

B.Sc. GE-II (Chemistry) I Year

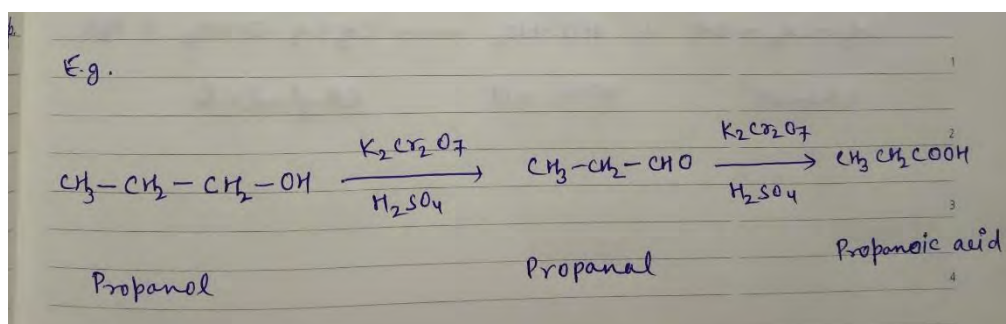
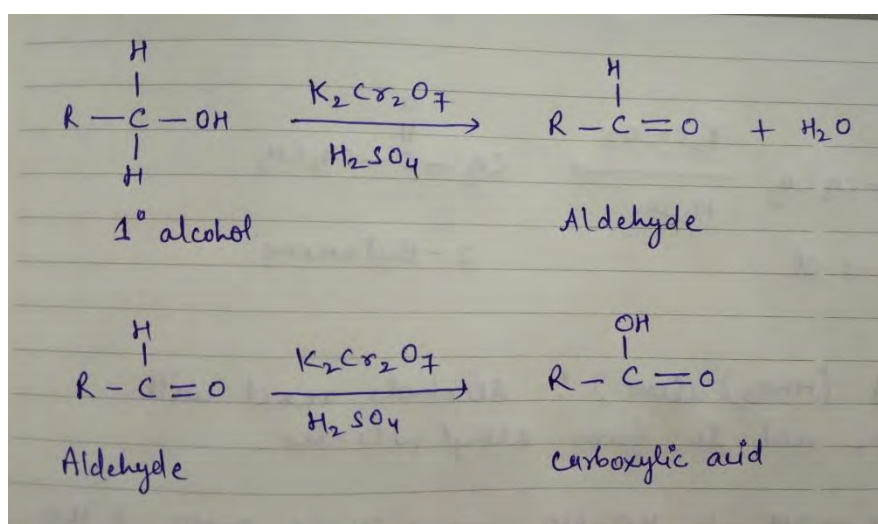
Chemistry- Chemical Energetics, Equilibria and Functional Organic Chemistry

Unit 6

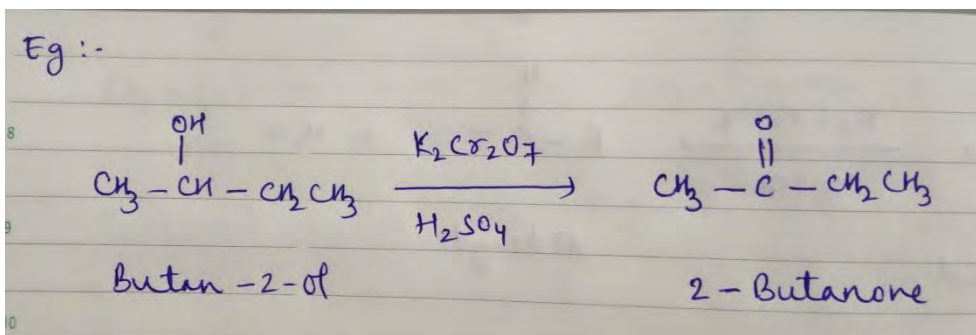
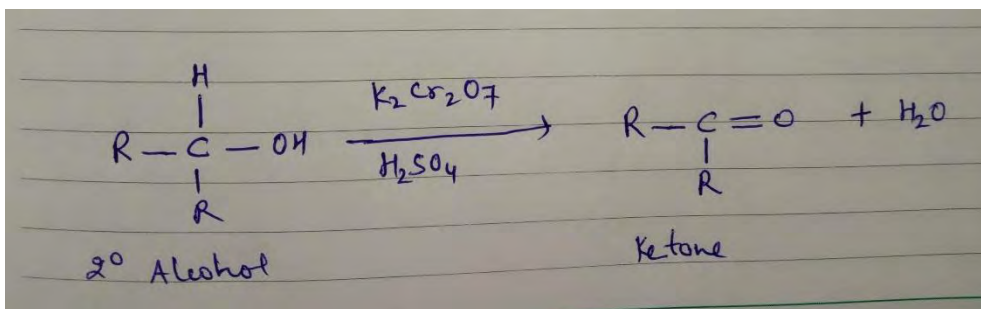
Alcohols, Phenols, Ether, aldehydes and Ketones

