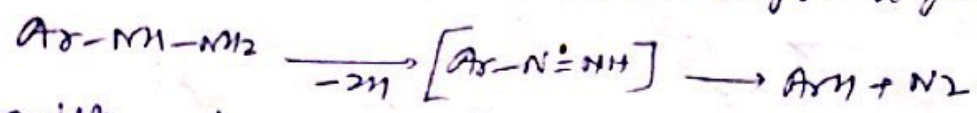
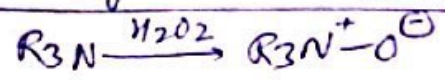


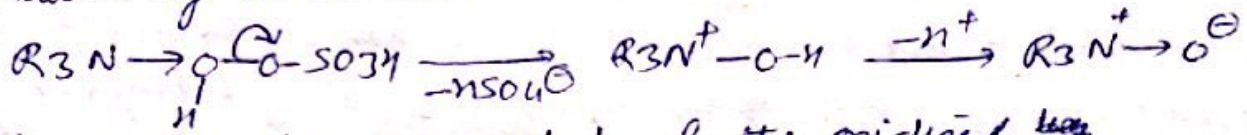
Hydrazo Compounds are oxidized to azo Compounds by several oxidising agents like NaOBr , HgO , $\text{K}_3\text{Fe}(\text{CN})_6$, MnO_2 , CuCl_2 etc. Dialkyl or diaryl hydrazines can also be oxidised by this method. Hydrazine, substituted only on one side also give azo Compounds but these are unstable and decompose to give N_2 and hydrocarbon.



(6) Oxidn of t-amine to amine oxide

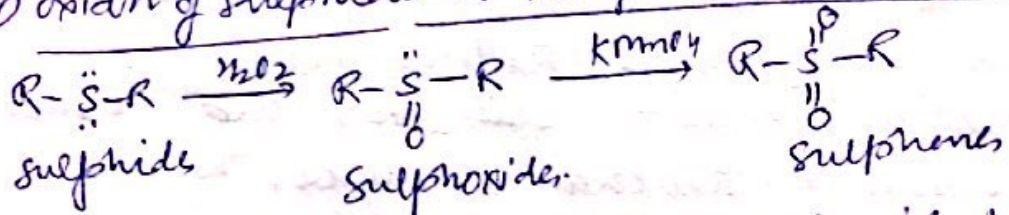


t-amine can be converted to amine oxide by oxidn, H_2O_2 is often used but per acids are also important reagents for this oxidn. Pyridine and its derivatives are oxidised by per acids only. Oxidation by Caro's acid occurs as -



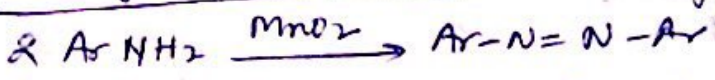
t-amine oxides can not be further oxidised.

(7) Oxidn of Sulphides to Sulphoxides and Sulphones



Sulphide can be oxidised to sulphoxides by 1 mole of 30% H_2O_2 or by t-BuOOH, Acetyl nitrate, NaIO_4 , Sod. per borate and per acids. Sulphoxides can be oxidised to sulphones by another mole of H_2O_2 , KMnO_4 , Na-perborate or pot. hydrogen per sulphate. If oxidising agent is present in large amounts, then sulphides can be directly converted to sulphones without isolation of sulphoxides.

(8) Oxidn of Amines to Azo or Azoxy Compds.

