

[USE OF REAGENTS]

[B.sc – III (HONS)]

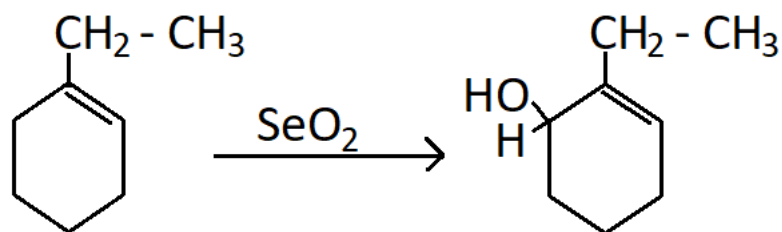
DR. SHASHI KUMAR

[ASSOCIATE PROFESSOR]

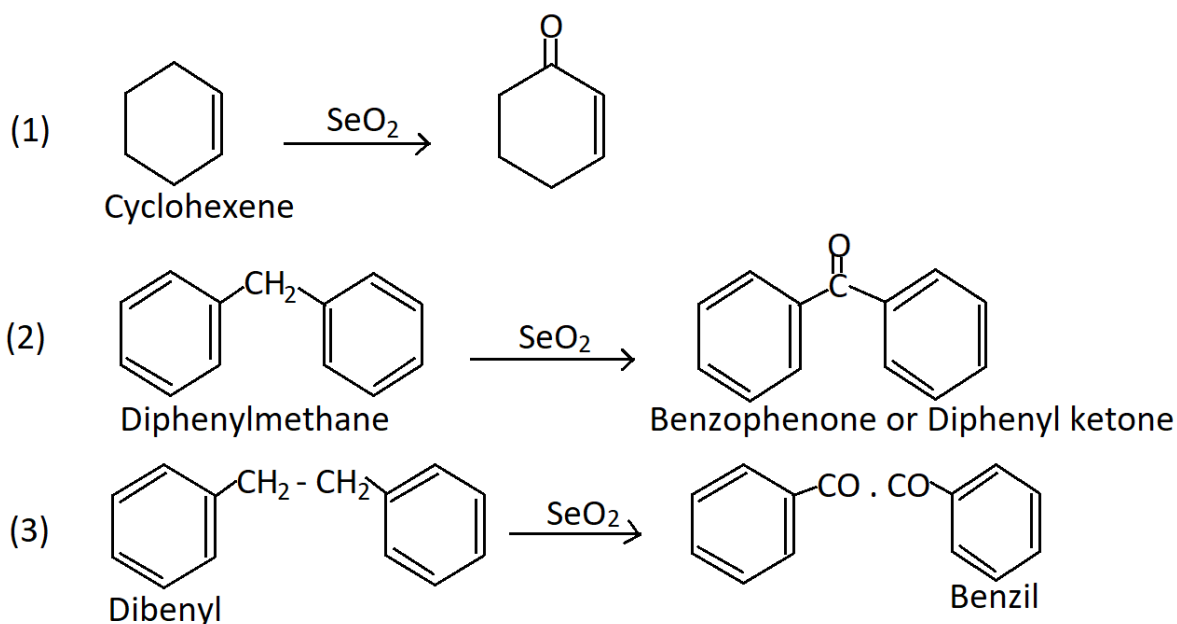
[HOD DEPARTMENT OF CHEMISTRY, G.J COLLEGE RAMBAG BIHTA (PATNA)]

[AUTHOR, GYAN PRAKASH]

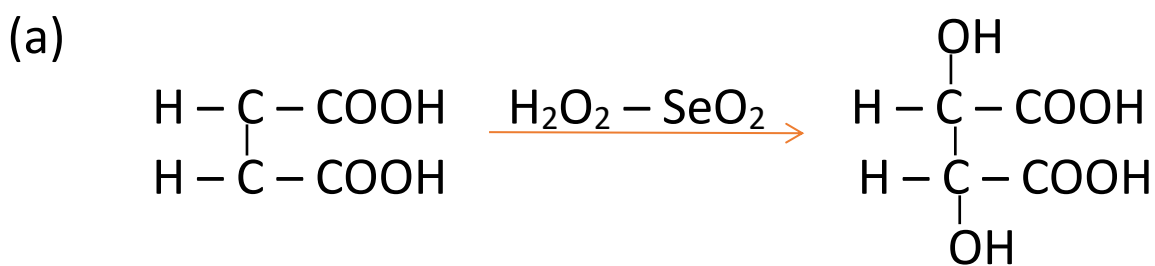
[22/12/2021]



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



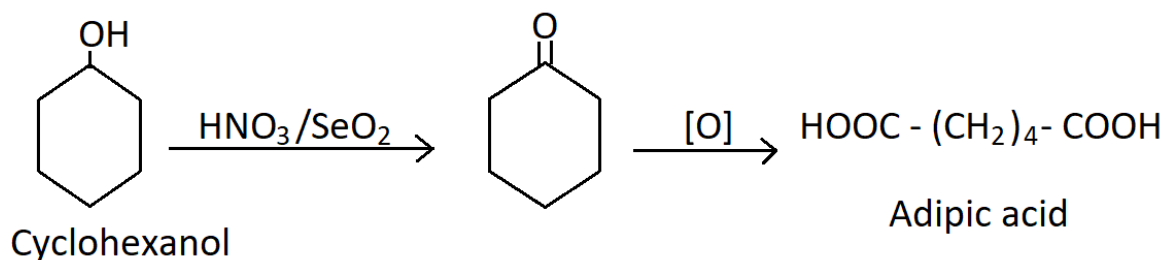
(3) As a catalyst :- SeO_2 catalyst some unsaturated compound to convert it into hydroxy compound by H_2O_2 .