### Oxidation of Alcohols

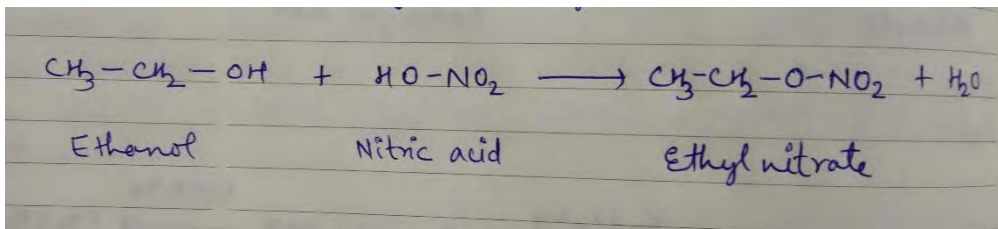
(c) Potassium dichromate ( $K_2Cr_2O_7$ ): When a primary alcohol is reacted with and sulphuric acid it converts firstly into an aldehyde and then quickly oxidizes to a carboxylic acid because the aldehyde has a H-atom attached to the carbonyl group ( $C=O$ ). The number of C – atoms remains same as that of parent compound.



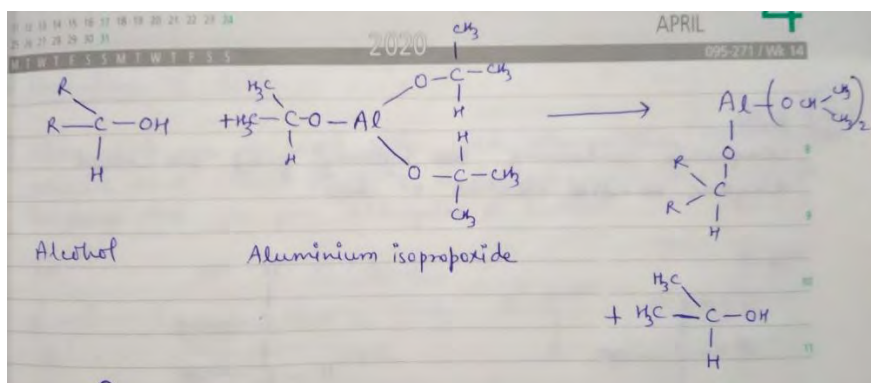
When Secondary alcohol is treated with potassium dichromate and sulphuric acid it is converted into a ketone having the same number of carbon atoms as that of parent compound. Since in a ketone no H-atom is present on the carbonyl carbon therefore, it is not further oxidized.

