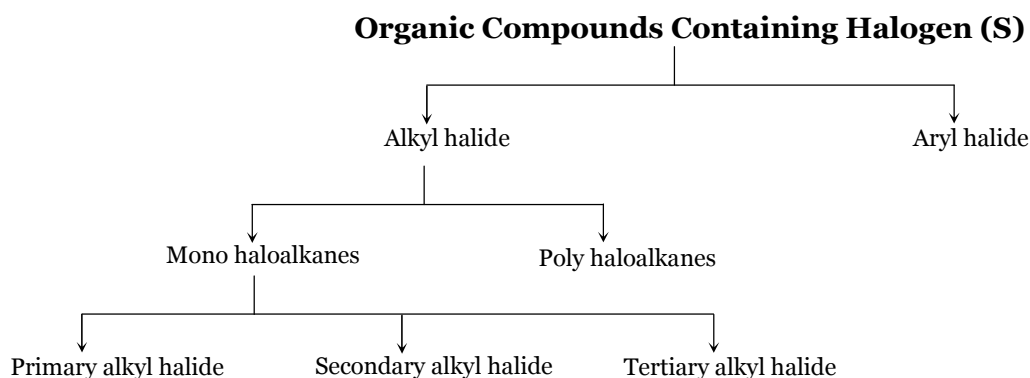


Halogen derivatives, Alcohols and Phenols

Halogen derivatives

Compounds derived from hydrocarbon by the replacement of one or more hydrogen atom (s) by the halogen atom (s) are known as halogen derivatives. The halogen derivatives of alkanes, alkenes, alkynes and arenes are known as alkyl halides (haloalkanes), alkenyl halides (haloalkenes), alkynyl halides (haloalkynes) and aryl halides (halobenzenes) respectively. Halogen derivatives may be classified as follows :



Alkyl Halides

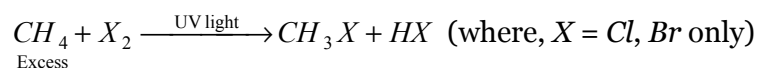
(1) **Monohaloalkanes** : These are halogen-substituted alkanes. The general formula is $C_nH_{2n+1}X$, where X is any halogen. Alkyl halides have been further classified, on the basis of nature of the carbon atom to which halogen is attached into following categories :

(i) *Primary alkyl halide* : The halogen is attached to primary carbon atom, i.e. RCH_2X .

(ii) *Secondary alkyl halide* : The halogen is attached to secondary carbon atom, i.e. $\begin{matrix} R \\ | \\ R-CH-X \end{matrix}$.

(iii) *Tertiary alkyl halide* : The halogen is attached to tertiary carbon atom, i.e. $\begin{matrix} R \\ | \\ R-C-X \\ | \\ R \end{matrix}$.

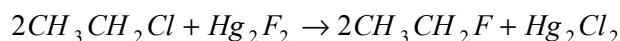
Preparation of alkyl halides : (1) By free radical halogenation of alkanes, e.g.



Note : □ The formation of *di, tri, tetra*-halides etc. (as side products) also takes place.

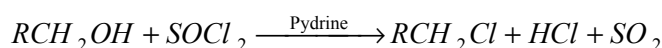
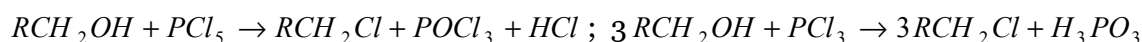
□ Iodination of alkanes is a reversible process, therefore, formation of iodoalkanes is possible only in the presence of oxidising agents such as HIO_3 , conc. HNO_3 etc., which oxidises the HI produced. Iodination with methane does not take place at all.

□ Fluorination of alkanes takes place with rupture of C – C bonds in higher alkanes. Therefore alkyl fluorides are generally prepared by halide exchange reactions. Alkyl fluorides are, therefore, prepared indirectly by heating alkyl chlorides with inorganic fluorides e.g. $AsF_3, SbF_3, AgF, Hg_2F_2$ etc. (Swarts reaction)



(2) By reaction of halogen acids (HX) to alkenes, e.g. $RCH = CH_2 + HX \rightarrow R \underset{\substack{| \\ X}}{C}H - CH_3$

(3) By reaction of PCl_5 or PCl_3 or $SOCl_2$ with alcohol :



(4) By reaction of alcohols with halogen acids : $RCH_2OH + HX \xrightarrow{ZnCl_2} RCH_2X + H_2O$

(5) By Hunsdiecker reaction : $RCOOAg + X_2 \rightarrow RX + AgX + CO_2$

Note : □ This reaction proceeds through free radical mechanism.

□ The yield of alkyl halide is $1^\circ > 2^\circ > 3^\circ$.

□ This reaction is used to reduce the length of carbon chain.

□ Only bromides are obtained in good yield in this reaction. The chlorides can also be obtained by this reaction but the yield is very low. Iodides however cannot be obtained because these form esters with silver salts. (Birnbaur Simonini reaction). $2RCO_2Ag + I_2 \rightarrow RCO_2R + CO_2 + 2AgI$

Properties :

Physical properties : (1) Lower members like CH_3Cl, CH_3Br, C_2H_5Cl are colourless gas while some of the higher members are colourless sweet smelling liquids. Higher homologues are odourless solids.

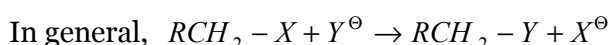
(2) The boiling point and density is in the order $R - F < R - Cl < R - Br < R - I$

Example	CH_3F	CH_3Cl	CH_3Br	CH_3I
B.P.(° C)	-78.4	-23.8	3.6	42.5
Density ($gm\ ml^{-1}$)	0.84	0.92	1.73	2.28

(3) They have very low solubilities in water but miscible with non-polar solvents.

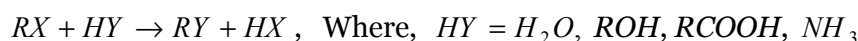
(4) These have a cumulative toxicity and are carcinogenic.

Chemical properties : (1) Alkyl halides undergo nucleophilic substitution reaction :

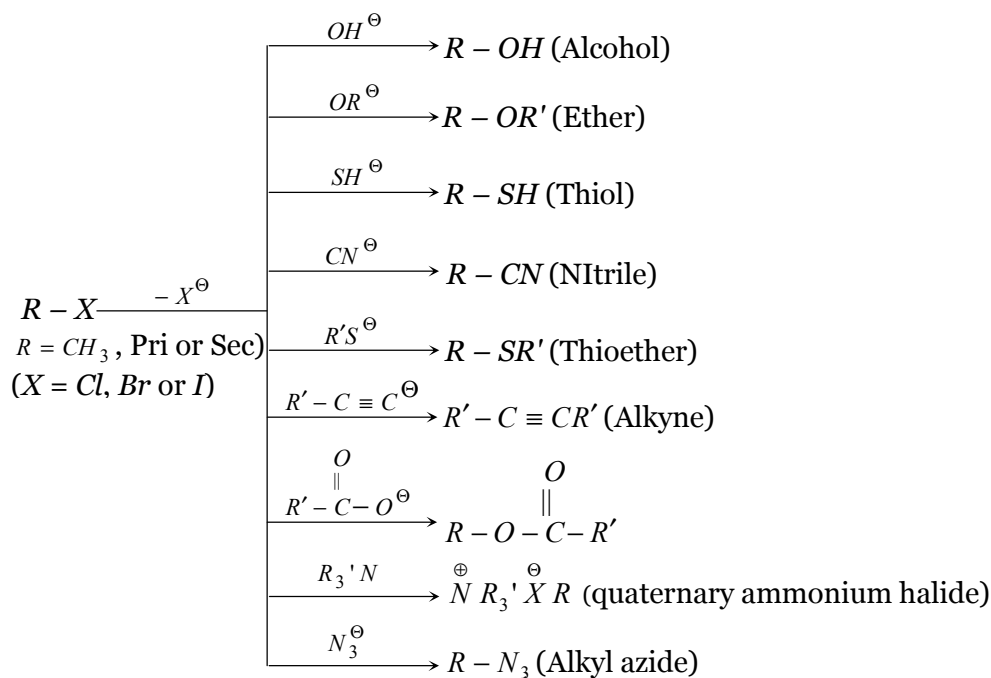


Where, $Y^\ominus = Cl^\ominus, Br^\ominus, OH^\ominus, RO^\ominus, RS^\ominus, CH_3COO^\ominus, CN^\ominus, R^\ominus, NH_2^\ominus, N_3^\ominus, NO_2^\ominus$

Similarly alkyl halide reacts with compound with general formula 'HY' as below



The general reactions are as follows :



Note : \square Reactivity of halides towards SN^1 -mechanism is $3^\circ > 2^\circ > 1^\circ$ and SN^2 -mechanism is $1^\circ > 2^\circ > 3^\circ$.

\square Polar solvents favour SN^1 while non polar solvents favour SN^2 mechanism.

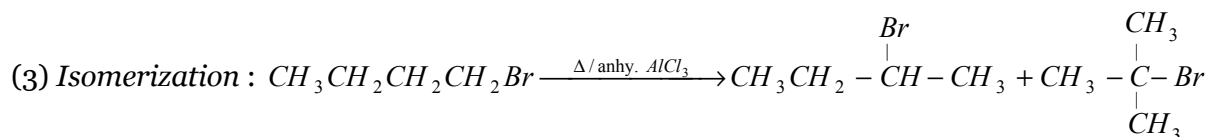
\square High concentration of nucleophiles favour SN^2 while low concentration SN^1 mechanism.

\square Rate of reaction in SN^1 mechanism do not depend upon the nature of the attacking nucleophile.

However, in SN^2 , rate depend on the strength of the attacking nucleophile.

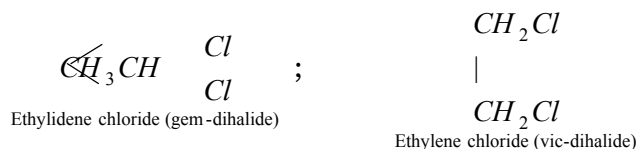
(2) Alkyl halides undergo dehydrohalogenation which is a β -elimination reaction in which halogen is lost from α -carbon atom while H is lost from β -carbon atom. This reaction is governed by **Saytzeff's rule**.

