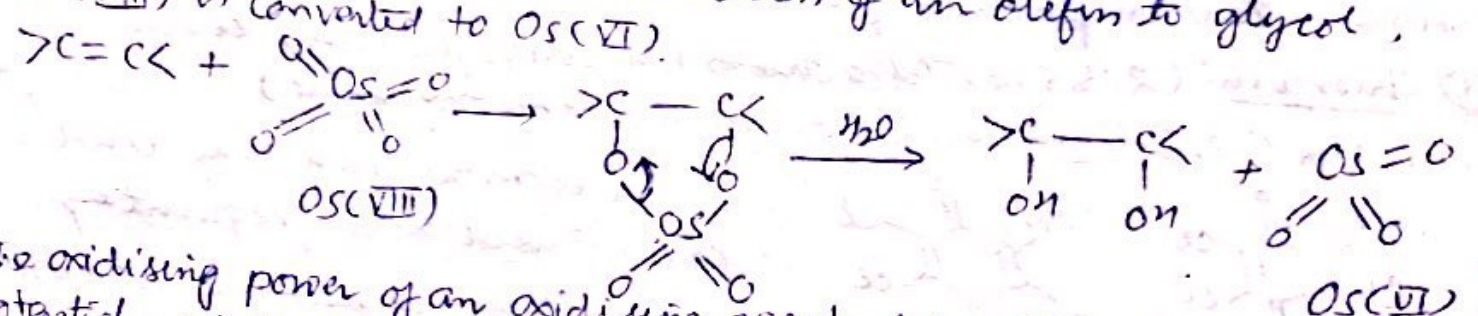


Oxidation is defined as, "loss of electrons or increase in oxidation no." but very few reactions are known, which involve direct transfer of electrons. Similarly the concept of change in oxidation number is also not easy to apply. eg. Carbon in propane has an oxidation no. of -2.67 while in butane it is -2.5. though these compounds were seldom thought to be in different oxidation states. Therefore a convenient definition of oxidation for organic compounds is -

"The addition or gain of oxygen or removal of hydrogen." eg. Oxidation of an alcohol to an aldehyde or carboxylic acid or ethylene into ethylene oxide, involves addition of oxygen, while oxidation of ethanol into acetaldehyde involves removal of hydrogen.

One of the important criteria to decide, whether a reaction is oxidation, is that the reagent used in the reaction, must be reduced. For example, in the conversion of an olefin to glycol,  $Os(VIII)$  is converted to  $Os(VI)$ .



The oxidising power of an oxidising agent depends on their oxidation potential, which is the "ability of a metal atom to be ionized to an ion, by losing electron." The oxidation of an organic compound is carried out by Transition metal compounds, containing Cu, Cr, Mn, Ru, Se Ag or Ce. pH of a medium also plays an important role in the oxidising power of a reagent.

Types of oxidation -

① Elimination of hydrogen - Oxidation of hydrocarbons

① Aromatisation of six memb. rings



Six memb aromatic rings can be aromatised in a no. of ways. Presence of one or more

double bonds in the ring facilitate aromatisation. The reaction is equally applicable to five or six membered heterocyclic rings.

In some cases on and -COOH groups are lost from the ring. Cyclic ketones are converted to phenols. There are three types of reagents which are widely used for affecting aromatisation.

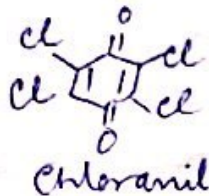
① Hydrogenation catalysts - such as Pt, Pd or Ni, substrate is heated with catalyst at about 300-350°C. Reaction can be carried out under mild conditions.

② Elemental Sulphur and Selenium - Combine with the hydrogen evolved to give H<sub>2</sub>S and H<sub>2</sub>Se respectively.

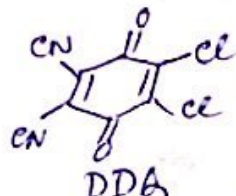
③ Quinones They become reduced to the corresponding hydroquinones. Two important quinones used for aromatisation are-

① Chloranil (2,3,5,6, Tetrachloro 1,4 benzoquinone) and

② DDA (2,3 dichloro, 5,6 dicyano, 1,4 benzoquinone)



Chloranil



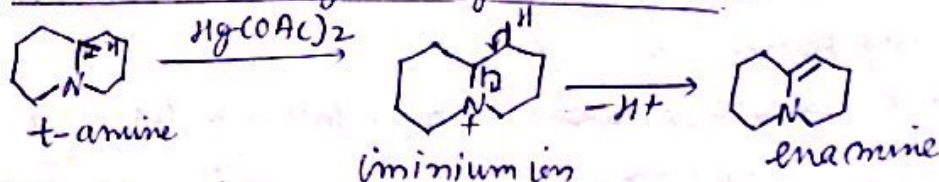
DDA

DDA is more reactive and can be used more frequently.