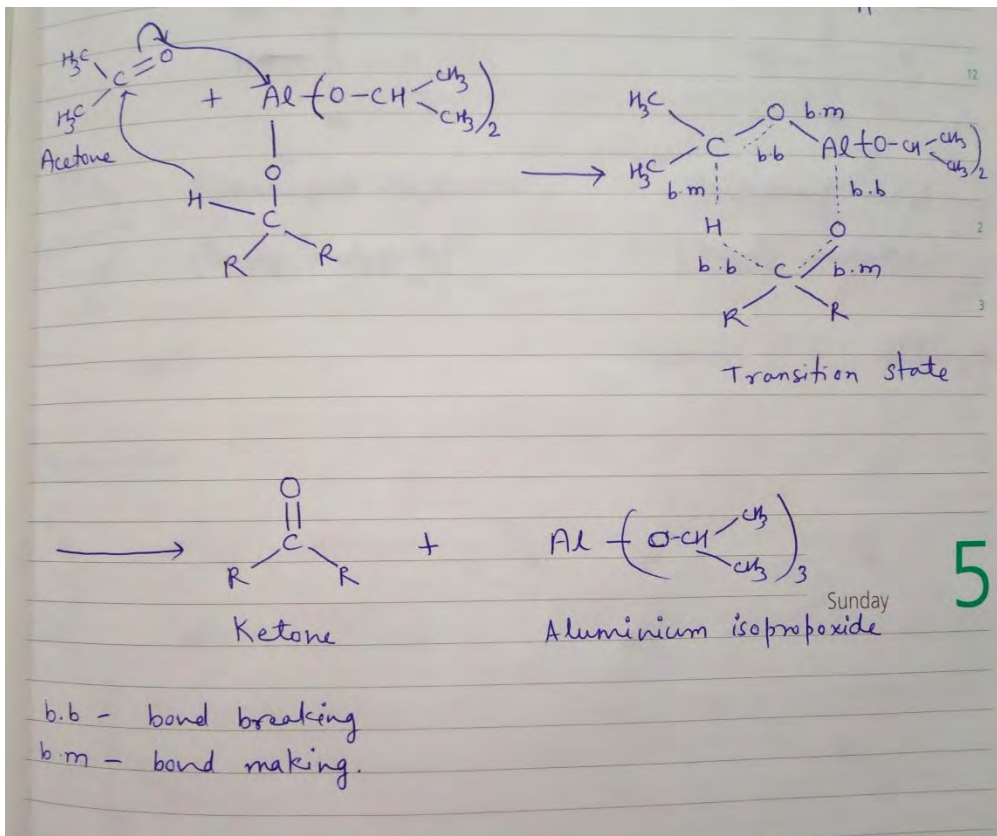


(d) Concentrated Nitric acid (HNO<sub>3</sub>): Alcohols react with nitric acid to form alkyl nitrates.



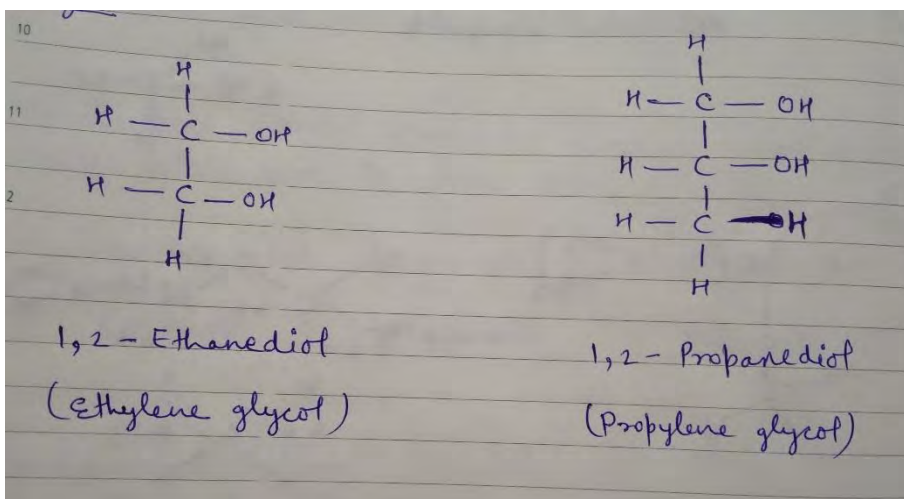
(e) Oppenauer's oxidation: Alcohols can also be oxidized by heating it with aluminium isopropoxide in the presence of acetone. This reaction is called Oppenauer's oxidation.