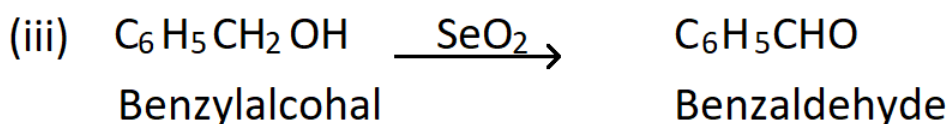
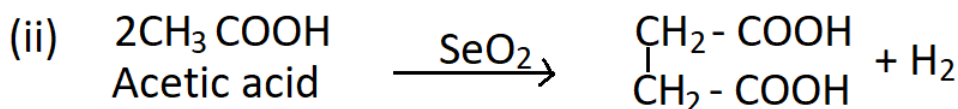
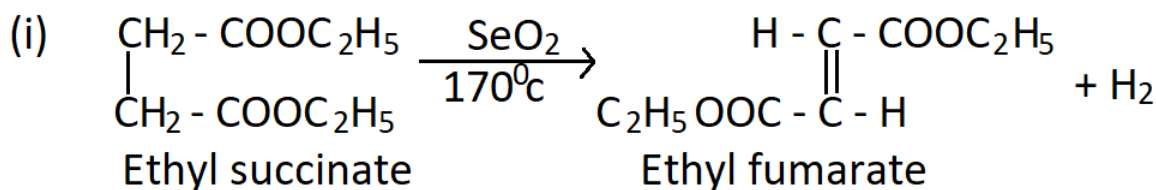
Maleic acid

Tartaric acid

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

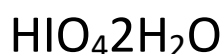
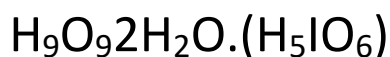


(4) In the dehydrogenation:-



“Periodic acid”

Introduction:-

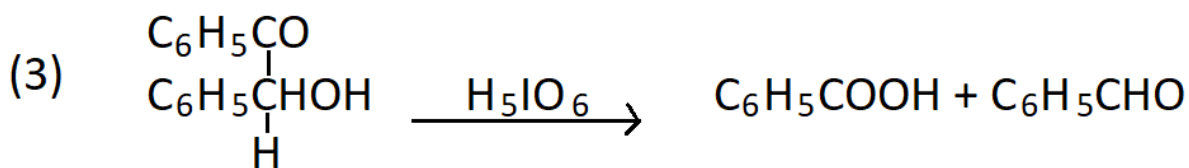
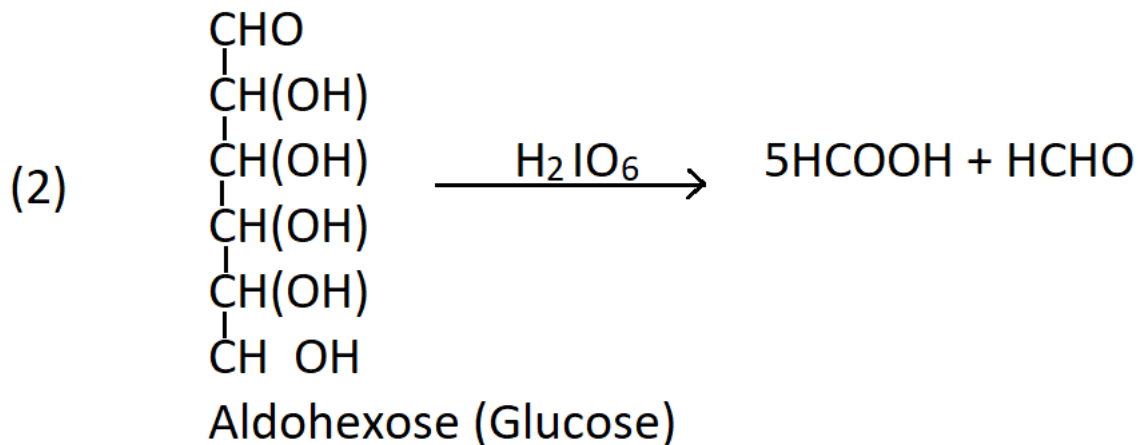
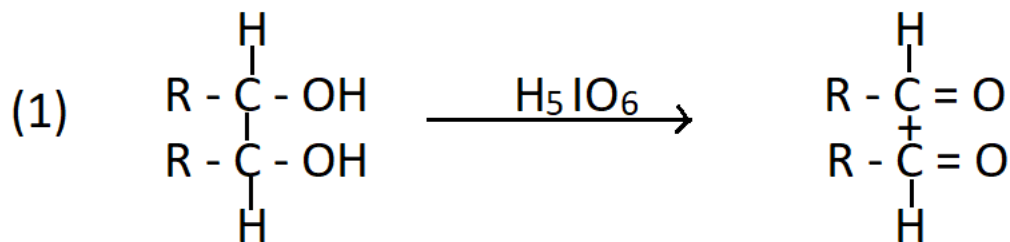


Very useful oxidising agent used in analytic and synthetic work. It is used for the oxidation of 1:2 diol α – hydroxy carbonyl compound and dicarbonyl compound into alkyl, ketone and acid depending upon the nature of the compound.