Note : \square Ease of dehydrohalogenation among halides : $3^\circ > 2^\circ > 1^\circ$.



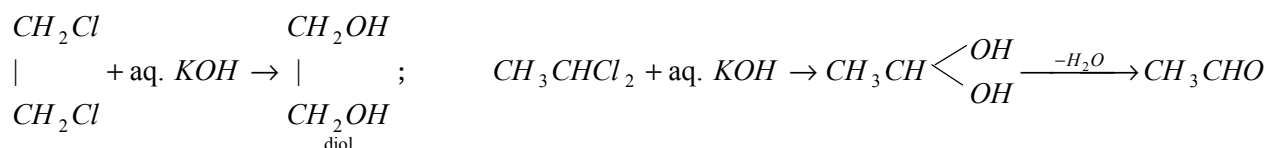
(2) **Dihaloalkanes** : These have been classified in two categories namely **Gem-dihalide** in which the two halogens are attached to same carbon atom and **vic-dihalide** in which the two halogens are attached to

adjacent carbon atom, e.g.



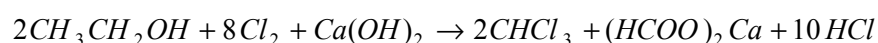
The vic-dihalides are prepared by reaction of halogens to alkene where as gem-dihalide are prepared by reaction of PCl_5 to aldehyde. $CH_2 = CH_2 + Cl_2 \rightarrow$ $\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$; $CH_3CH = O + PCl_5 \rightarrow CH_3CHCl_2 + POCl_3 + HCl$

The gem and vic-dihalides can be distinguished by reaction with aq. KOH :



(3) Trihaloalkanes

(i) **Chloroform** ($CHCl_3$) : It can be prepared by reaction of acetone or ethyl alcohol with bleaching powder.

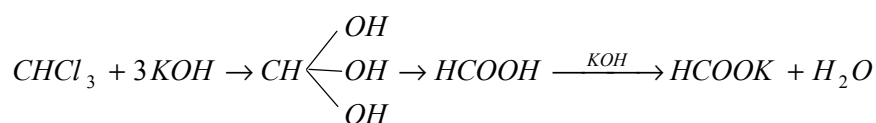


The important properties of $CHCl_3$ (sweet smelling liquid) are as follows :

(a) On oxidation it yields **phosgene** gas which is very poisonous : $CHCl_3 + [O] \xrightarrow[\text{air}]{\text{sun light}} \underset{\text{Phosgene}}{COCl_2} + HCl$

For medical purpose, the chloroform is filled in coloured bottles and kept in dark to avoid sunlight. Further the bottles are filled upto neck to avoid oxygen (air) and 1% C_2H_5OH is added to convert phosgene into harmless ethyl carbonate.

(b) Upon alkaline hydrolysis with KOH , chloroform gives potassium formate.

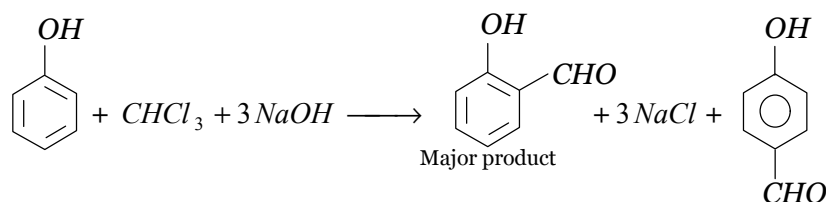


(c) With acetone it forms chloretone which is used as a hypnotic.

(d) When chloroform is warmed with a primary amine and alc. KOH , it forms isocyanide. The reaction is called carbylamine reaction, $RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$ (R = alkyl or aryl)

The carbene is the reaction intermediate.

(e) When $CHCl_3$ is treated with phenol in the presence of $NaOH$, salicylaldehyde is formed. The reaction is called Reimer Tiemann reaction.



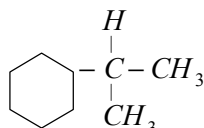
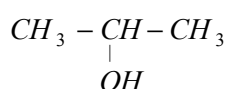
(ii) **Iodoform** : When methyl ketones $\left(\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{CH}_3 \end{array} \right)$ or alcohols having following structure reacts with I_2

and alkali (aq. $NaOH$ or aq. Na_2CO_3), a yellow solid of melting point $119^\circ C$ is obtained. The solid is called

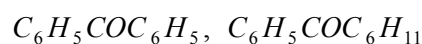
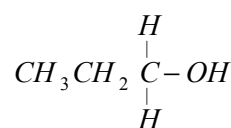
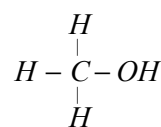
iodoform and the reaction is called Iodoformic. $R-\begin{array}{c} \text{H} \\ | \\ \text{C}-\text{CH}_3 \\ | \\ \text{OH} \end{array}$ (Where, $R = H$, alkyl, aryl)

As a rule all methyl ketones and alkanol-2 give +ve iodoform test, e.g.

Alcohols and ketones which gives +ve iodoform test

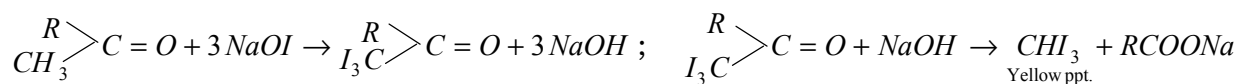


-ve Iodoform test (due to absence of $-CH_3$ gp.)



The reaction is as follows : $C_2H_5OH + 4I_2 + 6NaOH \rightarrow CHI_3 + HCOONa + 5NaI + H_2O$

The mechanism is as follows : $R-\begin{array}{c} \text{H} \\ | \\ \text{C}-\text{CH}_3 \\ | \\ \text{OH} \end{array} + NaOI \rightarrow \begin{array}{c} \text{R} \\ \diagup \\ \text{C} = \text{O} \\ \diagdown \\ \text{CH}_3 \end{array} + NaI + H_2O$

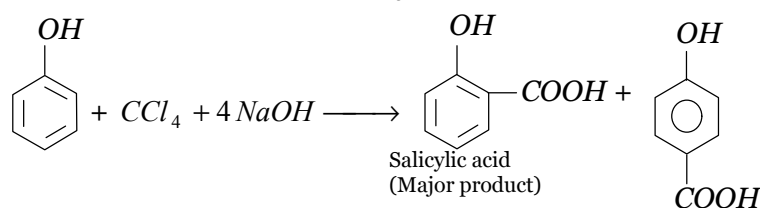


(4) Tetrahaloalkanes

(i) Freons is trade name of fluorochloromethanes having general formula CF_xCl_y , where $(x + y = 4)$.

(ii) The prefix per means that all H atoms of the hydrocarbons are replaced by fluorine atoms, e.g. perfluorooctane $CF_3(CF_2)_6CF_3$. These are chemically inert due to electrostatic force of attraction between δ^+ on C and δ^- on F .

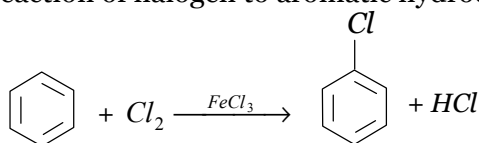
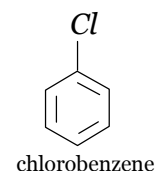
(iii) When CCl_4 instead of $CHCl_3$ is used in **Reimer Tiemann reaction** the product is salicylic acid.



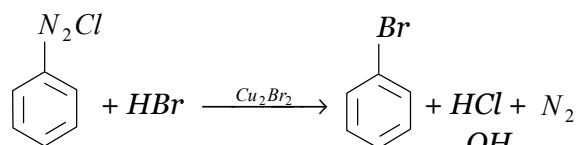
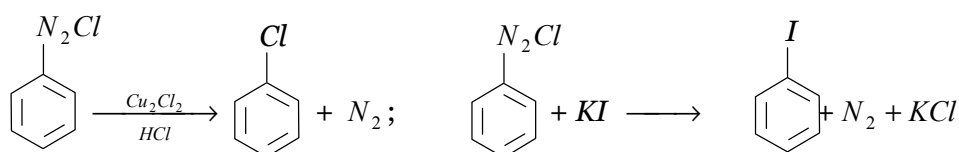
Aryl Halides

These are organic compounds in which halogen is directly attached to benzene ring, *e.g.*

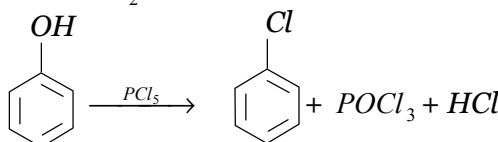
These can be prepared by reaction of halogen to aromatic hydrocarbon.