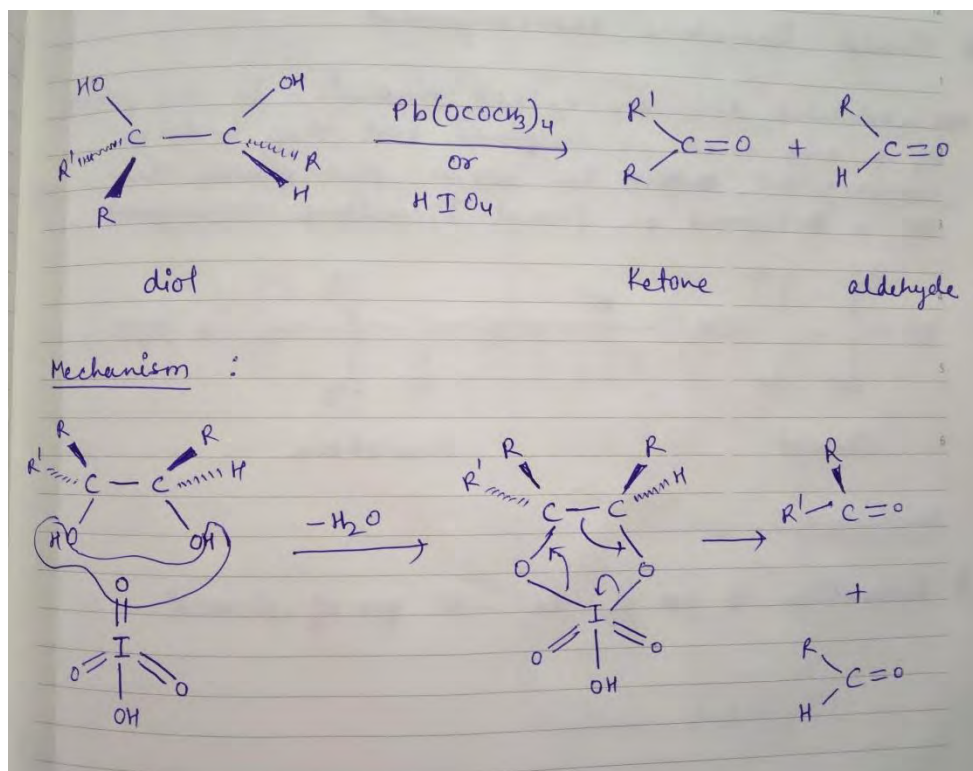
### (B) Diols

Compounds containing two hydroxyl group are called dihydric alcohols or diols.

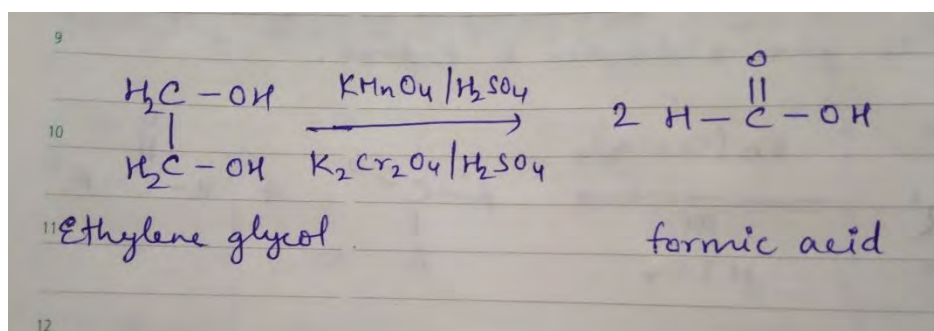


Oxidation of diols

- 1) When diols are oxidised with lead tetra-acetate  $[Pb(OAc)_4]$  or periodic acid ( $HIO_4$ ) it undergoes oxidative cleavage to form aldehyde and ketone.

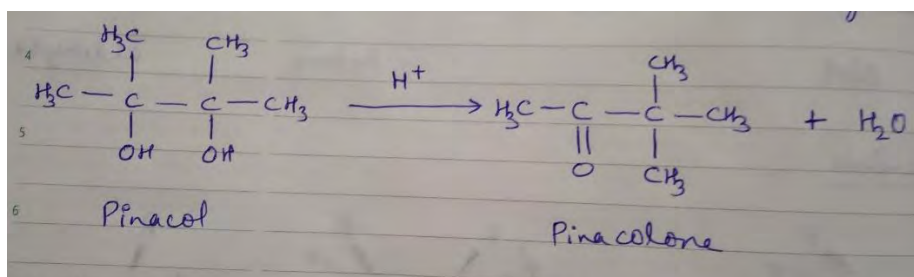


- 2) With  $KMnO_4$  or  $K_2Cr_2O_7$ : With potassium permanganate or acidic dichromates the diols are cleaved to form the respective carboxylic acids.



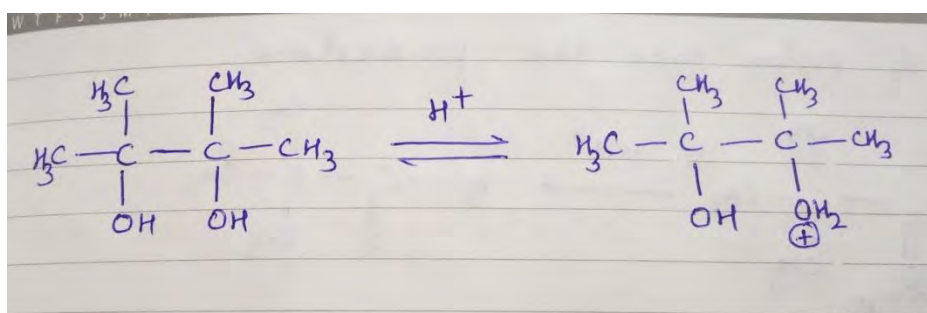
### Pinacol-Pinacolone rearrangement

Substituted 1,2-diols are called pinacols. In the presence of an acid like sulphuric acid they undergo rearrangement to form pinacolone. This is termed as Pinacol-Pinacolone rearrangement.