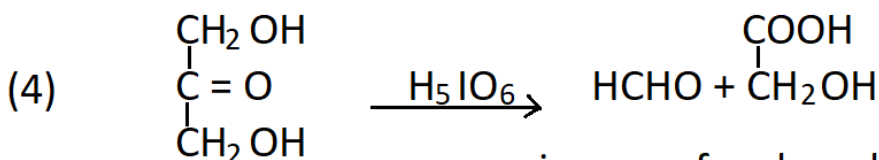


Perchloric acid (lq)

Application:- Oxidation purposes as well as in structure elucidation.

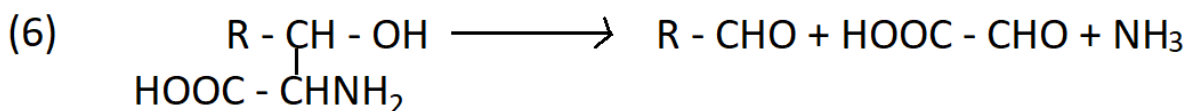
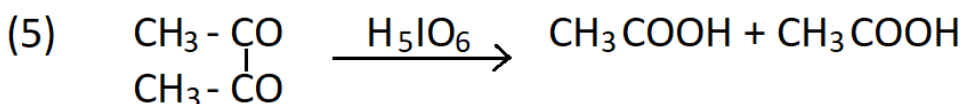


α - Hydroxyl carbonyl compound



is case of carbonyl only one charge takes place instead of two

α - hydroxy carbonyl compound

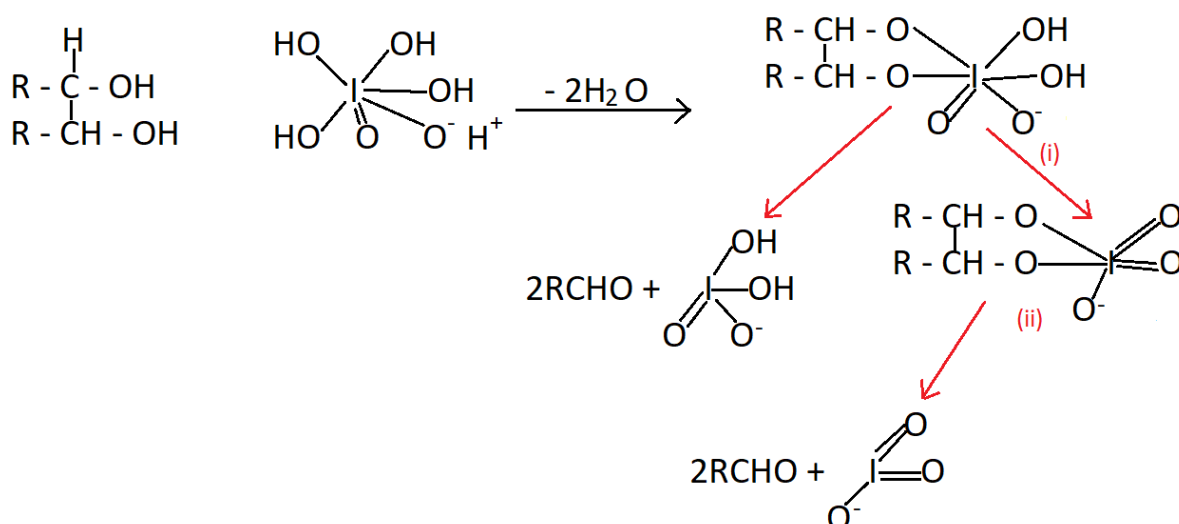


Eg:- $\begin{array}{c} | \\ \text{R} - \text{CH} - \text{OH} \\ | \\ \text{CHOH} \\ | \\ \text{CHOH} \\ | \\ \text{CHOH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ will consume 4 - moles of periodic acid to give R'CHO (from R'CHOH), HCOOH (from CHOH) and HCHO (from CH₂OH) and

HCHO (from CH₂OH). The formaldehyde, formic acid and other oxidised product are not further oxidised by periodic acid.

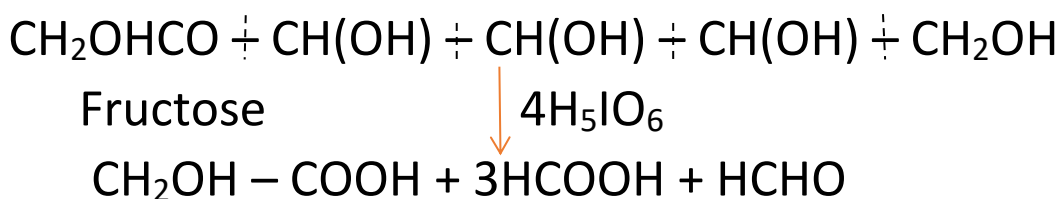
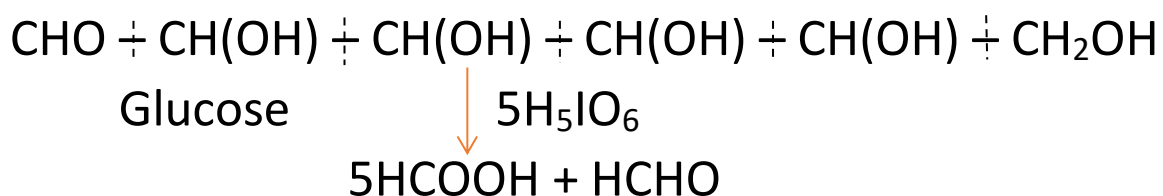
Since the H₅IO₆ can be very easily estimated. Thus, it can be very easily ascertained the amount of H₅IO₄ consumed by the method of titration by I₂. Similarly, HCHO, HCOOH can be estimated. Eg :- HCHO by dimedone. Thus, in this way we may know the complete structure of the compound.