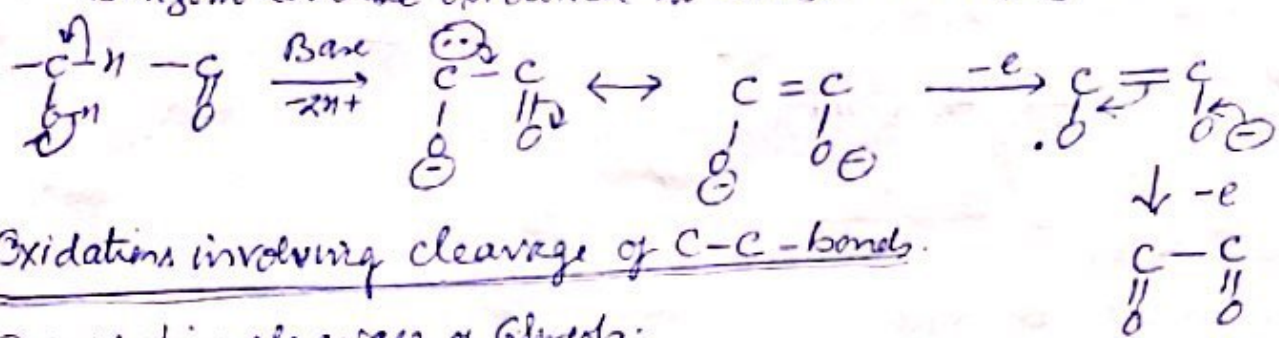


Primary aromatic amines can be oxidised to azo compounds by a variety of oxidising agents. Such as MnO_2 , $\text{Pb}(\text{OAc})_4$, O_2 etc. t-butyl hydroperoxide; has been used to oxidise certain primary amines to azoxy compounds.

Oxidation of α -Ketols

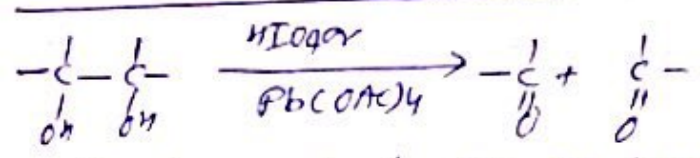
These systems are oxidised easily with one-electron oxidant ^{radical} in basic solution to α -dicarbonyl compounds. Carbanion formed in reaction with base, can donate one electron to the oxidant to give a delocalised radical; subsequent loss of second electron completes the reaction.

Benzoin can be oxidised to benzil in 90% yield.

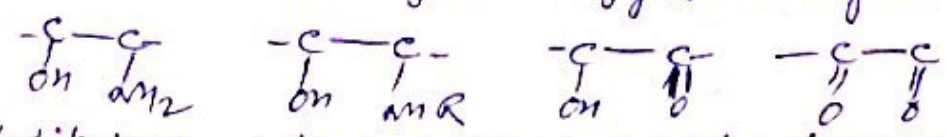


Oxidations involving cleavage of C-C-bonds.

① Oxidative cleavage of Glycols.



1,2 Glycols are easily cleaved under mild conditions with Pb(OAc)_4 or HIO_4 , products being 2 moles of aldehydes or 2 moles of ketones or 1 mole each of aldehyde and ketone both depending on the groups attached to carbon atoms. A no. of other oxidising agents have also been employed, such as KMnO_2 , Thallium (III) salts, permanganate, dichromate and Iodine triacetate etc, which cleave glycols giving carboxylic acid rather than aldehydes. The two reagents HIO_4 and Pb(OAc)_4 are complementary, the former is used extensively in aqueous solutions while the latter in organic solvents only. When three or more OH groups are located on adjacent carbon atoms, then the middle one is converted to formic acid. Similar cleavage is undergone by other compounds that contain nitrogen or oxygen at adjacent carbons.



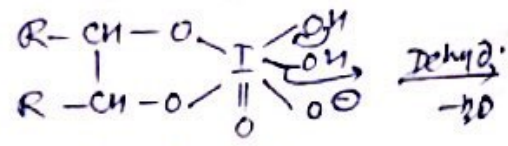
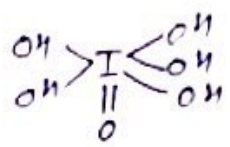
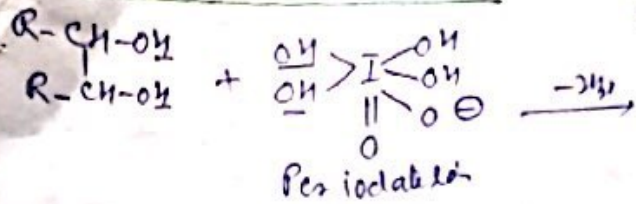
α -diketones, α -hydroxy ketones are also cleaved by alk. H_2O_2 . HIO_4 cleaves epoxides to aldehydes.

Oxidation of glycols.