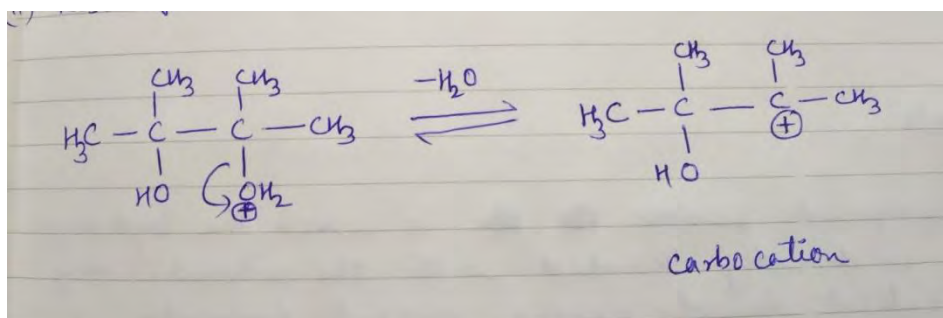


## Mechanism

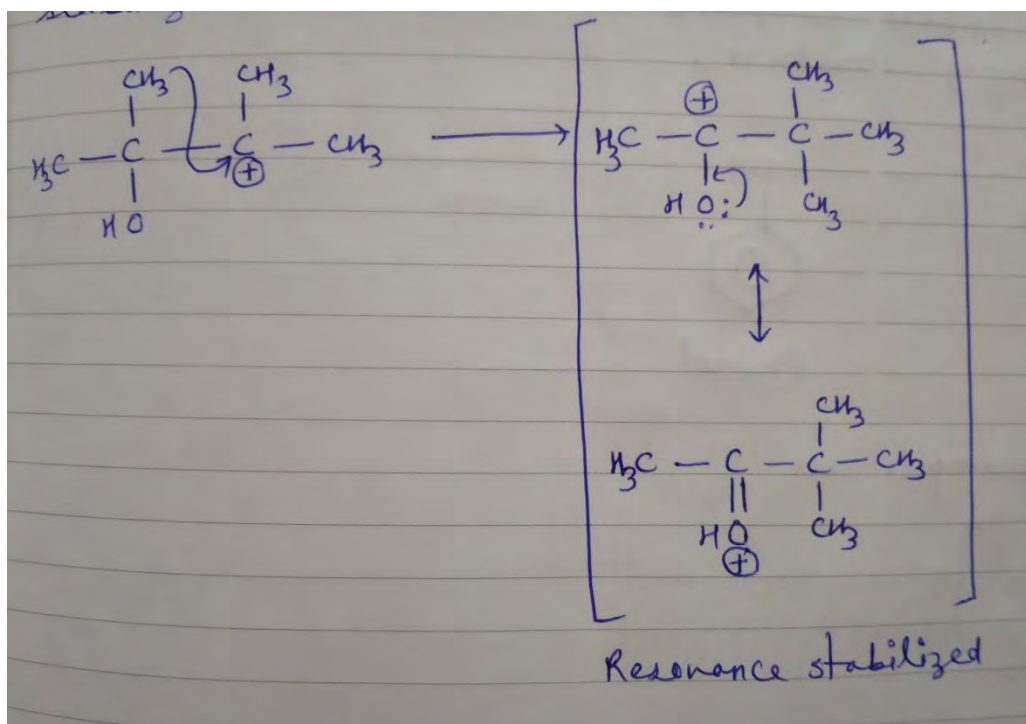
Step 1: Protonation of one of the hydroxyl group of pinacol.



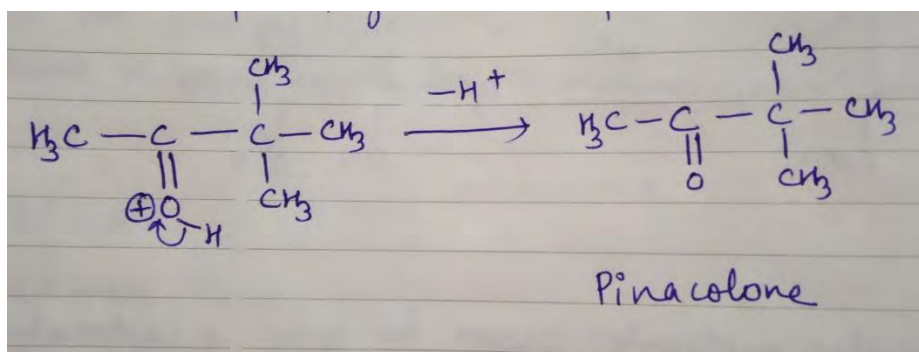
Step 2: Loss of water molecule occurs to form a carbocation.