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

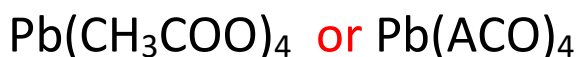


Analytical rules:-

Differentiation between glucose and fructose.



Lead tetra acetate:-



Red lead



Preparation:- It is prepared by the gradual addition of red lead to a mixture of acetic acid and AC_2O (anhydride) at 55 to 80⁰c on curling, the reaction product.

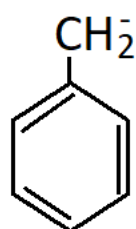
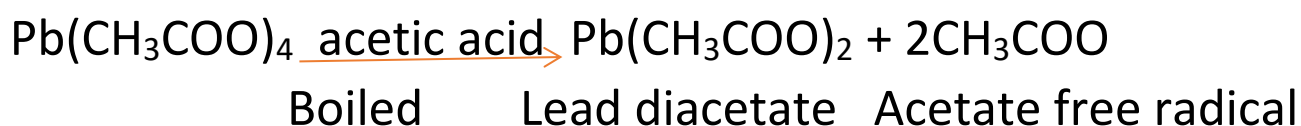


Red lead

Application:-

$\text{Pb}(\text{ACO})_4$ is generally implied as an acetoxyating methylating and oxidising agent.

Mechanism:- $\text{Pb}(\text{ACO})_4$ on boiling with glacial acetic acid gives $\text{Pb}(\text{CH}_3\text{COO})_2$ and two free acetoxy radicals as shown below.



Benzyl

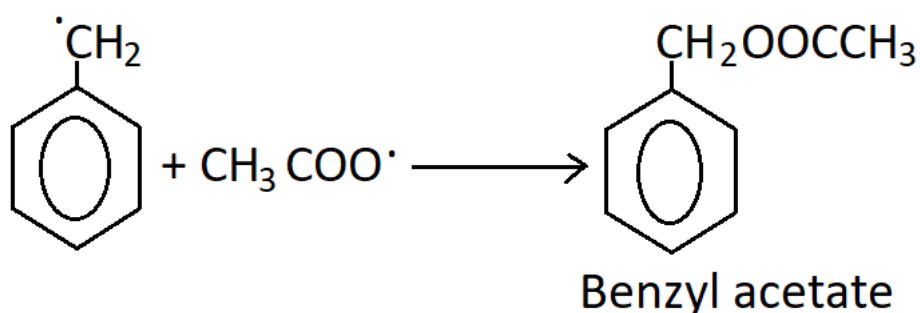
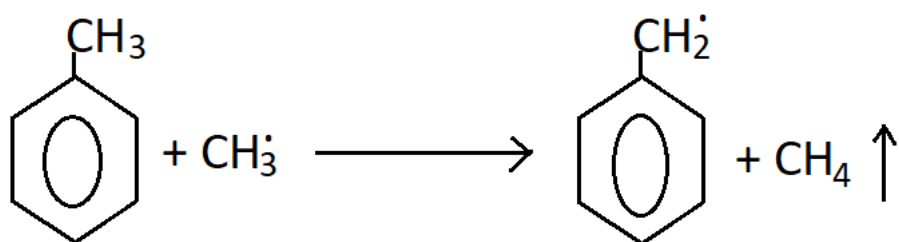
The free acetoxy radicals act as dehydrogenation agent in part and in part decompose to CO_2 and free methyl radical. The free methyl radical (CH_3) abstracts hydrogen

from the C – H bonds to give another free radical which takes up

acetoxy free – radical to give acetoxy derivation.

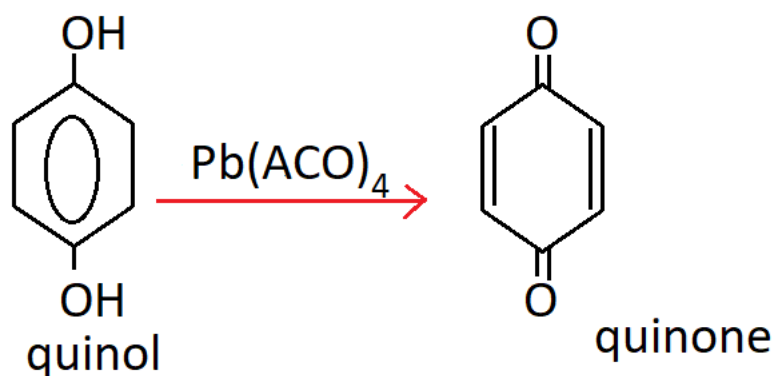


Eg:- With toluene the sequence of reactions is as follows.

