# [USE OF REAGENTS]

[B.sc – III (HONS)]

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# <u>"USE OF REAGENT"</u> <u>Selenium dioxide (SeO<sub>2</sub>):-</u>

<u>Preparation:-</u> It is prepared by the direct oxidation of selenium which burns in air with a blue flame. The oxidation is catalysed by nitrogen peroxide.

Se + O<sub>2</sub> air/N<sub>2</sub>O<sub>4</sub> SeO<sub>2</sub>

# Applications:-

- (1) In the oxidation of reactive methyl and methylene group without effecting the other carbonyl group.
- (a)  $CH_3CHO + SeO_2 \longrightarrow CHO + Se + H_2O$ Acetaldehyde Glyoxal
- (b)  $CH_3COCH_3 + SeO_2 \longrightarrow CH_3COCHO + Se + H_2O$ Acetone
- (c)  $C_6H_5COCH_3 + SeO_2 \longrightarrow C_6H_5COCHO + Se + H_2O$
- (2) In the allylic hydroxylation and oxidation.
- (a) Hydroxylation takes place on the  $\alpha$  position to the more highly substituted end of the double bond.

 $CH_3 \qquad CH_2 OH$  $CH_3 - C = CH - CH_3 \underline{SeO_2} CH_3 - C = CH - CH_3$ 

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

 $CH_3 - CH_2 - C = CH - CH_3 \underline{SeO_2} CH_3 - CH - C = CH - CH_3$ 

(c) When double bond is present in the ring oxidation takes place within the ring and at the  $\alpha$  – position to the more substituted end of the double bond.



During the oxidation of allylic compound the methylene group is oxidise to ketone.



(3) As a catalyst :- SeO<sub>2</sub> catalyst some unsaturated compound to convert it into hydroxy compound by  $H_2O_2$ .

(a) 
$$H - C - COOH$$
  $H_2O_2 - SeO_2$   $H - C - COOH$   
 $H - C - COOH$   $H - C - COOH$   $H - C - COOH$   
 $OH$ 

Maleic acid

Tartaric acid

(b) It also catalyses the oxidation of cyclohexanol to adipic acid.



#### Introduction:-

 $H_9O_92H_2O.(H_5IO_6)$ 

 $HIO_42H_2O$ 

Very useful oxidising agent used is analytic and synthetic work. It is used for the oxidation of 1:2 diol  $\alpha$  – hydroxy carbonyl compound and dicarbonyl compound in to alkyl, ketone and acid depending upon the nature of the compound.

Prof :-  $2HClO_4 + I_2 \longrightarrow 2HIO_4 + Cl_2$ Perchloric acid (lq)

<u>Application:-</u> Oxidation purposes as well as in structure elucidation.

(1) 
$$\begin{array}{c} H \\ R - C - OH \\ R - C - OH \\ H \\ \end{array} \qquad H_{5}IO_{6} \\ R - C = O \\ H \\ \end{array} \qquad R - C = O \\ H \\ \end{array}$$
(1) 
$$\begin{array}{c} R - C - OH \\ R - C = O \\ H \\ \end{array}$$
(2) 
$$\begin{array}{c} CHO \\ CH(OH) \\ \end{array}$$
(2) 
$$\begin{array}{c} C_{6}H_{5}CO \\ C_{6}H_{5}CO \\ C_{6}H_{5}CHOH \\ H \\ \end{array}$$
(3) 
$$\begin{array}{c} C_{6}H_{5}CO \\ C_{6}H_{5}CHOH \\ H \\ \end{array}$$
(4) 
$$\begin{array}{c} C_{1}E O \\ C_{1}E O \\ C_{1}E O \\ H \\ \end{array}$$
(5) 
$$\begin{array}{c} CH_{2}OH \\ CH_{2}OH \\ CH_{2}OH \\ \end{array}$$
(6) 
$$\begin{array}{c} R - CH - OH \\ CHO \\ CH_{2}OH \\ \end{array}$$
(7) 
$$\begin{array}{c} CHO \\ CH_{2}OH \\ CHO \\ CH_{2}OH \\ \end{array}$$
(8) 
$$\begin{array}{c} COOH \\ CHO \\ CHO \\ CH_{2}OH \\ \end{array}$$
(9) 
$$\begin{array}{c} COOH \\ CHO \\ CHO \\ CHO \\ CHO \\ CHO \\ CHO \\ \end{array}$$
(9) 
$$\begin{array}{c} CH_{3}-CO \\ CH_{3}-CO \\ CHO \\ CHO \\ CHO \\ \end{array}$$
(9) 
$$\begin{array}{c} CH_{3}-CO \\ CHO \\ CHO \\ CHO \\ CHO \\ \end{array}$$
(9) 
$$\begin{array}{c} R - CH - OH \\ - OH \\ CHO \\ CHO \\ \end{array}$$
(9) 
$$\begin{array}{c} R - CH - OH \\ - CHO \\ CHO \\ CHO \\ \end{array}$$
(9) 
$$\begin{array}{c} R - CH - OH \\ - CHO \\ CHO \\ CHO \\ \end{array}$$
(9) 
$$\begin{array}{c} R - CH - OH \\ - CHO \\ - CHO \\ - CHO \\ - CHO \\ \end{array}$$
(9) 
$$\begin{array}{c} R - CH - OH \\ - CHO \\ - CHO$$

