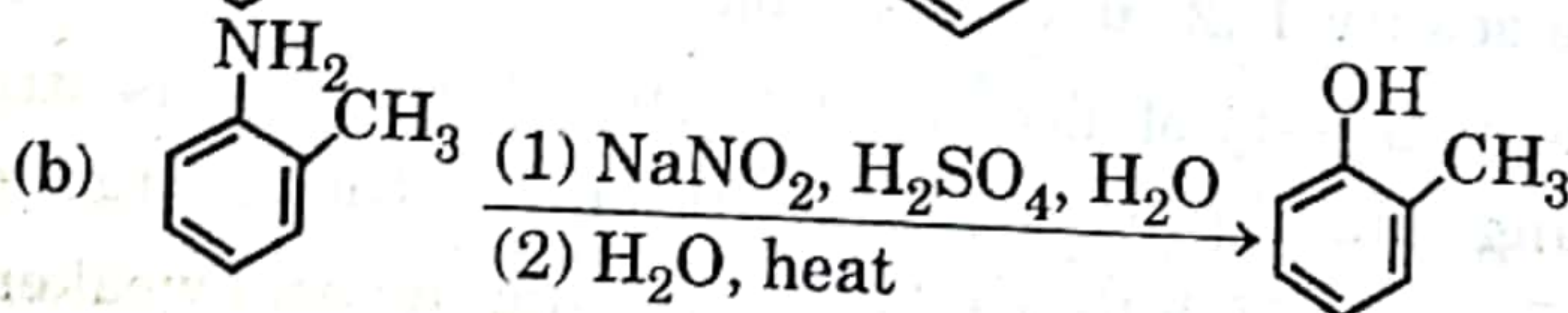
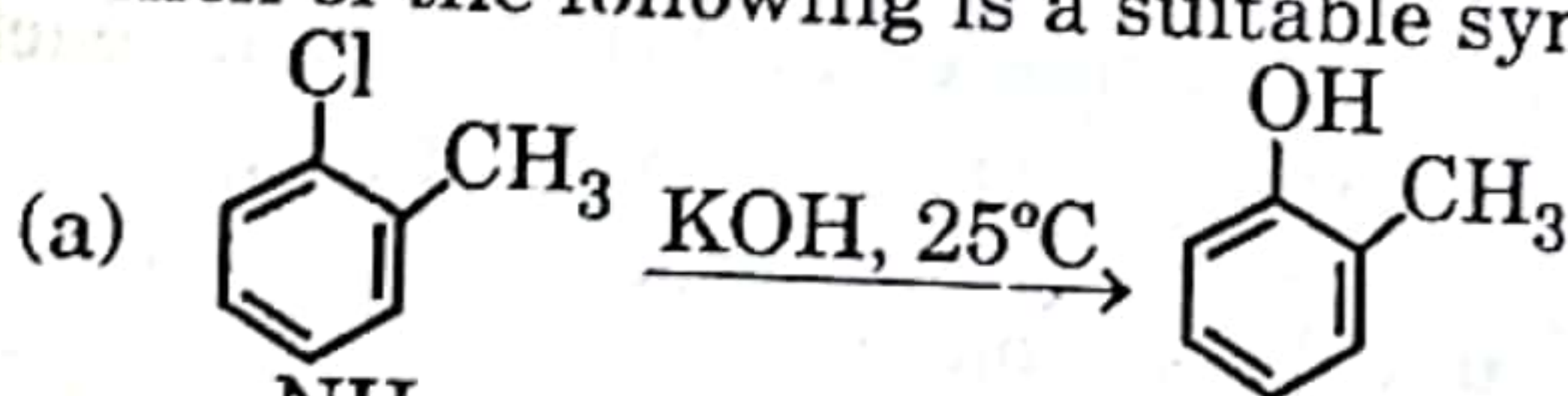
(b) $CH_3(CH_2)_4OH$

- (c) CH_3OH (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ **Ans: (b)**
3. The alkaline hydrolysis of an ester to form sodium salt of parent acid and alcohol is often referred to as.
(a) Saponification (b) Hardening (c) Hydroxylation (d) Condensation **Ans: (a)**
4. To distinguish among primary, secondary and tertiary alcohols, which one would use the following experimental method?
(a) Wittig reaction (b) Tollen's reagent
(c) Lucas test (d) Sandmeyer reaction **Ans: (c)**
5. Which of the compounds is the strongest acid?