(2) **By Sandmeyer's reaction** : When acid solution of diazonium salt is added to a solution of cuprous halide dissolved in corresponding halogen acid, aryl halides are obtained, *e.g.*



(3) By reaction of phenol with PCl_5 ,



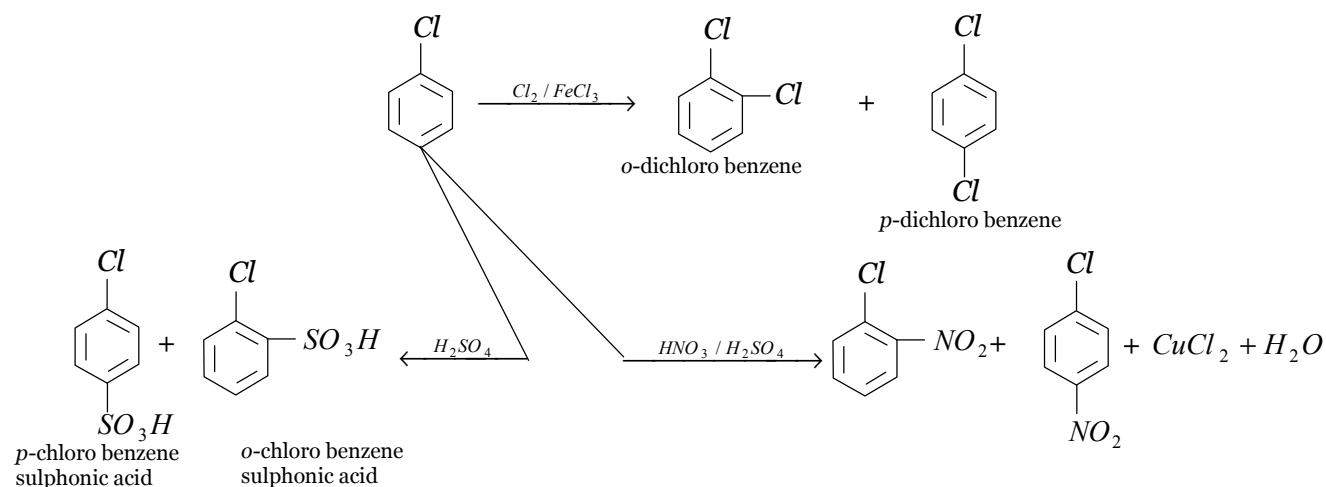
Properties

Physical properties : Aryl halides are generally colourless liquid or crystalline solid. They are soluble in organic solvents but insoluble in water. The boiling points and melting points are in the following order :

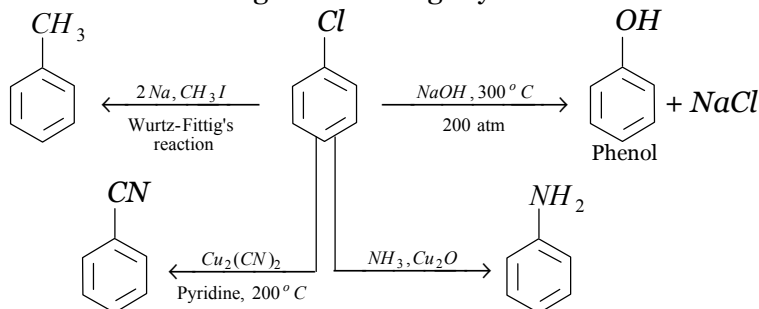
Aryl iodides > Bromides > Chlorides > Fluorides

Chemical properties : The properties can be discussed under two categories :

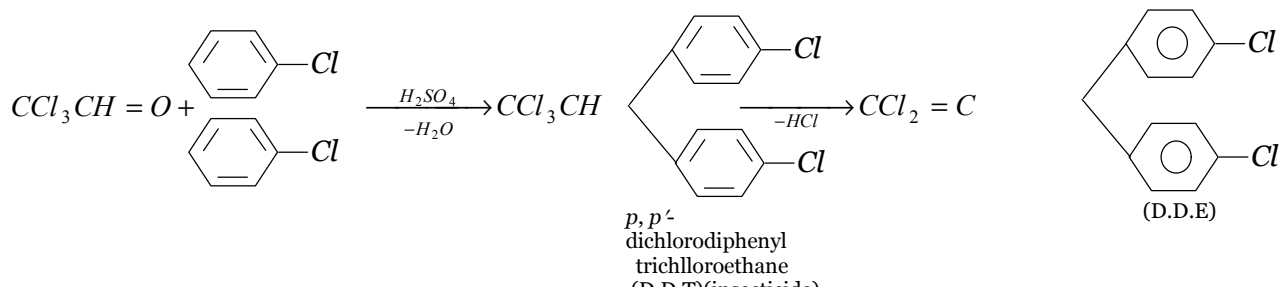
(1) *Properties due to benzene ring* : As halogen (s) are *ortho para* directing, the reactions are as follows :



(2) *Properties due to halogen atom* : Unlike alkyl halide, the aryl halides do not easily undergo nucleophile substitution reaction since halogen atom is tightly attached to benzene ring, e.g.

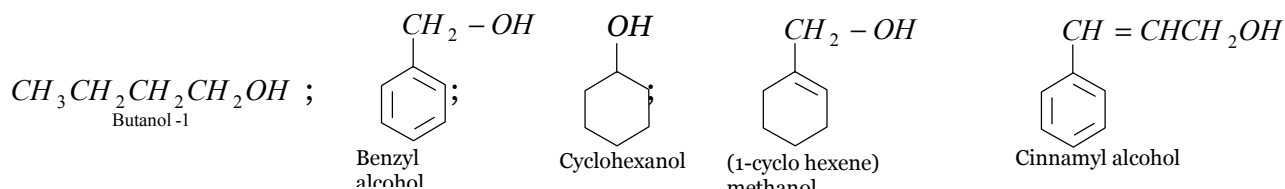


When chlorobenzene is heated with chloral in the presence of conc. H_2SO_4 , D.D.T. is formed. It is non biodegradable. It slowly changes to another compound, DDE by loss of a HCl molecule.

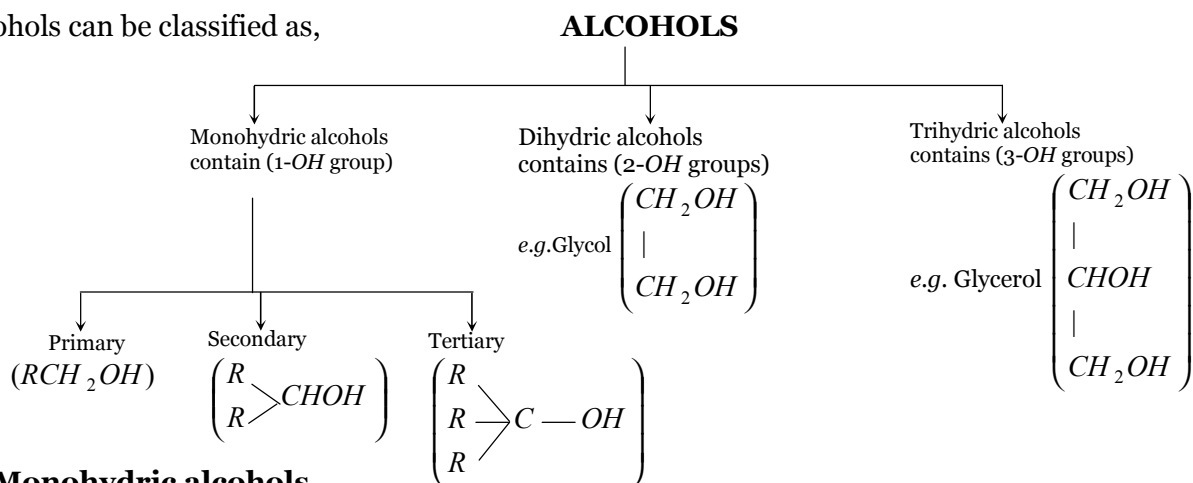


Alcohols

Alcohols are compounds of the general formula ROH , where R is alkyl or substituted alkyl group. The group may be open chain or cyclic, it may contain double bond, a halogen atom, an aromatic ring or additional hydroxyl groups, e.g.

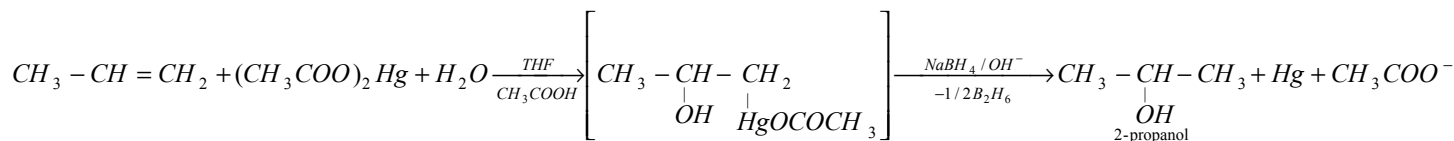


Alcohols can be classified as,



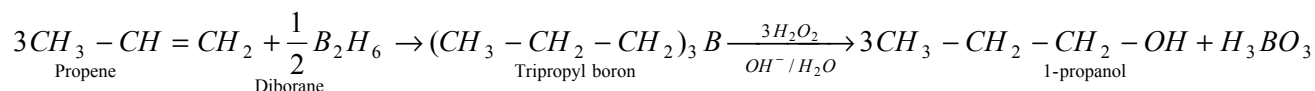
(1) Monohydric alcohols

Preparation : (i) By oxymercuration - demercuration reaction of alkene :

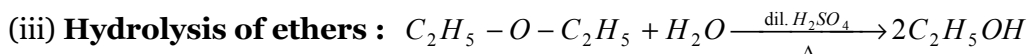


Note : □ It is fast and convenient. The addition of water to an alkene is anti-Markownikoff and free from rearrangement.

(ii) Hydroboration of alkene :

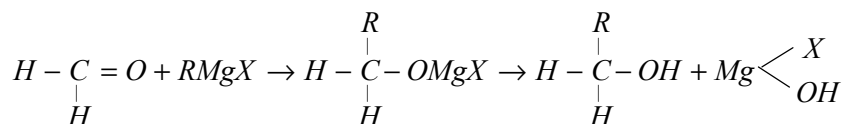


Note : □ In this reaction addition of water to an alkene is syn, anti-Markownikoff and free from rearrangement.

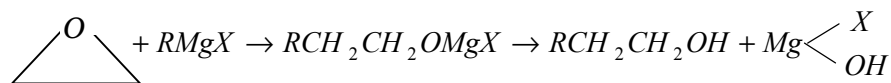


(iv) By reaction of Grignard reagent with formaldehyde/ other aldehydes/ ketones

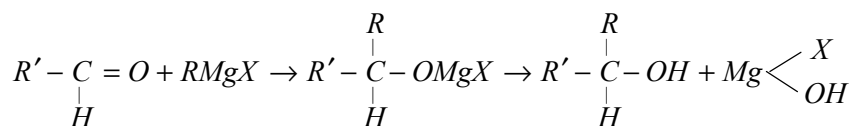
(a) When Grignard reagent reacts with $HCHO$, it forms primary alcohol.



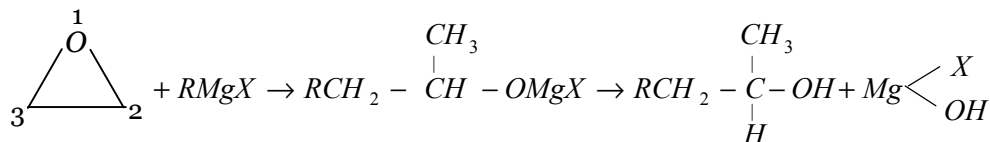
(b) **Oxirane** on reaction with Grignard reagent also forms primary alcohol.



