USE OF REAGENTS

For B.Sc. Part -3 (Hons) paper VII

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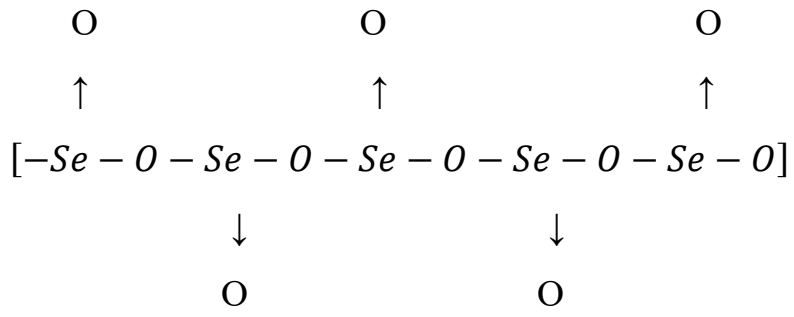
SELENIUM DIOXIDE

Selenium Dioxide is a powerful oxidising agent having structure as given below



PREPARATION

When Selenium is strongly heated with air in presence of traces of nitrogen peroxide as catalyst then we get Selenium oxide

$$Se + O_2 \rightarrow SeO_2$$

Properties & Application

Selenium dioxide is a dense white translucent solidlook like colourless needle like crystals . M.P. -340^{oC} .selenium dioxide dissolves in water toform selenous oxide .

Application:→ (1) SeO_2 is first used by H.L. Reley in1932 as oxidising agent in organic compounds. It oxidises so many compounds some of them mentioned below :→

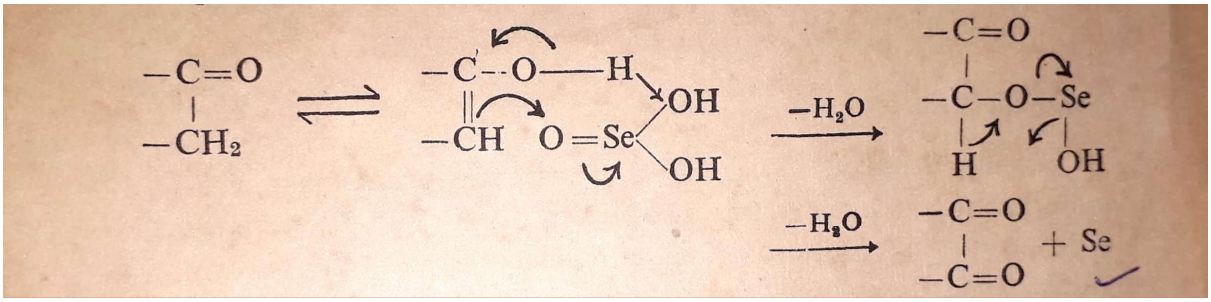
(a) SeO_2 oxidises a methyl or methylene group adjacent to the carbonyl group into a -CHO or > C=O group .

Eg IN presence of acetic acid It oxidises Acetaldehyde into glyoxal & acetone into methyl glyoxal

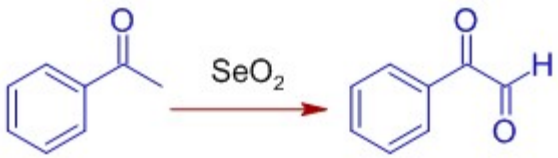
$$CH_3CHO + SeO_2 \rightarrow OHC\text{-}CHO + Se + H_2O$$

$CH_3COCH_3 + SeO_2 \rightarrow CH_3\,CO\,CHO + Se + H_2O$ (2)

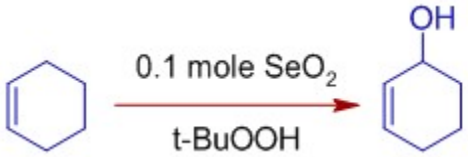
Mechanism of this reaction is as given below



(2) Acetophenone can be oxidized with SeO_2 to oxo(phenyl)acetaldehyde, a 1,2-dicarbonyl compound.



(3) Cyclohexane can be oxidised by the mixture of selenium dioxide and t-BuOOH into cyclohex-2-en-1-ol, an allylic alcohol.



(4) Allylic hydroxylation and oxidation :→ SeO_2 is used to oxidise Allyl group

(- CH_2 -CH = CH -)be either hydroxylated (-CH (OH) -CH -CH -)

Or oxidised into (-CO -CH =CH -) on allyl position.

Following rules govern the hydroxylation of allyl compounds .