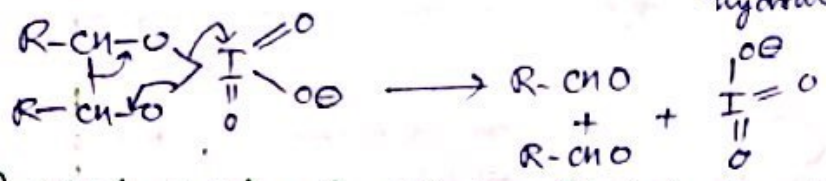
(7)

① Periodate oxidation of glycols.

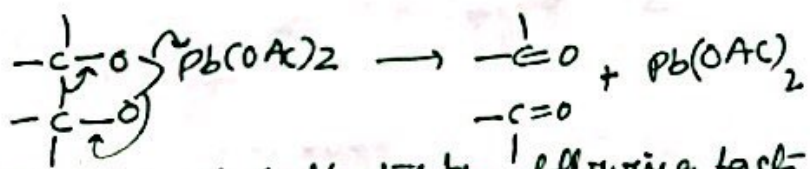
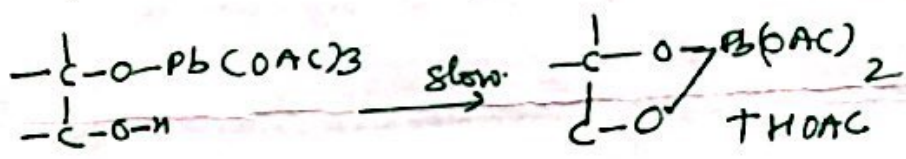
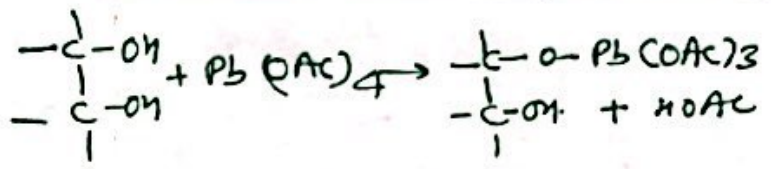
H_5IO_6 - Periodic acid or orthoperiodic acid
 \downarrow
 $HIO_4 \cdot 2H_2O$



Hydrated ion



② Mech. of glycol oxidn by $Pb(OAc)_4$. It was proposed by Criegee.

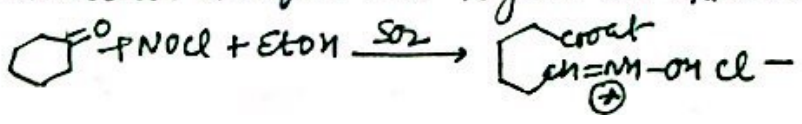


The mech. is supported by following facts -

- ① Kinetics are second order
 - ② Added acetic acid retards the rate of reaction
 - ③ cis-glycol reacts more rapidly than trans glycols.
- For periodic acid the mech. is quite similar

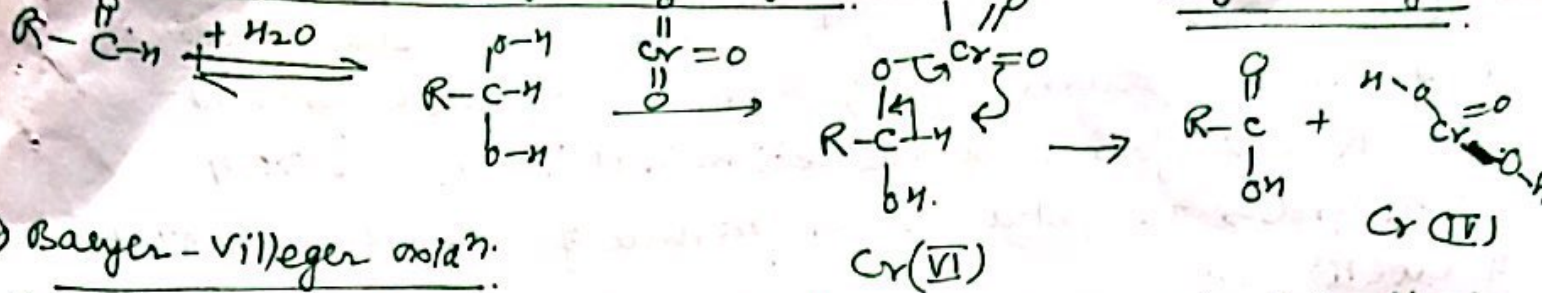
③ Oxidative cleavage of aldehydes, ketones and alcohols.