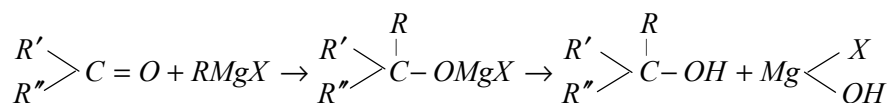
(c) Any aldehyde except formaldehyde when treated with Grignard reagent forms secondary alcohol.



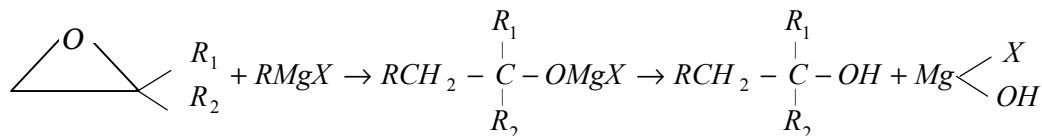
(d) When **2-alkyl oxirane** reacts with Grignard reagent, secondary alcohol is formed. The ring is opened from **least hindered site**.



(e) When ketone reacts with Grignard reagent, it forms tertiary alcohol.

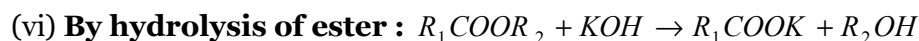
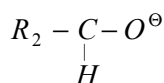


(f) When 2, 2-dialkyl oxirane reacts with Grignard reagent, it forms tertiary alcohol.

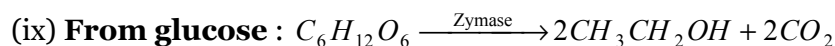
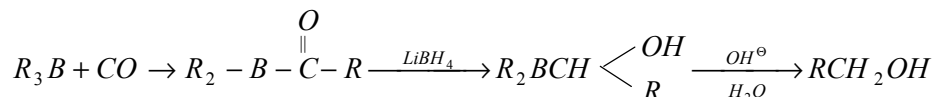


The reduction can be carried out by using H_2 /catalyst like Ni, Pt, Pd, LiAlH_4 , NaBH_4 , NaH , LiH . When the reduction is carried out by using metal/solvent combination it is known as Bouveault blanc reduction. The

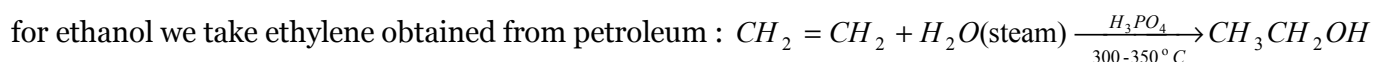
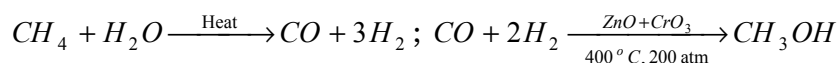
intermediates are : $\text{R} - \overset{\ominus}{\underset{\cdot}{\text{O}}} - \text{OEt}$; $\text{R} - \overset{\ominus}{\underset{\cdot}{\text{O}}} - \text{CH} - \text{OEt}$; $\text{R} - \overset{\ominus}{\underset{\cdot}{\text{C}}} \text{H}$. In case of metal hydride the reaction intermediate is



(vii) **By reaction of alkyl boride with CO :**



(ix) **Industrial method for methanol and ethanol are** as follows :

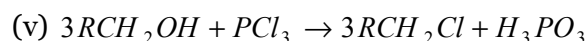
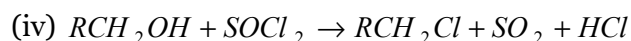
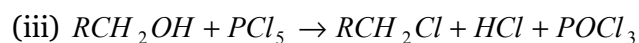
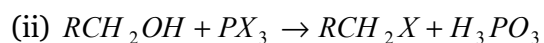
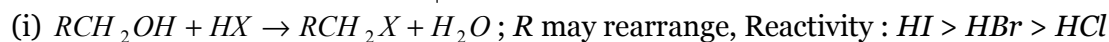


It is an *Oxo process*.

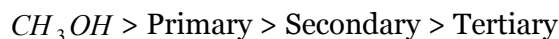
Physical properties: Alcohols are liquid with high boiling point due to intermolecular hydrogen bonding. Methanol, ethanol, both propyl alcohols and *tert*-butyl alcohol are completely miscible with water.

Chemical properties : Chemical properties of alcohols can be discussed under three categories :

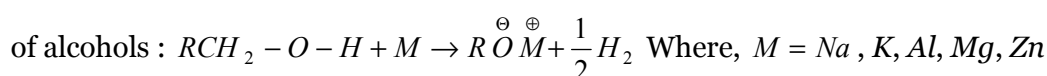
(1) **Reactions involving $\text{RCH}_2 - \text{OH}$ cleavage :** The reactivity order : Allyl > benzyl > *Tert* > *Sec* > *Pri*



(2) **Reactions involving $\text{RCH}_2 - \text{H}$ cleavage :** The order of reactivity :



(i) Alcohols react with metals like Na to form alkoxide and evolve H_2 . This reaction shows acidic nature



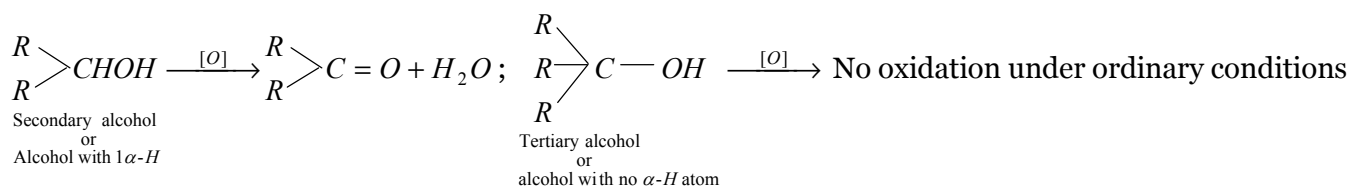
The relative acidity is : $\text{H}_2\text{O} > \text{ROH} > \text{RC} \equiv \text{CH} > \text{H}_2 > \text{NH}_3 > \text{RH}$

The relative basicity is : $\text{R}^{\ominus} > \text{N}^{\ominus} \text{H}_2 > \text{H}^{\ominus} > \text{RC} \equiv \text{C}^{\ominus} > \text{R}^{\ominus} \text{O} > \text{O}^{\ominus} \text{H}$

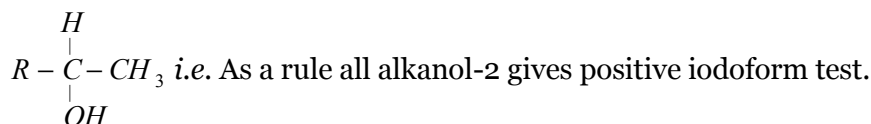


(3) **Miscellaneous** : (i) *Oxidation* : (a) Oxidation of alcohols : Number of α -H atoms \propto Oxidation rate of alcohol \propto Product yield e.g. $R-CH_2-OH \xrightarrow{[O]} RCHO + H_2O$

(Primary alcohol
or
Alcohol with 2 α -H)



(ii) *Iodoform test* : Alcohols having following structure gives positive iodoform test.



(iii) *Reaction with Lucas reagent* (anhydrous $ZnCl_2$ and conc. HCl) : Lucas reagent has been used to distinguish primary, secondary and tertiary alcohols :

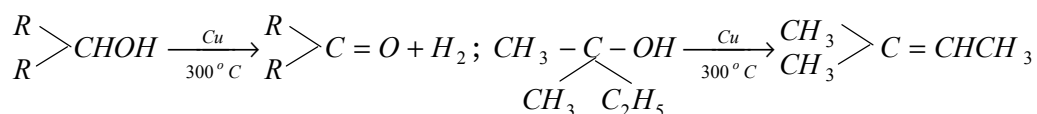
(a) Alkyl alcohol or tertiary alcohol $\xrightarrow{\text{Lucas Reagent}}$ White turbidity at once

The alkyl halide so formed is insoluble in the medium hence turbidity appears.

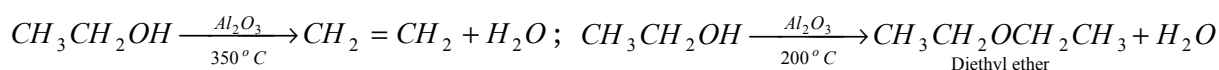
(b) Secondary alcohol + Lucas reagent \rightarrow Turbidity after 5 minutes

(c) primary alcohol + Lucas reagent \rightarrow No turbidity

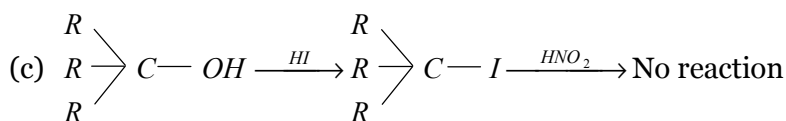
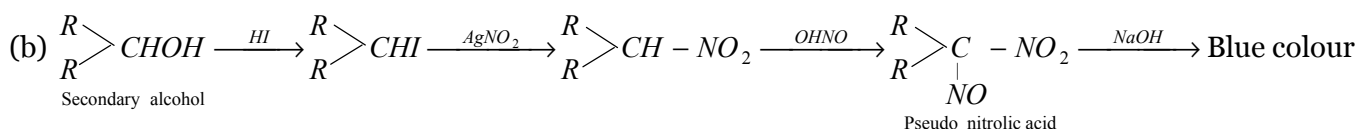
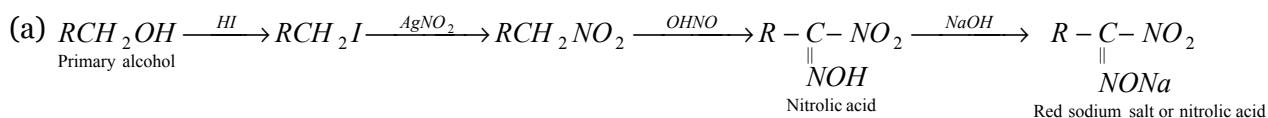
(iv) *Dehydrogenation* : $RCH_2OH \xrightarrow[300^\circ C]{Cu} RCHO + H_2$