(a) Hydroxylation takes place alpha to the more highly substituted end of the = bond

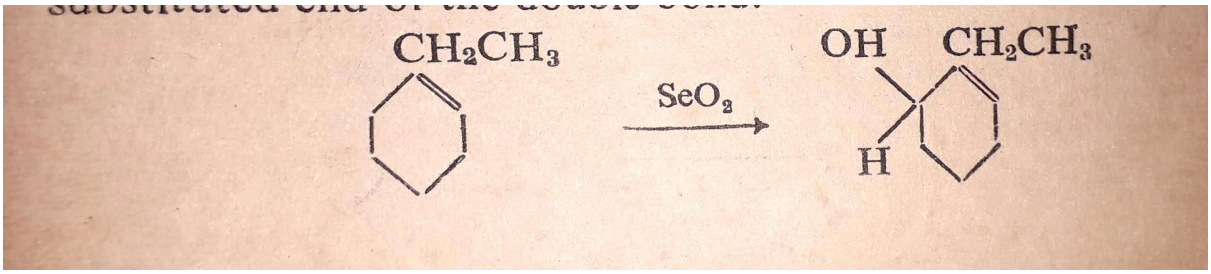
e.g.

$$CH_3\text{-}C(CH_3)=CH\text{-}CH_3 \xrightarrow{SeO_2} CH_3\text{-}C(CH_2OH)=CH\text{-}CH_3$$

(b) The order of preference of the group oxidised is $CH_2 > CH_3 > CH$

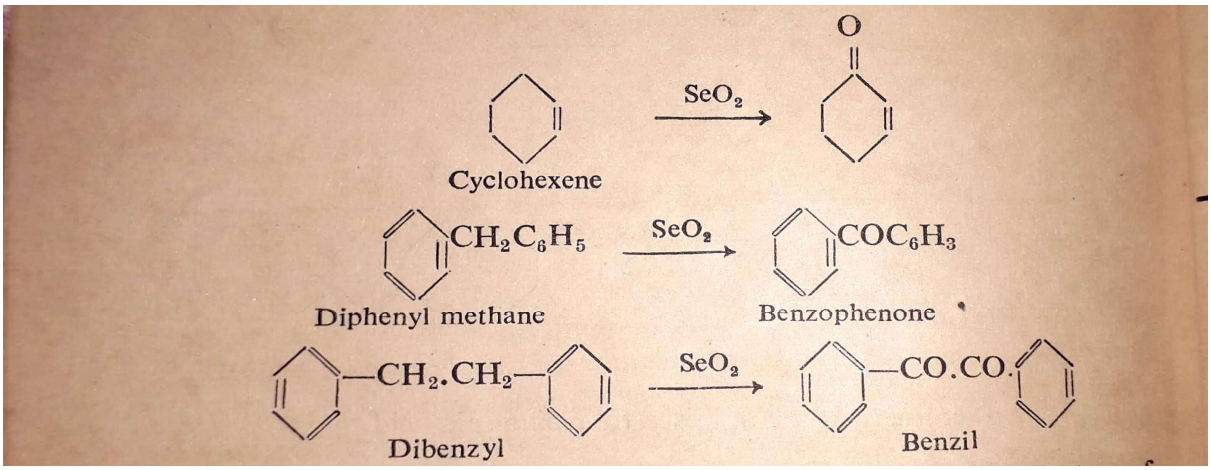
$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} = CH - CH_3 \xrightarrow{SeO_2} CH_2 - \underset{\displaystyle OH}{CH} - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} = CH - CH_3$$

(c) IF there is a double bond present in the ring ,oxidation takes place in the ring & alpha to the position to the more substituted end of the double bond

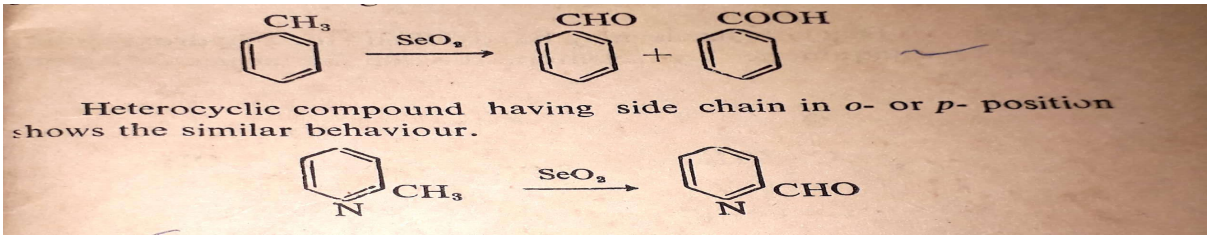


(d) During the oxidation of allylic compound methylene gr is oxidised to ketonic group

e.g.



(5) Selenium dioxide when heated with toluene at 250 – 350^0 C oxidises toluene into mixture of benzaldehyde and benzoic acid



##########Thanks ##########