Among other reagents are atoms/Pro<sub>2</sub>, MnO<sub>2</sub> and SeO<sub>2</sub>, Ph<sub>3</sub>COH/CF<sub>3</sub>COH and activated charcoal. In some cases

hydrogen serves to reduce another molecule of the substrate. The reaction being known as 'disproportionation reaction'.

② Dehydrogenation yielding C=C bonds.



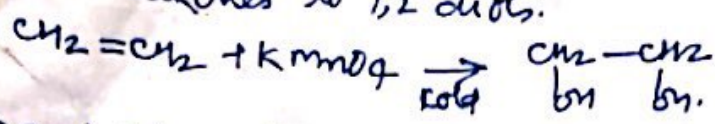
t-amine

iminium ion

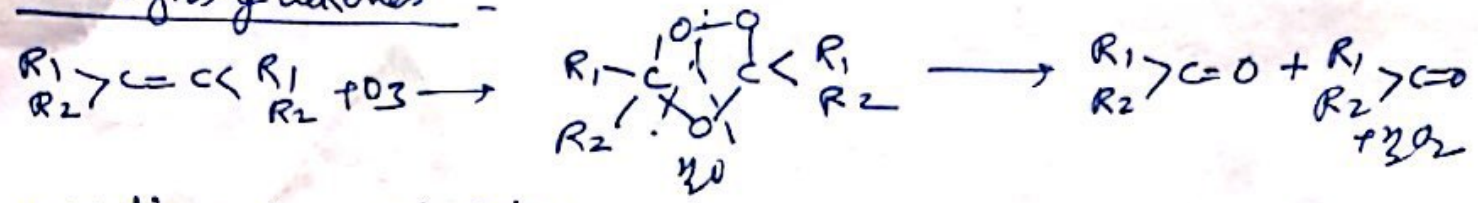
enamine

Dehydrogenation of an aliphatic compound to give a double bond in specific position is a rare reaction. An important example is the synthesis given by Leonard et. al. in which t-amine gives enamines, when treated with mercuric acetate.

2b) Alkenes - are hydroxylated,  $KMnO_4$  or  $OsO_4$  can be used to oxidise alkenes to 1,2 diols.

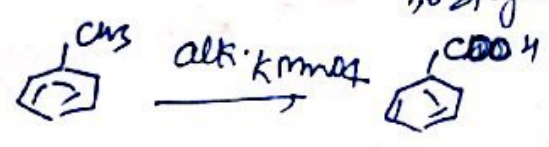
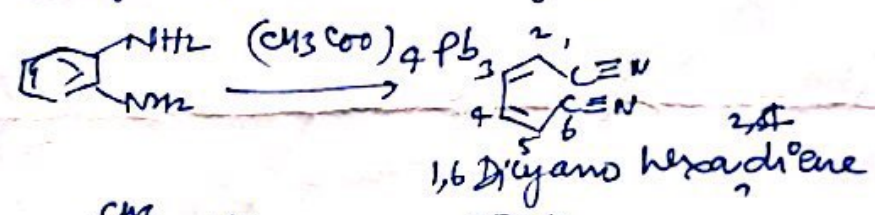
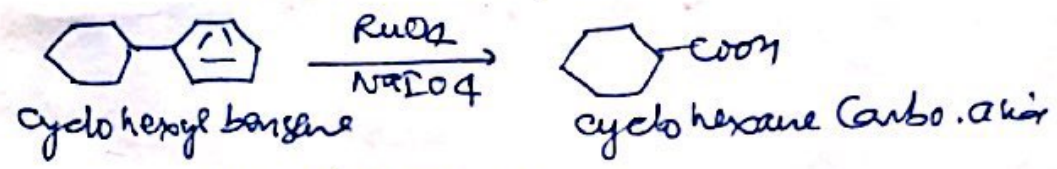
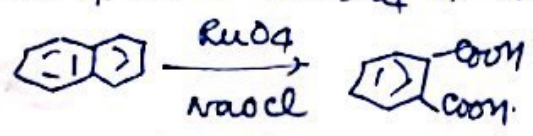


Ozonolysis of alkenes -

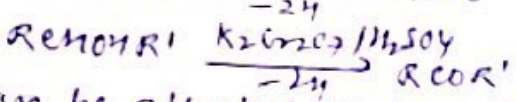
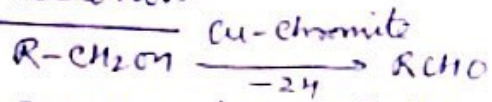


Oxidation of Aromatic Rings

Aromatic rings can be cleaved with strong oxidising agents such as  $K_2Cr_2O_7$  with  $HNO_3$  or  $NaOCl$ .