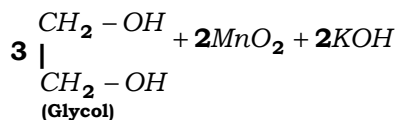
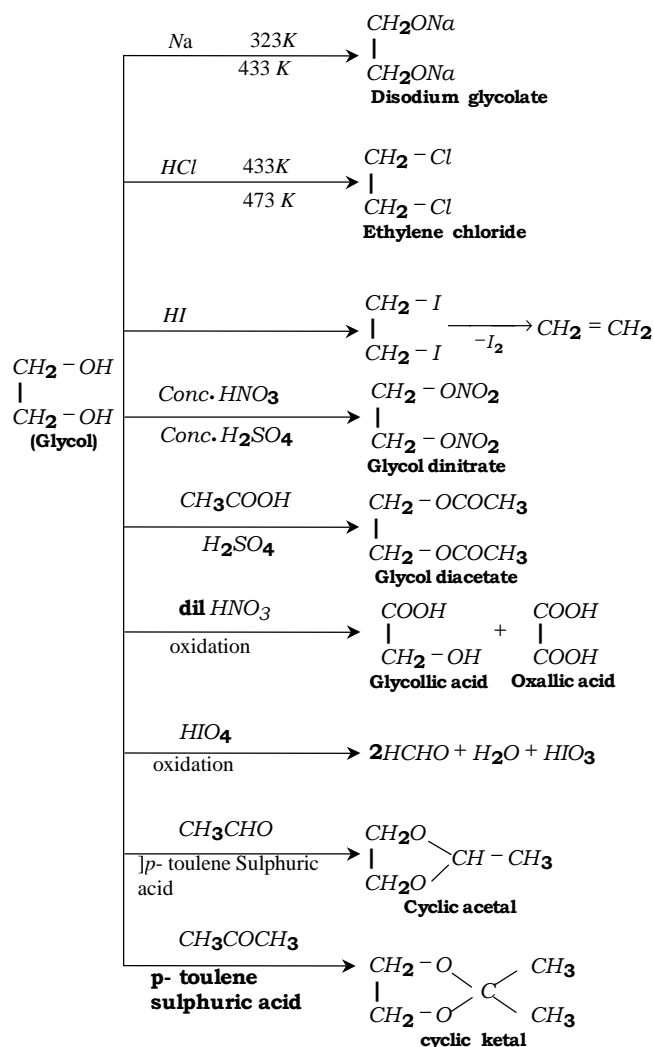


(v) When ethanol is heated with Al_2O_3 , it forms different depending upon temperature, e.g.

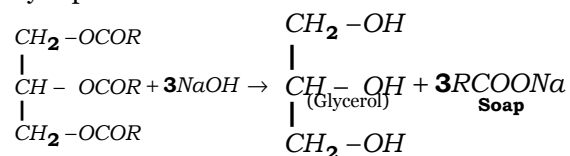
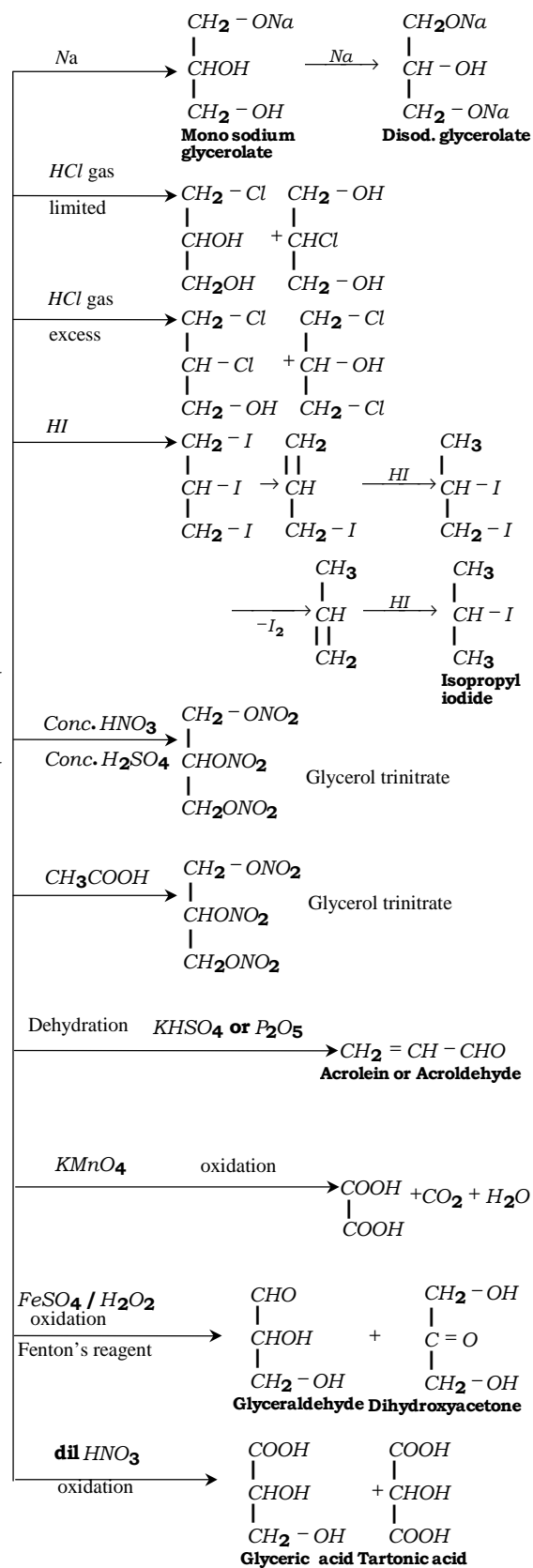


(vi) Primary, Secondary and Tertiary alcohols can be distinguished by *Victor Meyer's Method* :



(2) Dihydric alcohol
Glycol (Ethane - 1, 2- di-ol)
Preparation
Lab. Method

Chemical Properties

(3) Trihydric alcohol
Glycerol (Propan - 1, 2, 3 - triol)
Preparation

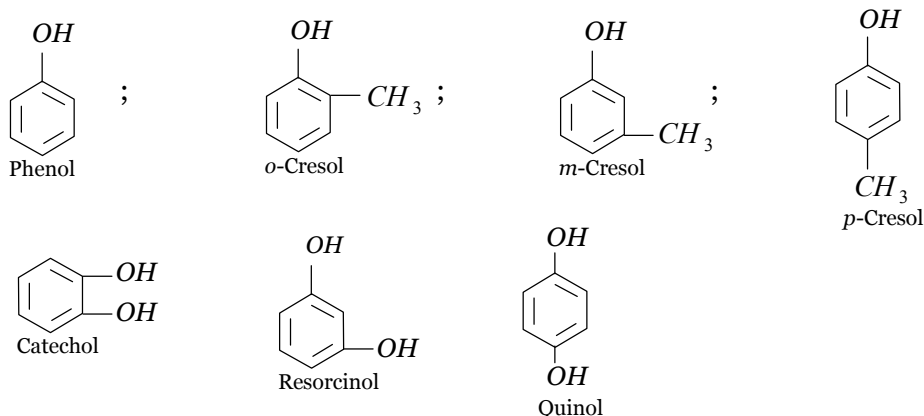
By saponification of oils and fats


Chemical Properties


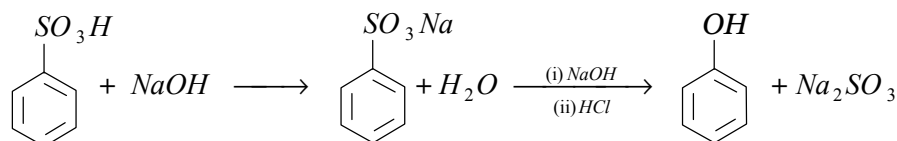
Glycerose

Phenols

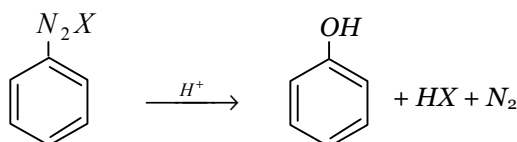
Phenols are the organic compounds in which $-OH$ group is directly linked to aromatic ring system. The simplest formula of such compound is phenol (C_6H_5OH). Structure of some common phenols is as follows :



Preparation : (1) Phenols can be prepared by reaction of benzene sulphonic acid with $NaOH$.



(2) Phenols can also be obtained by warming diazonium salt solution with hot dilute acid solution.



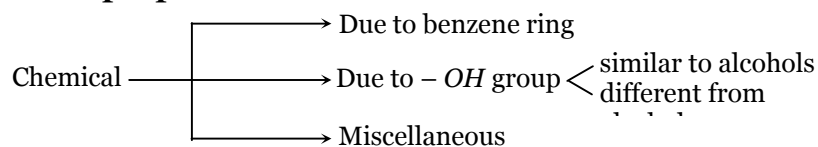
(3) Phenols can be prepared from aryl halides, Clc1ccccc1 + $NaOH$ $\xrightarrow[20]{3}$ Oc1ccccc1 + $NaCl$

(4) By reaction of phenolic acid with soda lime O=C(O)c1ccccc1 + $NaOH$ (CaO) $\xrightarrow{}$ Oc1ccccc1 + Na_2CO_3