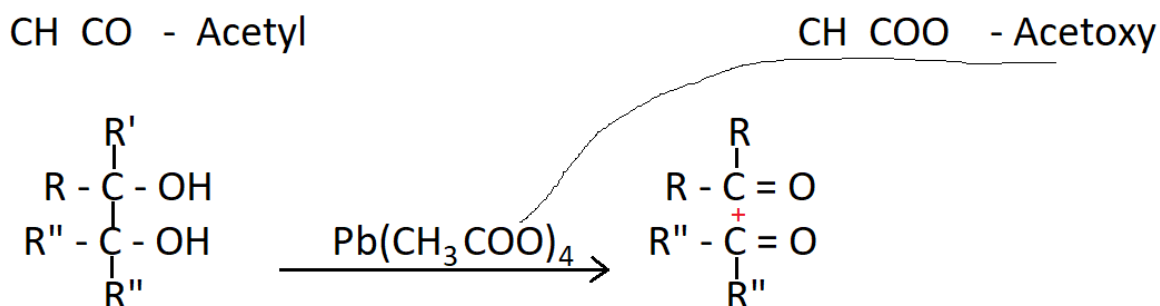


(i) As oxidising agent :-

Pb(CH₃COO)₄ is a very useful oxidising agent for hydroquinones to quinones and 1, 2 glucose to carbonyl compounds as show below.

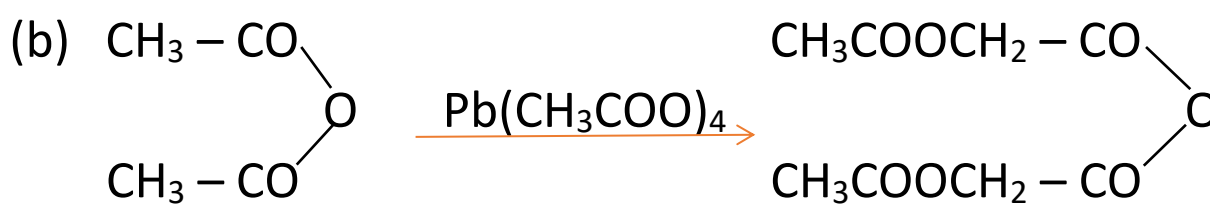
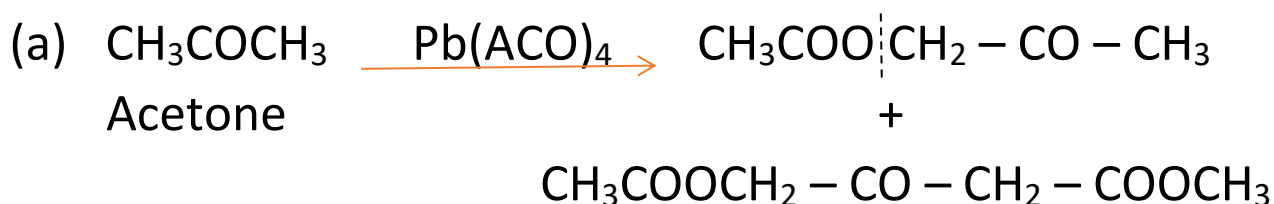


1:2 – glycols are oxidised at room temperature by $\text{Pb}(\text{ACO})_4$ aldehydes, ketones & both are formed according to the structure of the glycols.

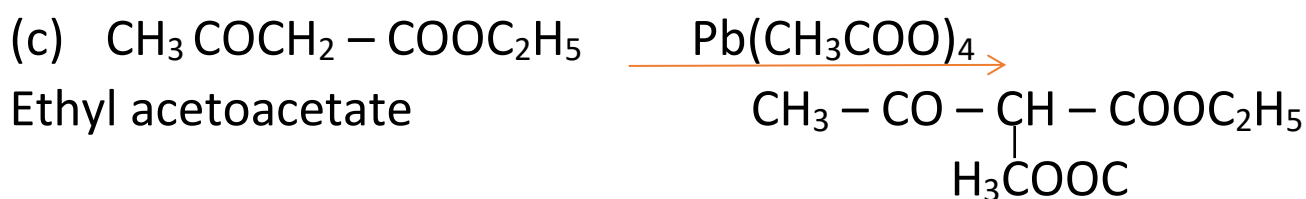


(ii) As acetoxyating agent:-

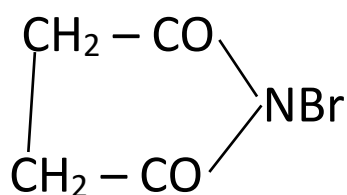
It is very useful acetoxyating agent for preparation purpose as applied to compounds containing an active methylene group because the reaction proceeds at a low temperature without any side reaction.



Acetic anhydride

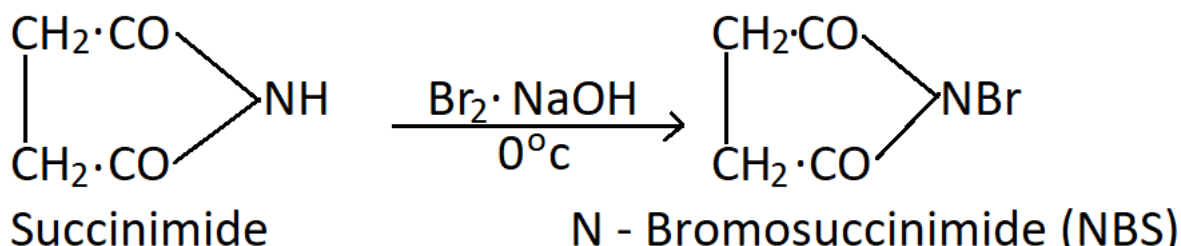


N – Bromo succinimide (NBS) :-



Preparation:-

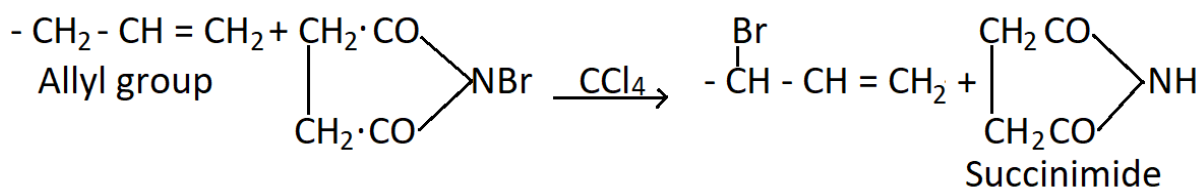
It is prepared by adding bromine to an ice, cold solution of succinimide in alkali when the reagent precipitates immediately.