Step 3: 1,2-shift of methyl group occurs to form a resonance stabilized carbocation.

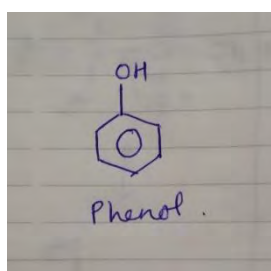


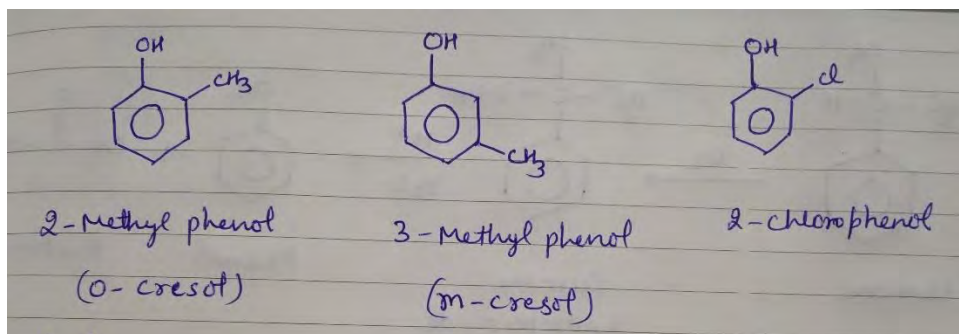
Step 4: Loss of proton gives pinacolone.



### (C) Phenols

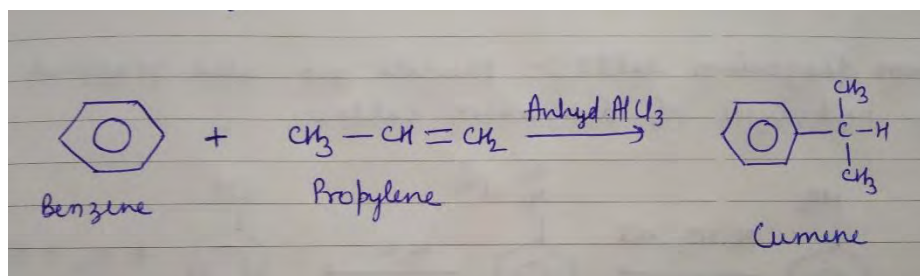
The compounds in which the hydroxyl group is attached directly with the aromatic ring are called phenols. They have general formula  $\text{Ar} - \text{OH}$  where, Ar is for Aryl group. The simplest one is phenol. For examples:



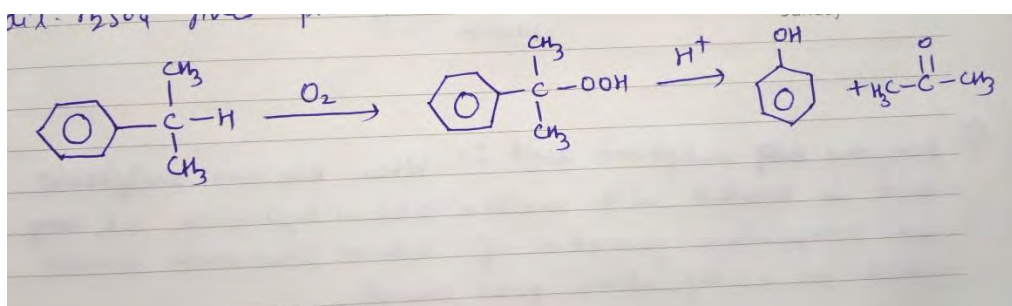


Methods of preparation of Phenols:

- (1) From Cumene: Cumene is prepared from propylene and benzene by Friedel Crafts reaction.



This cumene is oxidised in air ( $O_2$ ) to give Cumene hydroperoxide which on treating with dilute sulphuric acid forms phenol and acetone. This method is very useful on commercial scale.



- (2) From diazonium salts: Phenols are also prepared by the hydrolysis of diazonium salts.