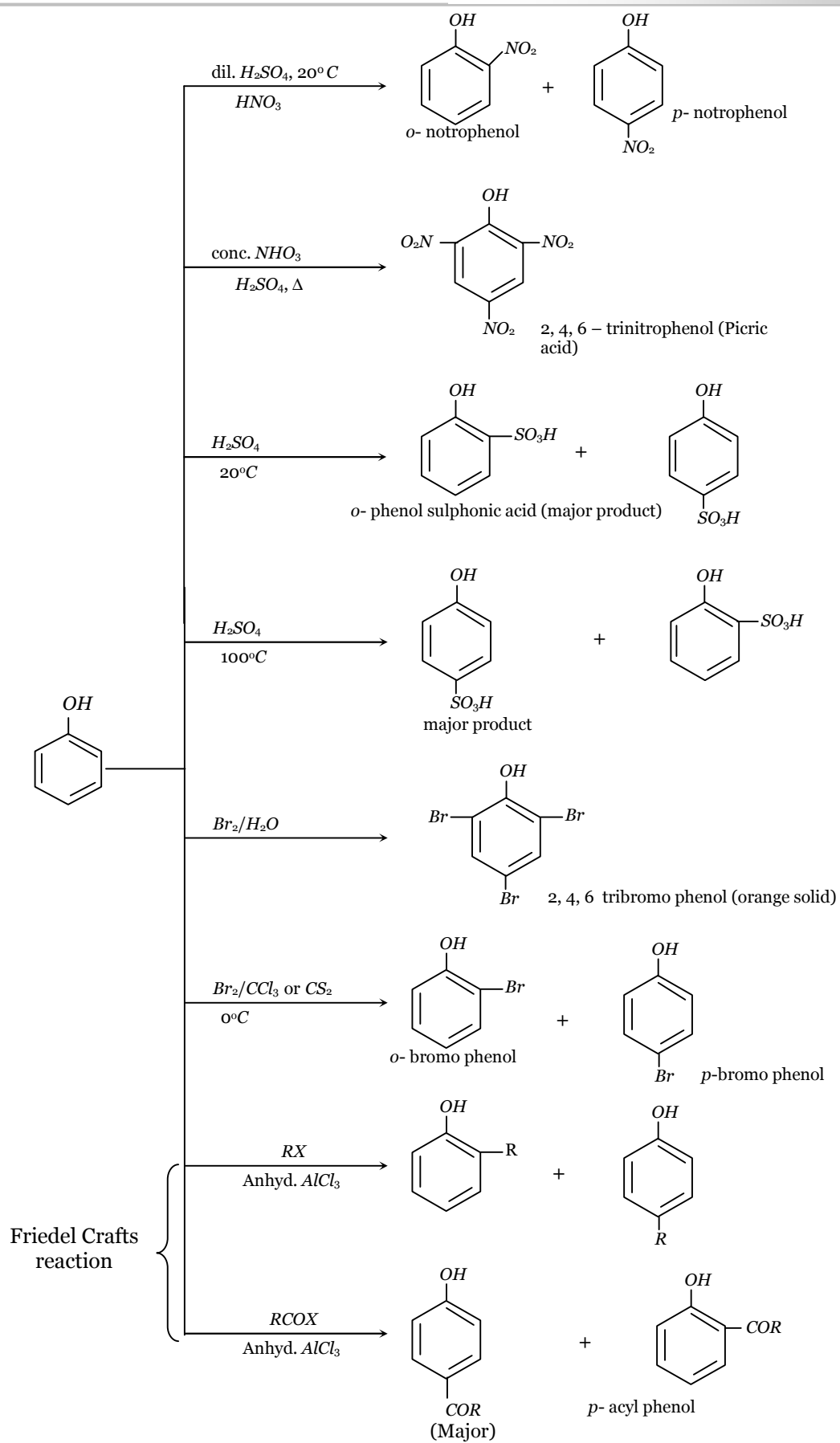
Physical properties : (1) Phenols are colourless liquid or crystalline solids. They turn pink due to oxidation.

(2) Phenols are weak acid and have high boiling point due to intermolecular hydrogen bonding.

Chemical properties :



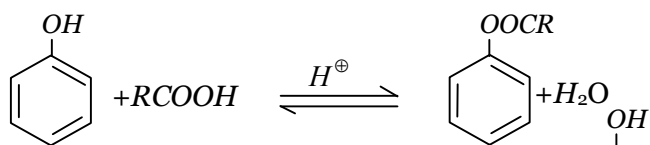
(1) **Properties due to benzene ring :** We have already discussed that $-OH$ group is *o-p* directing. The reactions due to benzene ring are briefly as follows :



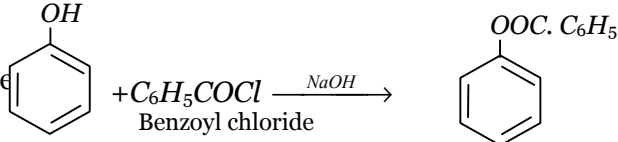
Note : □ It is important to note that Br_2 in water yields tri-bromo derivative but in CCl_4 only monobromoderivative. It is because of greater ionisation of Br_2 in water in comparison to that of CCl_4 in which the ionisation is very small.

(2) Reactions due to –OH groups which are similar to alcohols

(i) Reactions with acids : Ester formation occurs.



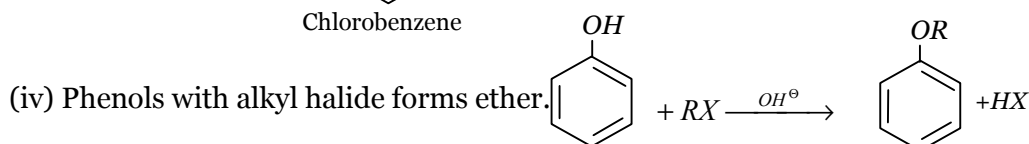
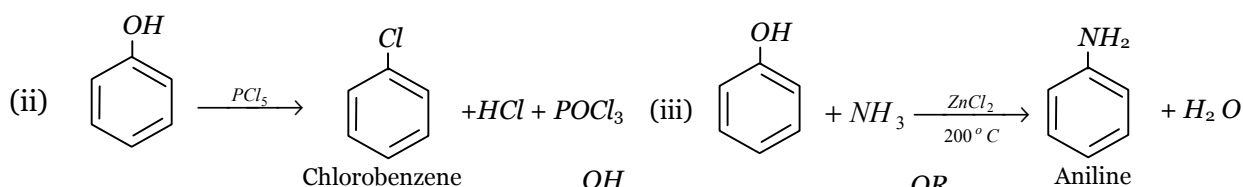
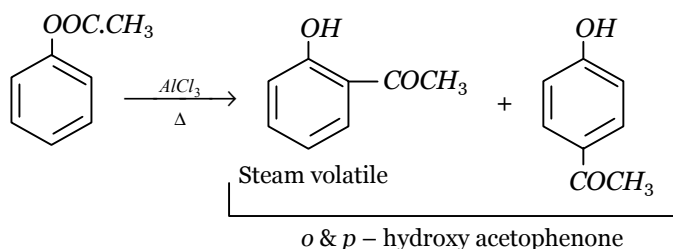
Esterification can also be carried out with acid chloride



Phenyl benzoate

The reaction is known as Schotten-Baumann reaction.

Further, when phenyl esters are treated with anhyd. $AlCl_3$ they undergo Fries rearrangement which involves migration of acyl group to *o*- or *p*- positions of the ring with respect to –OH group, to form phenolic ketones.

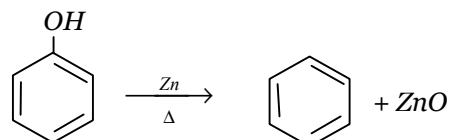


(3) Reactions in which phenol differs from alcohols

(i) Phenols gives colour with $FeCl_3$ due to formation of the complex, the exact nature of which is not known, but iron is hexavalent. The colours are as follows :

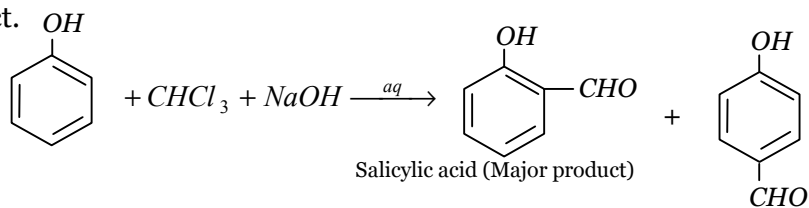
Phenol, Resorcinol, Salicylic acid	:	Violet colour
<i>p</i> -Hydroxy benzoic acid		
Catechol, <i>o</i> -cresol	:	Green
<i>m</i> -cresol, <i>p</i> -cresol	:	Blue or blue-violet
Quinol	:	Red

(ii) Phenols are acidic in nature.

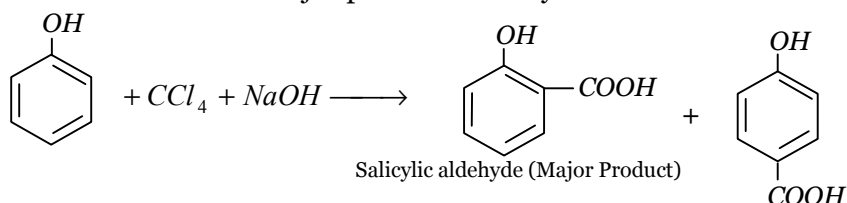


(iii) When phenol is distilled with Zn , $-OH$ group is removed.

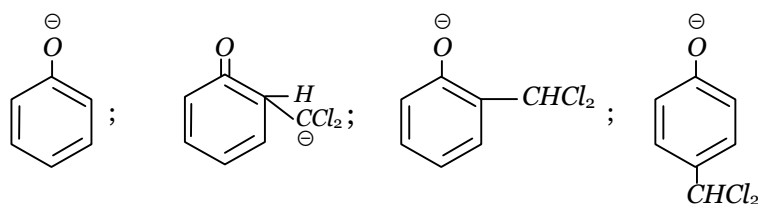
Reimer Tiemann Reaction : When phenol is refluxed with chloroform and $NaOH$, it forms salicylic aldehyde as major product.



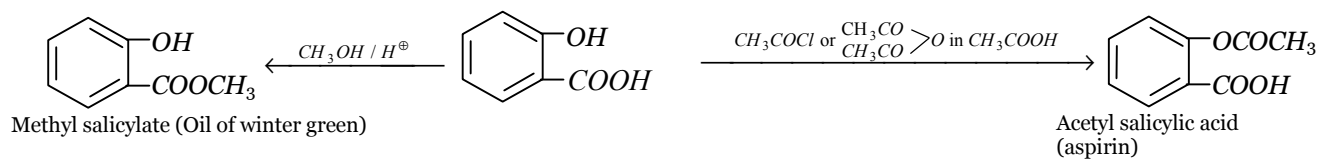
However, if $CCl_4 / NaOH$ is used the major product is salicylic acid.