Application (uses):-

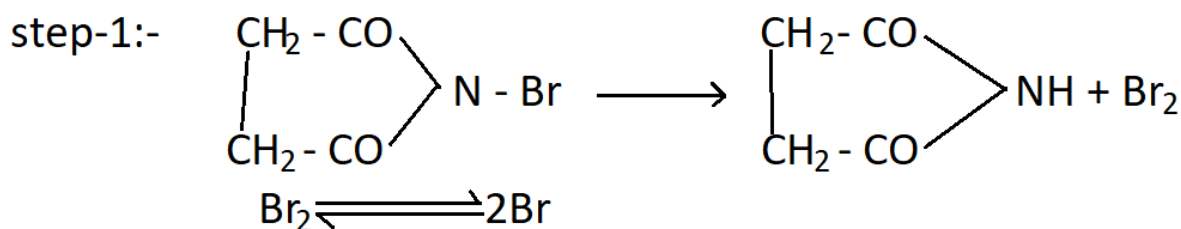
(A) NBS – is mainly used as a brominating reagent for the allylic and benzylic compounds (Whol – Ziegler reaction). This reaction is carried out in CCl_4 . Since the resulting succinimide is insoluble in CCl_4 .

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

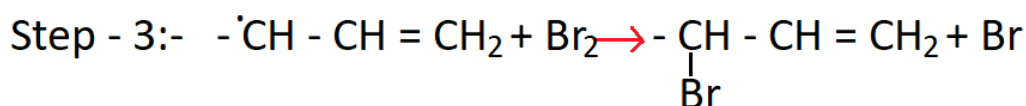
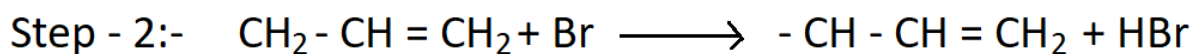


Mechanism :- Free radical mechanism.

Initiation:-

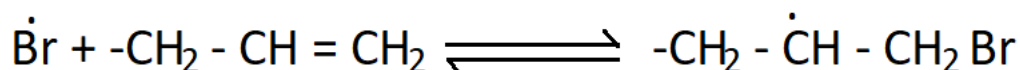


Propagation:-



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

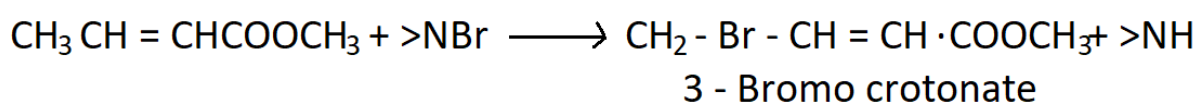
Here addition of bromine on double bond is not suitable due to low concentration of bromine and hence following reversible reaction does not allow this addition product.



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.



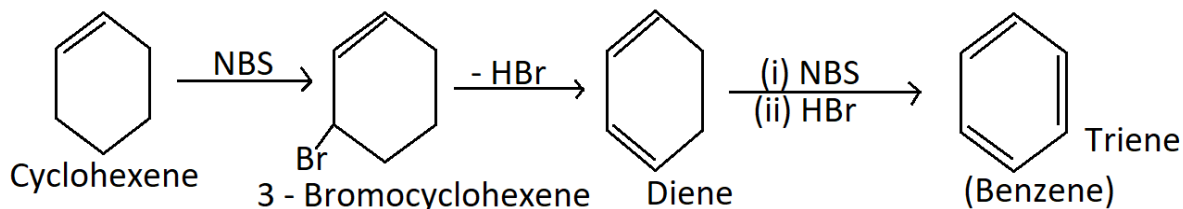
(b) In the conversion of vitamin A₁ + A₂.

(c) In the commercial production of cortisone.

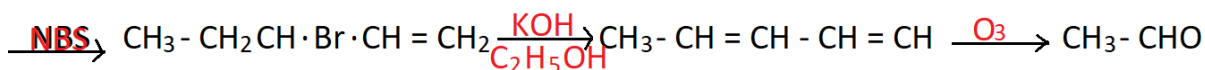
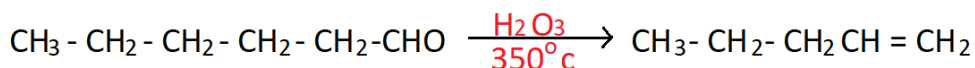
(d) In the commercial production of vitamin D₃.

(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 into a diene and a diene into a triene.