C1CCC(=O)CC1 $\xrightarrow{KMnO_4}$ $HOOC(CH_2)_4COOH$. Formation of adipic acid is an important example. Acid chromates and permanganate are most common oxidising agents. Pot. super oxide, under phase transfer conditions has also been used to cleave open chain ketones to give carboxylic acids. cyclic ketones can also be cleaved by $NOCl$ and alcohol in liquid SO_2 to give ω -oximino carboxylic ester



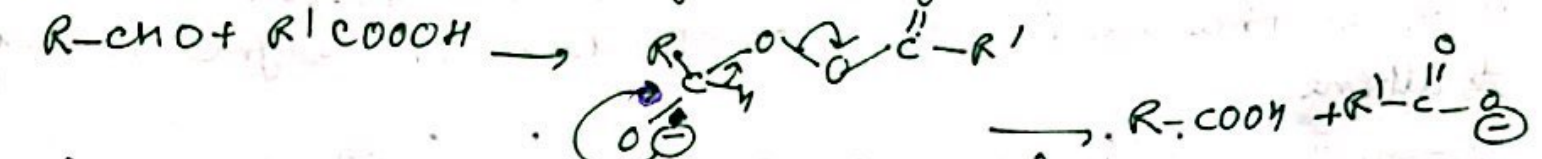
... ..

Mech. of Cr(VI) oxidn of an aldehyde.



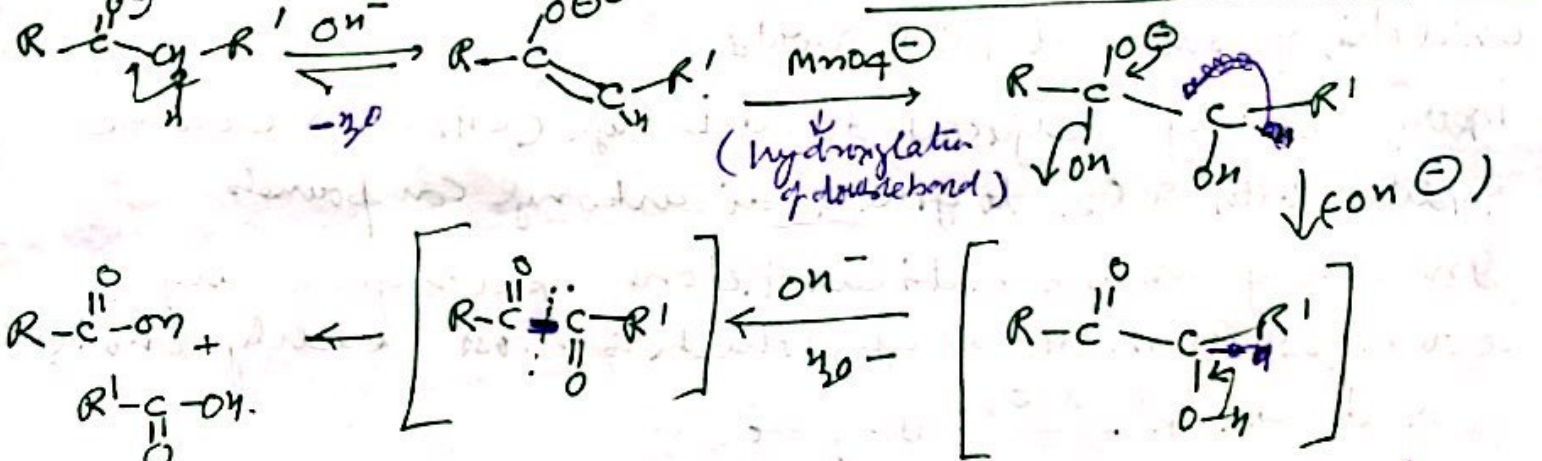
Baeyer-Villiger oxidn.