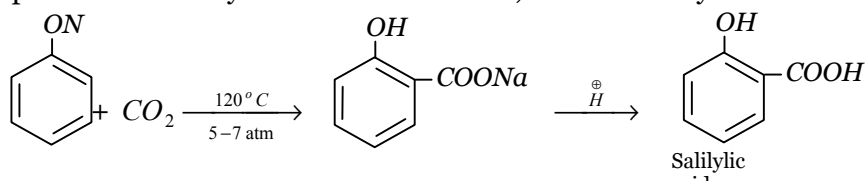
The reaction intermediates are as follows :



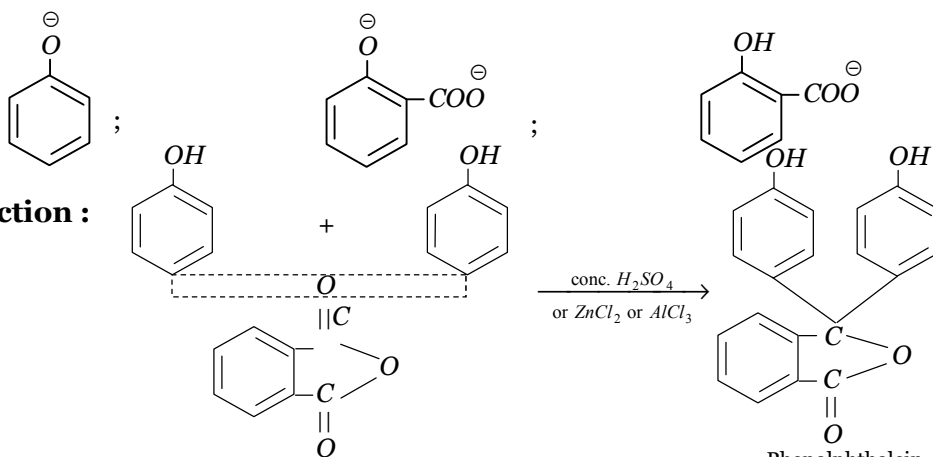
Salicylic acid is of great importance since it has been used to prepare some compounds.



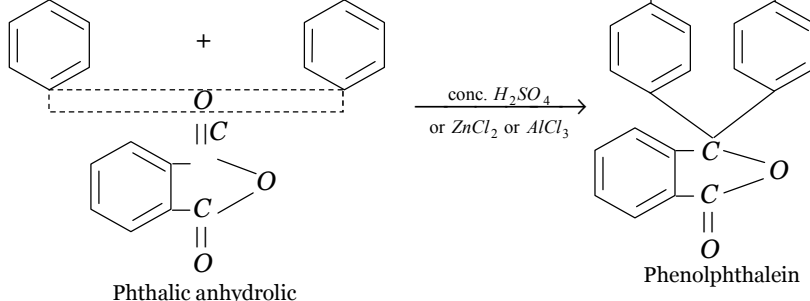
Kolbe reaction or Kolbe-Schmidt reaction : When sodium phenoxide reacts with CO_2 at $120^\circ C$ under 5-7 atmosphere followed by acidification with H^+ , it forms salicylic acid.



The reaction intermediate (s) are :

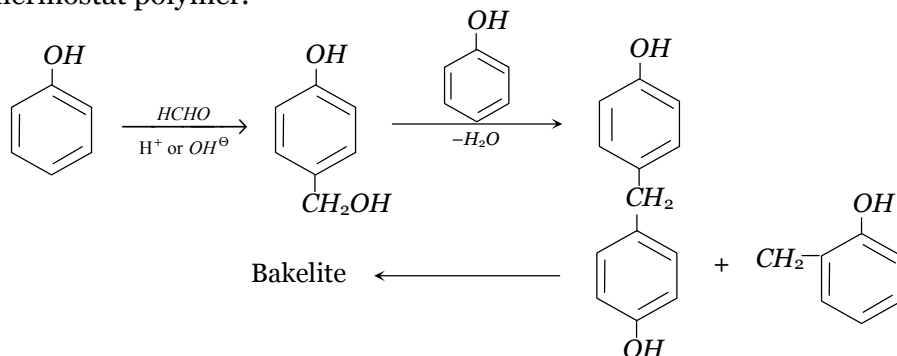


Phthalein reaction :



note that *H* para to *OH* is removed.

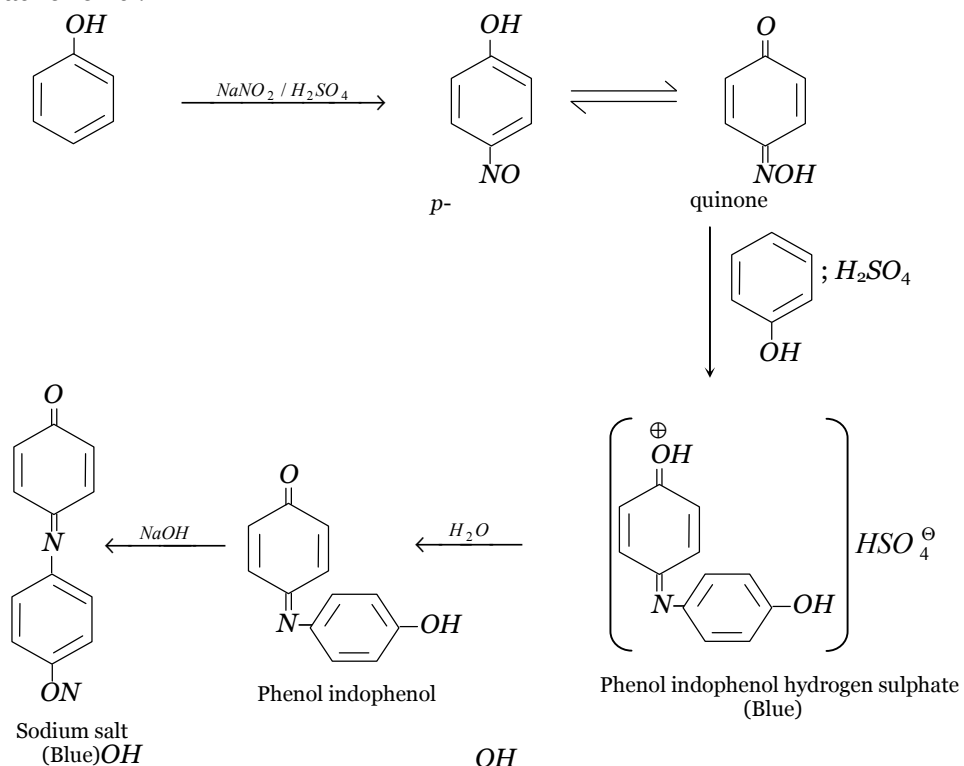
Ledrer-Manasse reaction : When phenol reacts with formaldehyde in the presence of acid or alkali, it forms bakelite, a thermostat polymer.



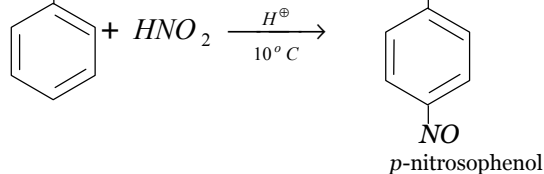
Liebermann's nitroso reaction

Phenol $\xrightarrow{NaNO_2 / \text{conc. } H_2SO_4}$ deep green or blue colour $\xrightarrow{H_2O}$ Red \xrightarrow{NaOH} green or blue colour

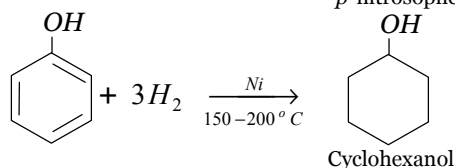
The reactions are as follows :



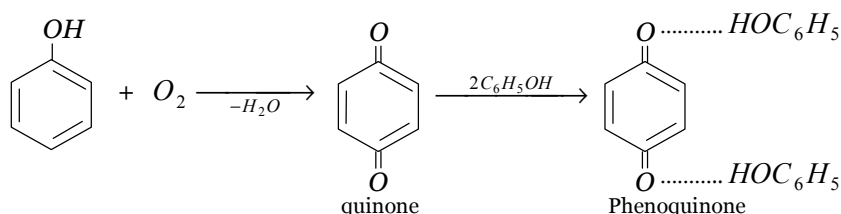
Nitrosation :



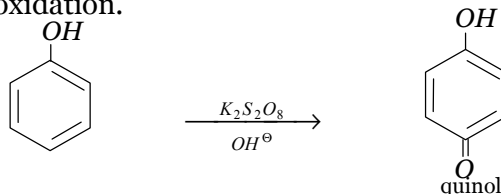
Hydrogenation :



Oxidation : Phenols turn pink or red or brown when exposed to air and light due to slow oxidation. The exact nature of these oxidation product is not known; but probable products are quinones and phenoquinones.



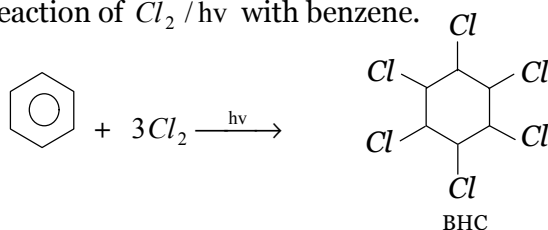
When phenols is oxidised with potassium persulphate in alkaline solution, it forms quinol and the reaction is known as Elbs persulphate oxidation.



Some important Points

Halogen derivatives

- (1) Many of alkyl halides burn with green edged flame.
- (2) C_2H_5Cl is used as a local anaesthetic.
- (3) C_2H_5SH (Ethyl mercaptan) is added to LPG (household cooking gas) to detect leakage. The compound has a typical smell.
- (4) CCl_4 is used to extinguish fire under the name pyrene.
- (5) CCl_4 resist hydrolysis with boiling water due to non availability of d -orbitals in C .
- (6) CCl_4 is an antihelminthic medicine against **hookworm**.
- (7) C_2Cl_6 is a solid and is known as **artificial camphor**.
- (8) Freon-14 is CF_4 , Freon-13 is CF_3Cl , Freon-12 is CF_2Cl_2 and Freon-11 is $CFCl_3$. All of these are used as refrigerant.
- (9) **Lindane** or **Gammaxane** or **666** is an isomer of BHC ($C_6H_6Cl_6$) and is used as insecticide against termites. It is obtained by reaction of $Cl_2 / h\nu$ with benzene.