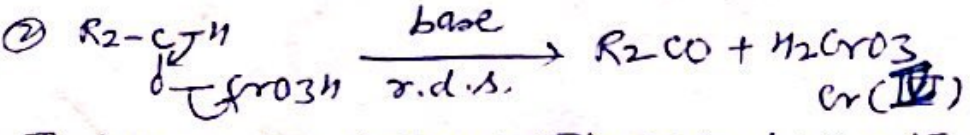
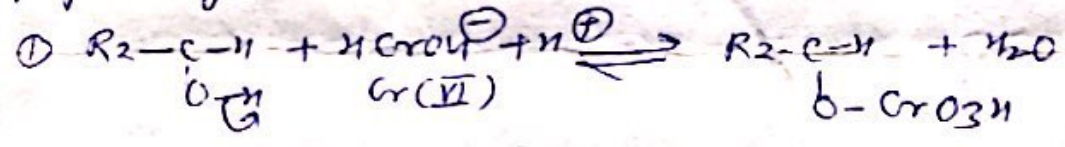


② Oxidation of alcohols



This oxidn can be affected in four ways - ① With strong oxidising agents sec alcohols are easily oxidised to ketones by acid dichromate, at room temperature. Other oxidising agents include  $KMnO_4$ ,  $Br_2$ ,  $MnO_2$ ,  $RuO_4$ . A soln of chromic acid and  $H_2SO_4$  in water is known as Jones Reagent. Which oxidises sec alcohols to ketones in higher yields, with out disturbing other double or triple bonds.  $MnO_2$  also is fairly specific reagent for  $OH$  groups to oxidise them to aldehydes or ketones. Primary alcohols are easily oxidised to aldehydes, but reaction proceeds further and aldehydes form acids immediately. This oxidation can be prevented by Dimethyl sulphoxide (Collins reagent), pyridinium dichromate Ceric Ammonium nitrate,  $Pb(OAc)_4$  etc.

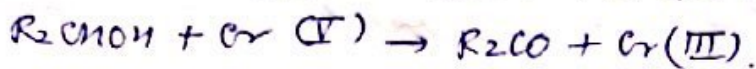
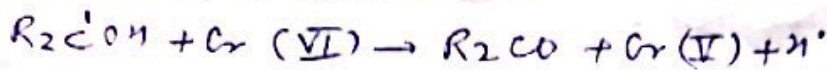
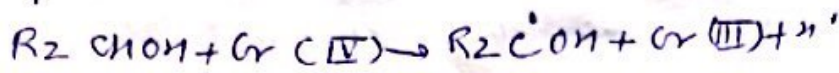
chromic acid oxidation of alcohols. Mech. of oxidation has been proposed by Westheimer.



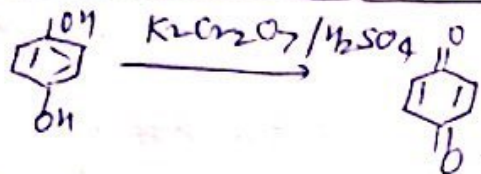
The base in the second step may be water, but in some cases no external base is required and proton is transferred directly to one of  $CrO_3H$ , oxygen. It has been suggested that some of the oxidising agents may work by hydride shift mechanism and some by free radical mechanism. (Oxidn by  $S_2O_8^{2-}$ )

② By catalytic dehydrogenation - These reactions are reversible

① With N-bromo succinimide - These compounds are chemoselective oxidising agents, and often oxidise OH groups, without disturbing other oxidisable groups. It does not oxidise aliphatic primary alcoholic group, but N-chloro succinimide does. With this reagent it is often possible to oxidise only one of several OH groups, that may be present in a molecule. Alkoxide ion, can be oxidised to aldehydes or ketone, in good yield by photooxidation with O<sub>2</sub>.

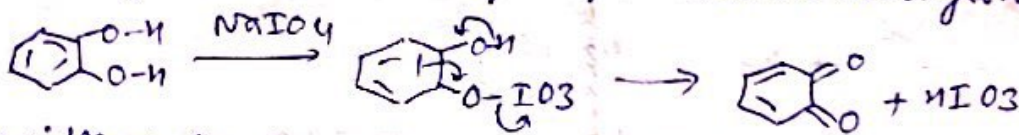


③ Oxidn of phenols and Aromatic amines to Quinones

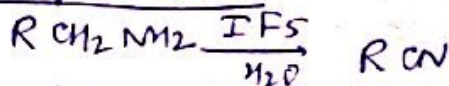


Ortho and para diols are easily oxidised to ortho and para quinones easily. The reaction has been successfully carried out with other groups para to -OH or -NH<sub>2</sub> like halogen, R, Me, Bu or even H.

Phenols, whose para-positions are unoccupied can be oxidised to ortho-quinones with diphenyl, seleninic anhydride or NaIO<sub>4</sub>.



④ Oxidn of Amines



This reaction can be carried out by treating amine with IFS, Pb(OAc)<sub>4</sub>, Nickel peroxide, silver picolinate, N-bromo succinimide etc, amines are sometimes dehydrogenated to imines, which is formed by dehydrogenation with Pt-black, may react with another molecule of the same or different amine to give an aminal, which loses NH<sub>3</sub> or RNH<sub>2</sub> to give sec. or tert amine. eg. Reaction between N-methyl benzyl amine and N-methyl butyl amine to form N-butyl N-methyl benzylamine