Aldehydes also form an intermediate like peroxycarboxylic like that of a ketone which rearranges to an acid

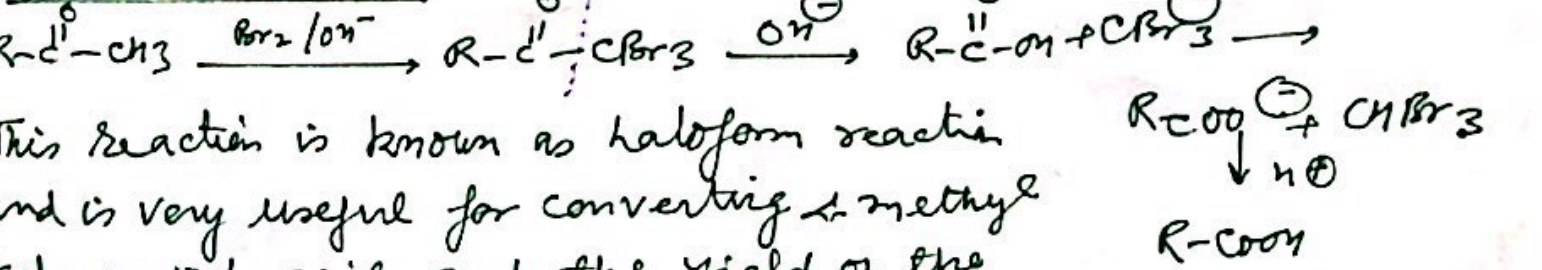


oxidn of ketones. (can also be oxidised)

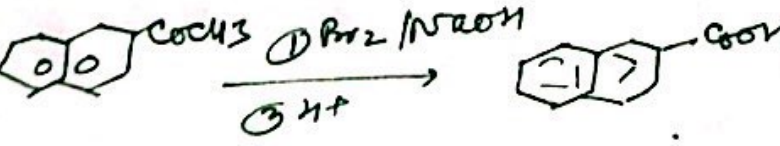
by nitric acid or alk. KMnO₄ - these strong oxidising agents convert ketones into carboxylic acids. The mech. for KMnO₄ oxidn is as



By halogens in alkali



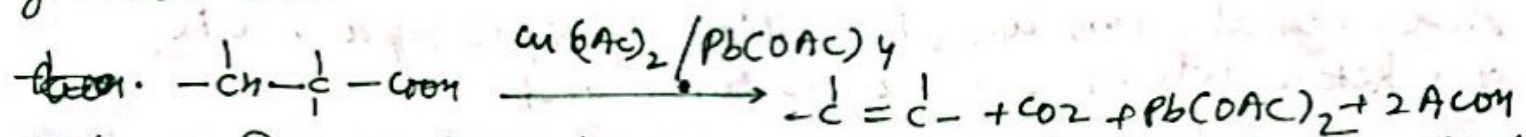
This reaction is known as haloform reaction and is very useful for converting α-methyl ketones into acids and the yield of the product is excellent.



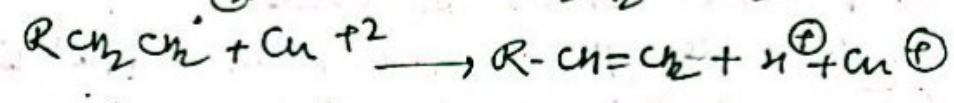
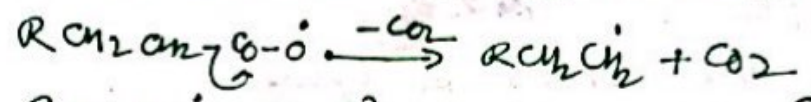
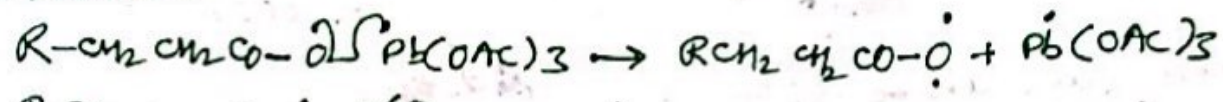
Oxidative decarboxylation of acids (oxidation of carboxylic acids) (3B)

Carboxylic acids can be decarboxylated by lead tetra acetate. Decarboxylation occurs and if a β -hydrogen is present the alkene is formed by the elimination of H and COOH.

High yields are obtained in presence of catalytic amount of Cu(II) salts.



Mech. is Free radical type. Cu(II) ions oxidise free radicals to alkene.



Oxidation of saturated C-H groups.