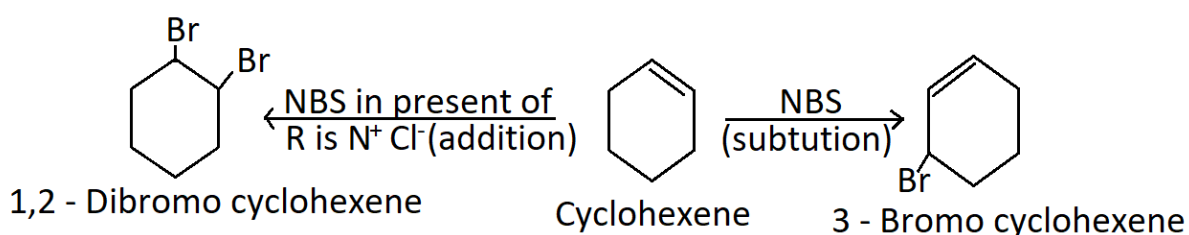


(g) NBS also provides a means of degrading the olefinic compounds by splitting of the carbon atoms, viz.



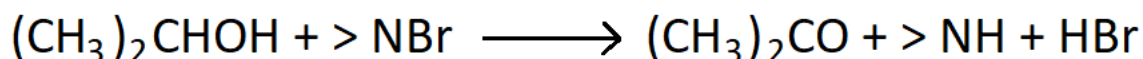
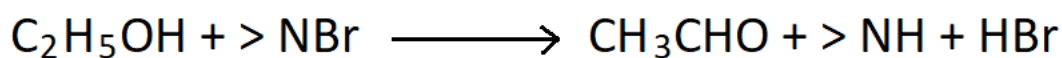
(h) It must be noted that NBS may also produce addition product as well as substitution product but the yield of the addition product is very small under ordinary conditions.

However, in the presence of tetraalkyl ammonium salts, the addition product is the main product.



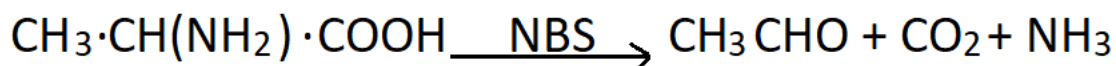
(B) As an oxidising agent:-

Like other oxidising agents, NBS oxidises primary alcohols into aldehydes and secondary alcohols into ketones.



(C) Other reactions :-

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



“Periodic acid ($\text{HIO}_4 \cdot 2\text{H}_2\text{O}$)”:-

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

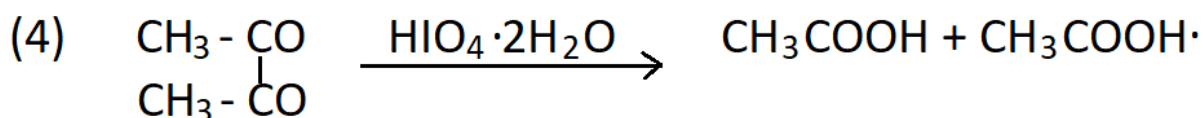
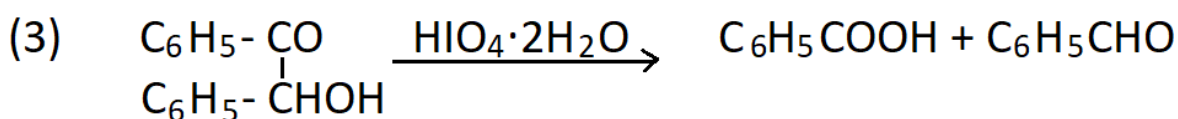
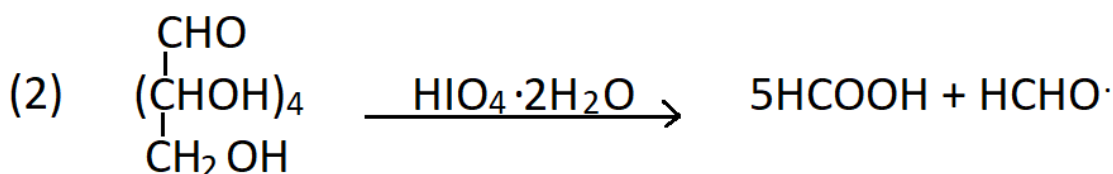
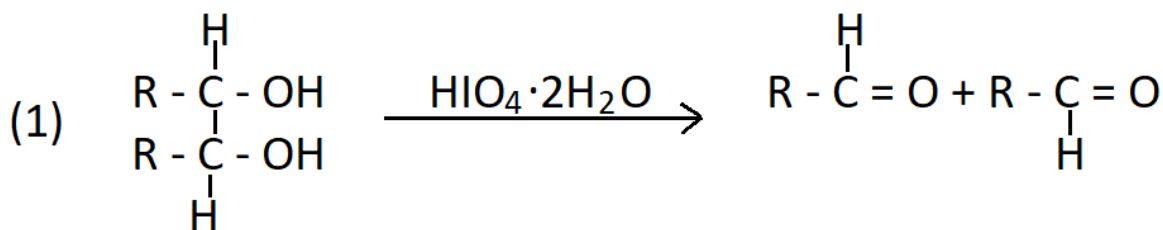
Preparation:-



Perchloric acid

Application:-

Oxidation purposes as well as in structure elucidation.