HCHO (from CH<sub>2</sub>OH). The formaldehyde, formic acid and other oxidised product are not further oxidised by periodic acid.

Since the H<sub>5</sub>IO<sub>6</sub> can be very easily estimated. Thus, it can be very easily ascertained the amount of H<sub>5</sub>IO<sub>4</sub> consumed by the method of titration by I<sub>2</sub>. Similarly, HCHO, HCOOH can be estimated. Eg :- HCHO by dimedone. Thus, in this way we may know the complete structure of the compound.

Mechanism:- It is used either as neutral or slightly acidic aqueous solution. It reacts by the intermediate i or ii.



Differentiation between glucose and fructose.

 $CHO + CH(OH) + CH(OH) + CH(OH) + CH(OH) + CH_2OH$ Glucose 5H₅IO<sub>6</sub> 5HCOOH + HCHO $CH_2OHCO + CH(OH) + CH(OH) + CH(OH) + CH_2OH$ Fructose  $4H_5IO_6$ CH<sub>2</sub>OH – COOH + 3HCOOH + HCHO

Lead tetra acetate:-

Pb(CH<sub>3</sub>COO)<sub>4</sub> or Pb(ACO)<sub>4</sub>

 $Pb_{3}O_{4} + CH_{3}COOH \longrightarrow Pb(CH_{3}COOH)_{4}$ 

Red lead

 $CH_3CO - O - COCH_2$ 

<u>Preparation:-</u> It is prepared by the gradual addition of red lead to a mixture of acetic acid and AC<sub>2</sub>O (anhydride) at 55 to 80<sup>o</sup>c on curling, the reaction product.

 $Pb_3O_4 + 8CH_3COOH \longrightarrow Pb(CH_3COO)_4 + 2Pb(CH_3COO)_2 + 4H_2O$ Red lead

Application:-

Pb(ACO)<sub>4</sub> is generally implied as an acetoxylating methylating and oxidising agent.

<u>Mechanism:-</u> Pb(ACO)<sub>4</sub> on boiling with glacial acetic acid gives Pb(CH<sub>3</sub>COO)<sub>2</sub> and two free acetoxy radicals as shown below.

Lead diacetate Acetate free radical

Pb(CH<sub>3</sub>COO)<sub>4</sub> acetic acid Pb(CH<sub>3</sub>COO)<sub>2</sub> + 2CH<sub>3</sub>COO



The free acetoxy radicals act as dehydrogenation agent in part and in part decompose to CO<sub>2</sub> and free methyl radical. The free methyl radical (CH<sub>3</sub>) abstracts hydrogen from the C – H bonds to give another free radical which takes up

acetoxyl free - radical to give acetoxyl derivation.

 $H - R + CH_3COO \longrightarrow CH_3COOH + R$  $CH_3COO \longrightarrow CH_3 + CO_2^{\uparrow}$ 

Eg:- With toluene the sequence of reactions is as follows.



# (i) <u>As oxidising agent :-</u>

Pb(CH<sub>3</sub>COO)<sub>4</sub> is a very useful oxidising agent for hydro quinones to quinones and 1, 2 glucose to carbonyl compounds as show below.



1:2 – glycols are oxidised at room temperature by Pb(ACO)<sub>4</sub> aldehydes, ketones 8 both are formed according to the structure of the glycols.



#### (ii) As acetoxylating agent:-

It is very useful acetoxylating agent for preparation purpose as applied to compounds containing an active methylene group because the reaction proceeds at a low temperature without any side reaction.