**Ans: (d)**

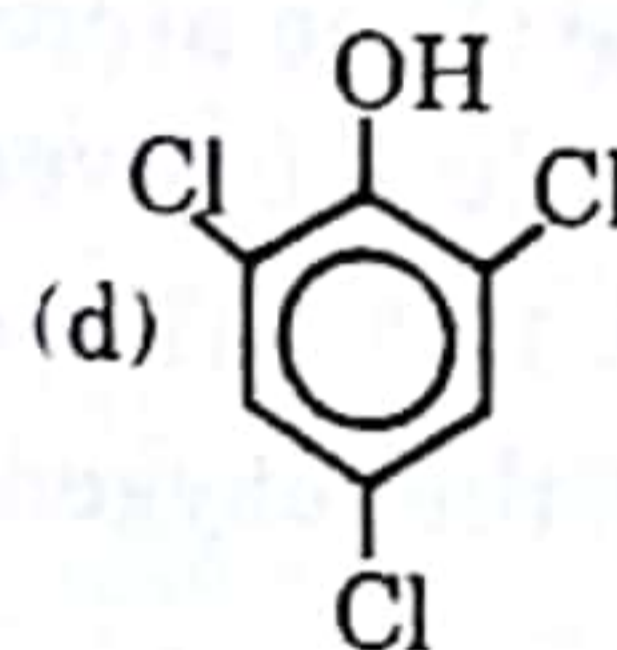
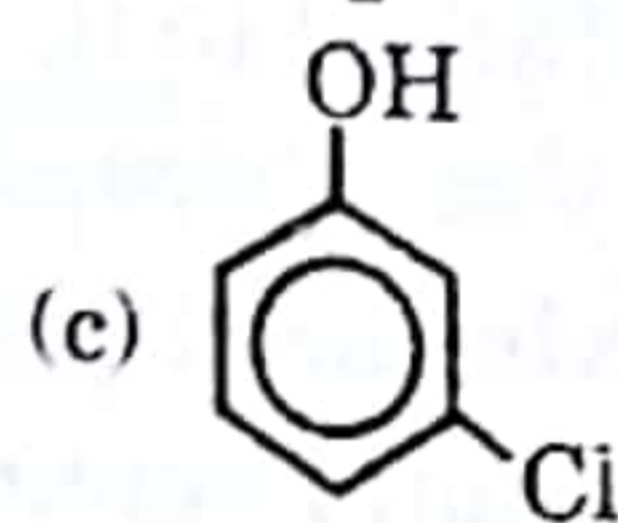
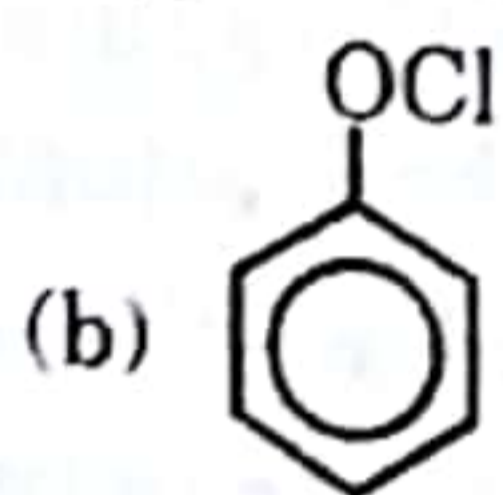
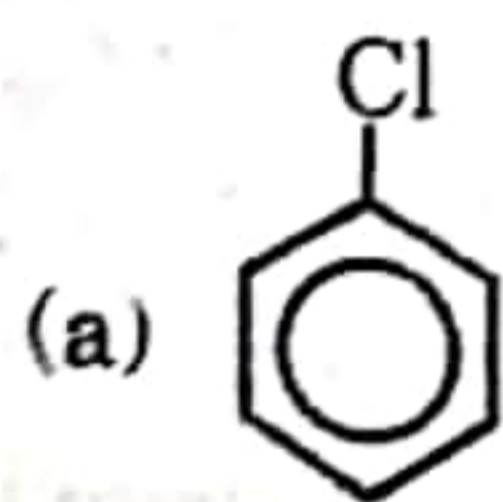
6. Which of the following compounds is expected to exhibit the highest boiling point?
(a) $\text{CH}_3\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{OCH}_2\text{CH}_3$ (c) $\text{CH}_3\text{CH}_2\text{CH}_3$ (d) $\text{CH}_3\text{CH}_2\text{CHO}$ **Ans: (a)**
7. Ethylene glycol is a
(a) secondary alcohol (b) diol (c) tertiary alcohol (d) triol **Ans: (b)**
8. Which of the following is used in the manufacture of explosives?
(a) ethanol (b) glycol (c) glycerine (d) acetaldehyde **Ans: (c)**
9. The final product of oxidation of glycol with nitric acid is:
(a) formaldehyde (b) mesoxalic acid (c) oxalic acid (d) formic acid **Ans: (c)**
10. Phenol is
(a) a weaker base than NH_3 (b) neutral
(c) an acid stronger than carboxylic acid.
(d) an acid weaker than carboxylic acid. **Ans: (d)**

11. Which of the following is a suitable synthesis of *o*-methylphenol?

**Ans: (b)**

12. Which of the following reagents will oxidize isopropyl alcohol to acetone.
(a) CrO_3 in glacial acetic acid (b) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$

- (c) $\text{KMnO}_4, \text{H}^+$ (d) all of the above **Ans:(d)**
13. Which of the following is the most appropriate reagent for the oxidation of secondary alcohols to ketones
 (a) CrO_3 in pyridine (b) $\text{CrO}_3 + \text{dil H}_2\text{SO}_4 + \text{acetone}$
 (c) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ (d) $\text{KMnO}_4 + \text{KOH}$ **Ans:(b)**
14. Oxygen atom carrying a positive charge and bonded to three other atoms or groups is called
 (a) carbonium ion (b) carbocation
 (c) oxonium ion (d) protonium ion **Ans:(c)**
15. Which of the following statements is incorrect about ethers.
 (a) Polyethers are used as antibiotics (b) Dioxane is a crown ether
 (c) Diethyl ether is used as general anesthetic in hospitals.
 (d) Crown ethers are cyclic polyethers. **Ans:(b)**
16. Which of the following reagents can be used to distinguish between phenol and benzyl alcohol.
 (a) aq. bromine (b) acetyl chloride
 (c) dil HCl (d) alkaline KMnO_4 **Ans:(a)**
17. What is the formula of the safer and more effective germicide which can be produced by treating phenol with aq. Cl_2 .

**Ans: (d)**