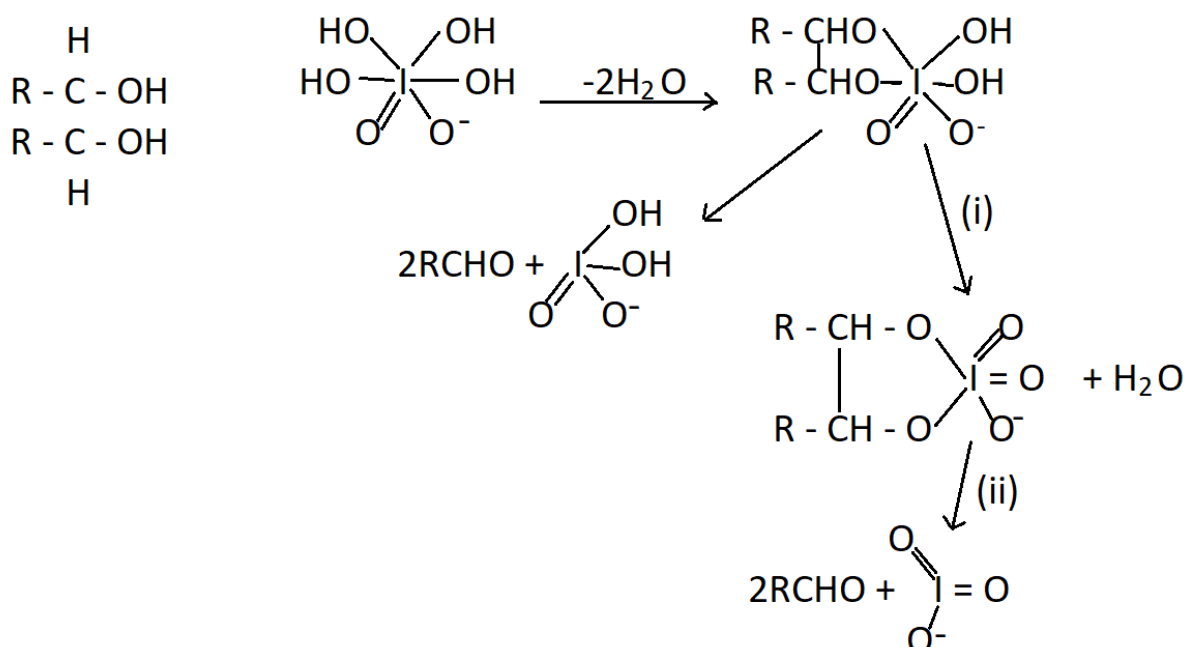


$R - CH - OH + CHOH + CHOH + CHOH + CH_2OH$ will consume 4 – moles of periodic acid to give $R'CHO$ (from $R'CHOH$), $HCOOH$ (from $CHOH$) and $HCHO$ (from CH_2OH) and $HCHO$ (from CH_2OH). The formaldehyde formic acid and other oxidised product are not further oxidised by periodic acid.

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.

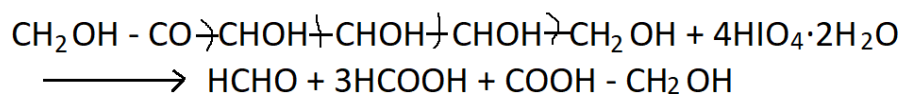
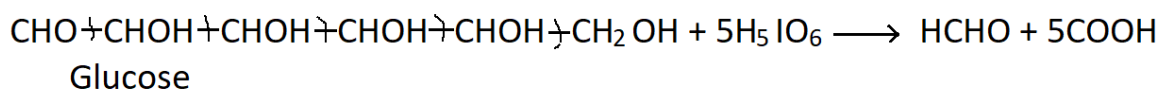
Mechanism:-

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

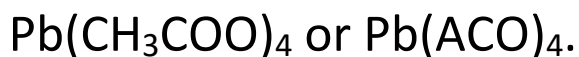


Analytical uses:-

Differentiation between glucose and fructose.

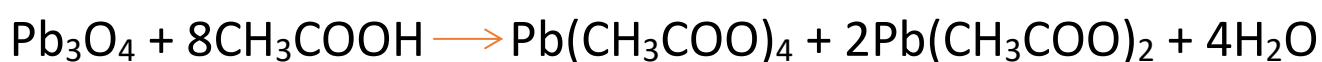


Lead tetra – acetate:-



“Preparation”:-

It is prepared by the gradual addition of red lead to a manufacture of acetic acid and AC_2O (anhydride) at 55 to 86°C on cooling the reaction product. $\text{Pb}(\text{ACO})_4$ separates out which can be recrystallised from acetic acid.



Red lead

Application:-

$\text{Pb}(\text{ACO})_4$ is generally employed as an acetoxylating and oxidising agent.

Bromine (Br_2) :-

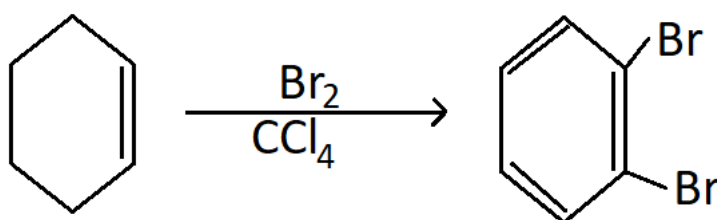
Bromine is a deep – red, only liquid with a sharp smell it is toxic.

Uses:-

Bromine is used in many areas such as agricultural chemicals, dyestuffs, insecticides, pharmaceuticals and chemical intermediates. Some uses are being phased out for environmental reasons, but new uses continue to be found.

Bromine compounds can be used as flame retardants. They are added to furniture from plastic casing for electronics and textiles to make them less flammable. However, the use of bromine as a flame retardant has been phased out in the USA because of toxicity concerns.

(i) Treatment of an alkene with Br_2 to give vicinal dibromides.



(iii) It is used in the recognition of substances which react with Br_2 .

(a) Bromine water is commonly used to test for the presence of an alkene which contains a double covalent bond which reacts with the bromine water which changes its colour from an intense yellow to a 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).