- (a)  $CH_3COCH_3 \xrightarrow{Pb(ACO)_4} CH_3COOCH_2 CO CH_3$ Acetone +
- $\begin{array}{c} CH_{3}COOCH_{2}-CO-CH_{2}-COOCH_{3}\\ (b) CH_{3}-CO \\ O \\ CH_{3}-CO \end{array} \xrightarrow{Pb(CH_{3}COO)_{4}} CH_{3}COOCH_{2}-CO \\ CH_{3}COOCH_{2}-CO \end{array}$

Acetic anhydride

(c)  $CH_3 COCH_2 - COOC_2H_5$   $Pb(CH_3COO)_4$ Ethyl acetoacetate  $CH_3 - CO - CH - COOC_2H_5$  $H_3COOC$ 

<u>N – Bromo succinimide (NBS) :-</u>



#### Preparation:-

It is preposed by adding bromine to an ice, cold solution of succinimide in alkali when the reagent precipitates immediately.



# Application (uses):-

(A) NBS – is mainly used as a brominating reagent for the allylic and benzylic compounds (whol – ziegler reaction). This reaction is carried out in CCl<sub>4</sub>. Since the resulting succinimide is insoluble in CCl<sub>4</sub>.

Ziegler in 1942 introduced NBS as a selective brominating agent since it normally brominates the ethylenic compounds in the allylic position.

- 
$$CH_2$$
 -  $CH = CH_2 + CH_2 \cdot CO$   
Allyl group  
 $CH_2 \cdot CO$   
 $NBr CCl_4$   
 $CH_2 \cdot CH - CH = CH_2 + CH_2 CO$   
 $CH_2 CO$   
 $CH_2 CO$   
 $CH_2 CO$ 

<u>Mechanism :-</u> Free radical mechanism. <u>Initiation:-</u>



Propagation:-

Step - 2:-  $CH_2 - CH = CH_2 + Br \longrightarrow - CH - CH = CH_2 + HBr$ Step - 3:-  $-CH - CH = CH_2 + Br_2 \rightarrow - CH - CH = CH_2 + Br$ 

The allylene free radical formed in step – 2 is an irrepressible section and stabilized through resonance.

Here addition of bromine on double bond is not suitable due to low concentration of bromine and hence following reversible reaction does not allow this addition product.

 $\dot{Br}$  + -CH<sub>2</sub> - CH = CH<sub>2</sub>  $\longrightarrow$  -CH<sub>2</sub> -  $\dot{CH}$  - CH<sub>2</sub> Br

#### Examples:-

(a) Preparation of bromo acid ester:-

NBS react with methyl crotonate to form 3 – bromo crotonate which is a valuable synthetic reagent and is used in reformatsky reaction eg;- in the synthesis of vitamin A.  $CH_3 CH = CHCOOCH_3 + >NBr \longrightarrow CH_2 - Br - CH = CH \cdot COOCH_3 + >NH$ 

 $CH_3 CH = CHCOOCH_3 + 2NBr \longrightarrow CH_2 - Br - CH = CH \cdot COOCH_3 + 2NBr \longrightarrow CH_2 - Br - CH + Br$ 

- (b) In the conversion of vitamin  $A_1 + A_2$ .
- (c) In the commercial production of cortisone.
- (d) In the commercial production of vitamin D<sub>3</sub>.
- (e) NBS is also used during the synthesis of some important organic natural products such as reserpine, colchicine, patulin, etc.

 (f) Allylic bromination with NBS is very useful for converting a monosaturated compound in to diene and a diene in to triene.



(g) NBS also provides a means of degrading the olefinic compounds by splitting of the carbon atoms, viz.

 $CH_3 - CH_2 -$ 

<u>NBS</u>, CH<sub>3</sub>- CH<sub>2</sub>CH ⋅ Br · CH = CH<sub>2</sub> $\xrightarrow{\text{KOH}}$ CH<sub>3</sub>- CH = CH - CH = CH  $\xrightarrow{O_3}$  CH<sub>3</sub>- CHO

(h) It must be noted that NBS may also produce addition product is addition to substitution product but the yield is very small under ordinary condition.

However, is presence of tetra alkyl ammonium salts addition product is the main product.



(B) As an oxidising agent:-

Like other oxidising agents, NBS oxidises primary alcohol in to aldehydes and secondary alcohol in to ketones.

 $C_2H_5OH + > NBr \longrightarrow CH_3CHO + > NH + HBr$ 

 $(CH_3)_2CHOH + > NBr \longrightarrow (CH_3)_2CO + > NH + HBr$ 

# (C) Other reactions :-

Barakat (1955) and Luck (1957) showed that  $\alpha$  – amino acids prepared and proteins are decarboxylated on fixation with NBS on aqueous solution.

 $CH_3 \cdot CH(NH_2) \cdot COOH$  <u>NBS</u>  $CH_3 CHO + CO_2 + NH_3$ 

# <u>"Periodic acid (HIO<sub>4</sub>·2H<sub>2</sub>O)":-</u>

It is very useful oxidising agent used in any synthetic work. It is used for the oxidation of 1:2 diol,  $\alpha$  – hydroxy carbonyl compound and carbonyl compound in to aldehyde, ketone and acid depending upon the nature of the compound.