(10) **Westron** (acetylene tetrachloride) is used as a good industrial solvent for oil, fats,, paints and varnishes etc.

(11) Iodoform has antiseptic properties because on coming in contact with organic matter of skin it decomposes to give free iodine which is an antiseptic.

(12) Chloretone is a sleep inducing medicine (hypnotic). Phosgene is harmful poisonous gas used in warfare.

Chloropicrin is a tear gas and insecticide.

Alcohols

(1) *Wood spirit* : Methyl alcohol (CH_3OH) is called wood spirit. It is obtained by destructive distillation of wood. Drinking of methanol causes blindness.

(2) *Grain alcohol*. Ethyl alcohol (C_2H_5OH) is called grain alcohol. It is used in preparation of various beverages, by using different percentages.

(3) *Proof, over proof and under proof spirit*. An alcohol-water mixture containing 57.1% alcohol by volume or 49.3% by weight is called proof spirit. A sample having higher percentage of ethyl alcohol in comparison to proof spirit is called over proof spirit (O.P.) and the one having lower percentage is called under proof spirit (U.P.).

e.g., 10 O.P. means 100 ml of given sample contains alcohol as 110 ml of proof spirit. 10 U.P. means 100 ml of given sample contains as much alcohol as present in 90 ml of proof spirit.

(4) *Methylated spirit of denatured spirit*. Ethyl alcohol containing 5 to 10% methyl alcohol is called methylated spirit. It is unfit for drinking purposes. Widespread deaths due to liquor poisoning occur mainly due to the presence of methyl alcohol. It is also called denatured spirit. Denaturing can also be done by adding 0.5% pyridine, petroleum naphtha, rubber distillate (caoutchoucine) or $CuSO_4$.

(5) *Power alcohol*. A mixture of 80% petrol, 20% ethyl alcohol with co-solvent benzene is called power alcohol. It is used to run automobiles.

(6) *Absolute alcohol*. 100% ethanol is called absolute alcohol. It is generally prepared by azeotropic distillation.

(7) *Rectified spirit*. Ethyl alcohol (95.87%) + water (4.13%) mixture is known as rectified spirit.

(8) Pyroligneous acid contains acetic acid (10%), methyl alcohol (2.5%) and acetone (0.5%).

(9) Fusel oil is mixture of *n*-propyl alcohol, *n*-butyl alcohol, *n*-amyl alcohol and isoamyl alcohol.

(10) Argol is potassium hydrogen tartarate. It is used to manufacture tartaric acid.

(11) Tincture of iodine is 2-3% alcoholic solution of iodine.

(12) In the oxidation of alcohol by acidified $K_2Cr_2O_7$, its colour changes from orange to green due to the formation of $Cr_2(SO_4)_3$.

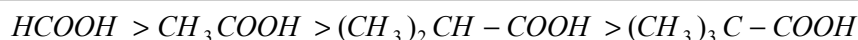
(13) 3° alcohols are resistant to oxidation due to lack of α -hydrogen.

(14) 1° alcohols on dehydrogenation with red hot copper form aldehydes, 2° alcohols form ketones and 3° alcohols form alkenes by dehydration.

(15) Fischer-Speier esterification, $CH_3COOH + HOC_2H_5 \xrightarrow{\text{dry HCl}} CH_3COOC_2H_5 + H_2O$
Acetic acid Ethyl alcohol Ethyl acetate

(16) The rates of esterification of three types of alcohols ($R'O-H$) are quite different and can be employed in their distinction. The percentages of esters obtained by 1° , 2° and 3° alcohols with acetic acid are 45.7%, 5.4% and 1.4% respectively (because reactivity order is $1^\circ > 2^\circ > 3^\circ$).

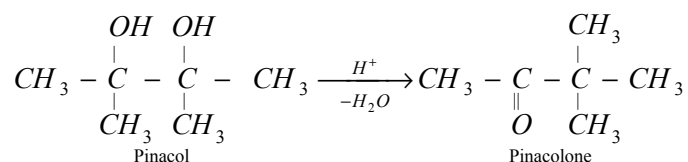
(17) In the esterification reaction, the water formed is removed by *Dean and Stark* apparatus. It should be noted that, bulkier the acid or alcohol, slower is the rate (due to steric hinderance), Decreasing order of rate of reaction of different alcohols and acids is, $CH_3OH > C_2H_5OH > (CH_3)_2CHOH > (CH_3)_3C-OH$



(18) Alcohols cannot be dehydrated using anhydrous $CaCl_2$ because it forms an addition compound, $CaCl_2 \cdot 4CH_3OH$.

(19) The name *fermentation* has been derived from Latin word *fervere* meaning to boil, as during this process there is lot of frothing due to evolution of CO_2 and this gives the appearance of boiling liquid. Favourable conditions for fermentation are (i) Optimum temperature ($25 - 30^\circ C$), (ii) A low concentration of solution, (iii) Presence of certain inorganic compounds (like $(NH_4)_2SO_4$, phosphate etc.) which acts as food for the ferment cells.

(20) *Pinacol-Pinacolone rearrangement*. The reaction involves dehydration of diols through the formation of carbocation intermediate which rearranges to more stable compound.

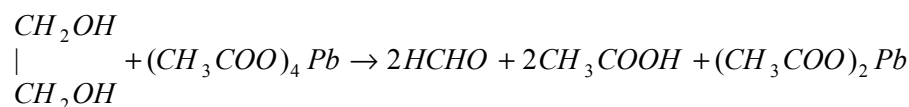


(21) Order of acidity : $H_2O > ROH(1^\circ) > ROH(2^\circ) > ROH(3^\circ) > RC \equiv CH \gg \gg RCH_3$

(22) Hydroxylation of alkene can be carried out either by cold alkaline $KMnO_4$ or peroxy formic acid (HCO_2OH). Hydroxylation by either reagent is stereoselective and stereospecific. Cold alkaline $KMnO_4$ gives *syn* addition and peroxy acid gives *anti* addition.

(23) The reaction of glycol with ketone is used in the protection of keto group in the reactions where it is to be protected.

(24) Oxidation of glycol with lead tetracetate give formaldehyde.

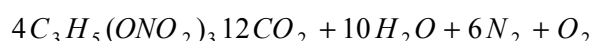


(25) Glycol is used as an antifreeze for automobile radiators and as a coolant for aeroplane aviation petrol under the name prestone.

(26) Glyceryl trinitrate is an inorganic ester.

(27) Glyceryl trinitrate is colourless, oily liquid insoluble in water and is called **Nobel's oil**.

(28) On detonating it explodes violently giving CO_2, N_2, O_2 as gaseous products.



(29) It is a safer explosive when absorbed on keiselguhr and is known as dynamite.

(30) Its mixture with cellulose nitrate is known as blasting galletin or geilgnite.

(31) Its mixture with cellulose nitrate (gun cotton) and vaseline is called cordite. It is a smokeless powder.

(32) Nobel's oil is also used in the treatment of angina pectoris and asthma.

(33) *Dunstan's test for glycerol*. A drop of phenolphthalein is added to approx. 5 ml. of borax solution. The pink colour appears. On adding 2-3 drops of glycerol, the pink colour disappears. The pink colour reappears on heating and disappears on cooling again.

Phenols

(1) Aqueous solution of phenol is also called carbolic acid.

(2) 2, 4, 6-Trinitrophenol is called picric acid.

(3) Phenol is stronger acid as compared to ethanol but weaker acid as compared to acetic acid.

(4) Groups with +M effect and +I effect decrease the acid strength.

(5) Groups with +M effect and -I effect decrease the acidity at *p*-position, but at *m*-position, the acidity is increased due to -I effect.

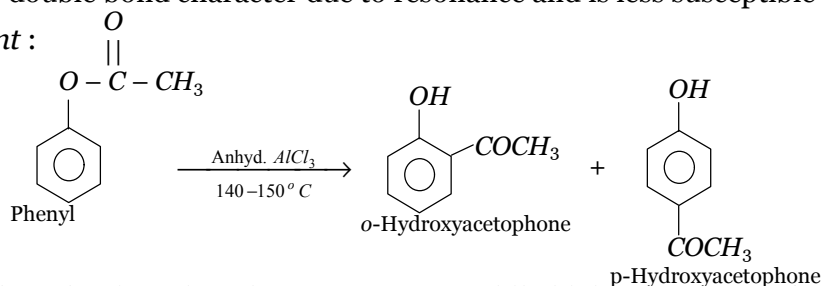
(6) Benzene-1, 3, 5-triol is also called phloroglucinol.

(7) In general, acid strength increases as

Cresols << *Phenol* << *p*-Chlorophenol << *m*-Nitrophenol << *o*-Nitrophenol < *p*-Nitrophenol << *Picric acid*

(8) *Ph-O* bond acquires double bond character due to resonance and is less susceptible to cleavage.

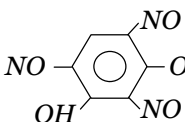
(9) *Fries rearrangement* :



The *p*-isomer is formed predominantly at low temperature while high temperature favours the formation of *o*

(10) Phenol on condensation with resorcinol in the presence of conc. H_2SO_4 give fluorescein.

(11) In the Reimer-Tiemann reaction, the electrophile used is : CCl_2 (dichloromethylene).

(12)  is also called as 2, 4, 6-trinitroresorcinol or styphnic acid.

(13) The solubilities of *o*, *m* and *p*-nitrophenol in water increases in the order $o < m < p$. In fact *o*-nitrophenol contains intramolecular *H*-bonds.

(14) Phenols cannot be converted into esters by direct reaction with carboxylic acids whereas alcohols can be. This is due to the fact that the esterification reaction is exothermic for alcohols but slightly endothermic for phenols.

(15) In Elb's persulphate oxidation the second -OH group is mainly introduced at the *p*-position but if this position is occupied than at *o*-positions.