Preparation:-

 $2\text{HClO}_4 + \text{I}_2 \longrightarrow 2\text{HIO}_4 + \text{Cl}_2$ 

Perchloric acid

**Application:-**

Oxidation purposes as well as in structure elucidation.

(1) 
$$\begin{array}{ccc} H & H \\ R - C - OH & H O_4 \cdot 2H_2 O \\ R - C - OH & H \end{array} \xrightarrow{H} R - C = O + R - C = O \\ H \\ H \end{array}$$

(2) 
$$(CHOH)_4$$
  $HIO_4 \cdot 2H_2O$   $5HCOOH + HCHO^{-1}$   
 $CH_2 OH$ 

(3) 
$$C_6H_5 - CO HIO_4 \cdot 2H_2O C_6H_5COOH + C_6H_5CHO C_6H_5 - CHOH$$

$$(4) \quad \begin{array}{c} CH_3 - CO \\ CH_3 - CO \end{array} \xrightarrow{HIO_4 \cdot 2H_2O} \quad CH_3COOH + CH_3COOH \cdot \\ \end{array}$$

 $R - CH - OH + CHOH + CHOH + CHOH + CH_2OH will consume$ 4 – moles of periodic acid to give R'CHO (from R'CHOH), HCOOH (from CHOH) and HCHO (from CH<sub>2</sub>OH) and HCHO (from CH<sub>2</sub>OH). The formaldehyde formic acid and other oxidised product are not further oxidised by periodic acid.

Since, the  $H_5IO_6$  can be very easily estimated. Thus, it can be very easily ascertained the amount of  $HIO_4 \cdot 2H_2O$ consumed by the method of titration by  $I_2$ . Similarly HCHO.HCOOH can be estimated eg:- HCHO by dimedone. Thus, in this way we know the complete structure of the compound.

#### Mechanism:-

It is used either as neutral or slightly acidic aqueous solution. It reacts by the intermediate i or ii.



#### Analytical uses:-

Differentiation between glucose and fructose.

 $\label{eq:choh} CHOH+CHOH+CHOH+CHOH+CHOH+CHOH+CHOH+SCOOH\\ Glucose$ 

 $CH_{2}OH - CO \rightarrow CHOH + CHOH \rightarrow CHOH \rightarrow CH_{2}OH + 4HIO_{4} \cdot 2H_{2}O$  $\longrightarrow HCHO + 3HCOOH + COOH - CH_{2}OH$ 

#### Lead tetra – acetate:-

 $Pb(CH_{3}COO)_{4} \text{ or } Pb(ACO)_{4}.$   $Pb_{3}O_{4} + CH_{3}COOH \longrightarrow Pb(CH_{3}COO)_{4}$ <u>"Preparation":-</u>

It is prepared by the gradual addition of red lead to a manufacture of acetic acid and AC<sub>2</sub>O (anhydride) at 55 to  $86^{\circ}$ c on cooling the reaction product. Pb(ACO)<sub>4</sub> separates out which can be recrystallised from acetic acid. Pb<sub>3</sub>O<sub>4</sub> + 8CH<sub>3</sub>COOH  $\longrightarrow$  Pb(CH<sub>3</sub>COO)<sub>4</sub> + 2Pb(CH<sub>3</sub>COO)<sub>2</sub> + 4H<sub>2</sub>O

Red lead

### Application:-

Pb(ACO)<sub>4</sub> is generally employed as on acetoxylating and oxidising agent.

# Bromine (Br<sub>2</sub>) :-

Bromine is a deep – red, only liquid with a shape smell it is toxic.

#### Uses:-

Bromine is used in many are as such as agricultural chemicals, dyestuffs, insecticides pharmaceuticals and chemicals intermediates. Some users are being phased out for environment reason, but new uses continued to be found. Bromine compounds can be used as flame retardants. They are added to furniture from plastic casing for electrons and textiles to more than less flammable. However, the use of bromine as from retardant has been phased out in USA bcz of toxicity concerns.

(i) Treatment of alkene with Br<sub>2</sub> to give vicinal dibromides.



- (iii) It is used in recognition of substances which react with Br<sub>2</sub>.
- (a) Bromine water is commonly used to test for the presence of alkene which contains a double covalent bond which reacts with the bromine water which change its colour form an intense yellow to colourless solution.
- (b) Bromine water is also commonly used to check for the presence of an aldehyde group in compounds. In this solution as well as the colour of bromine water is changed to colourless from yellow (oxidation process).

 $RCHO + H_2O \quad Br_2 \quad R - COOH + 2HBr$