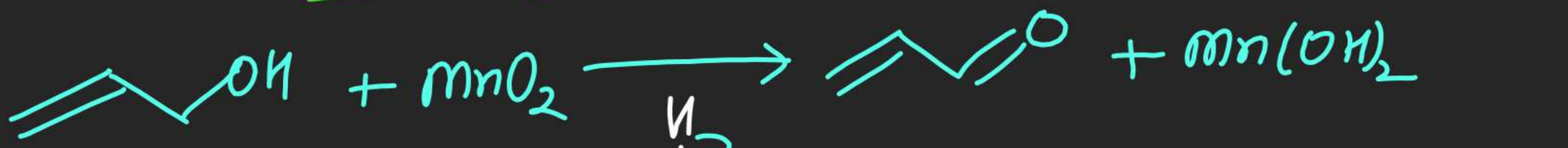
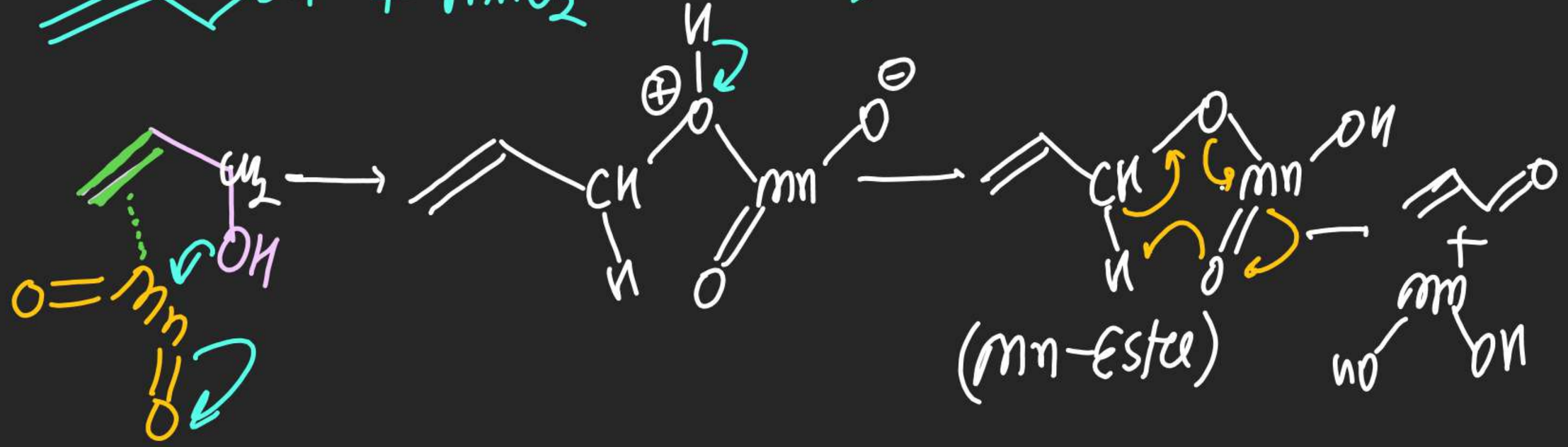
(10) By MnO_2 :-

⇒ Mild Oxidising agent

⇒ MnO_2 Oxidises Allylic & Benzylic 1° & 2° Alcohols

(13) 

Mechⁿ :-



Note: ① MnO_2 interacts with πe^- Cloud of Allylic & Benzylic πe^- density hence alcohol near to this site gets oxidised.

② Formation of Conjugated Product.

(14)

(15)

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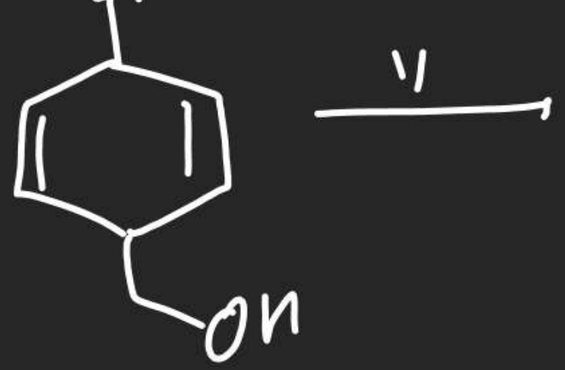
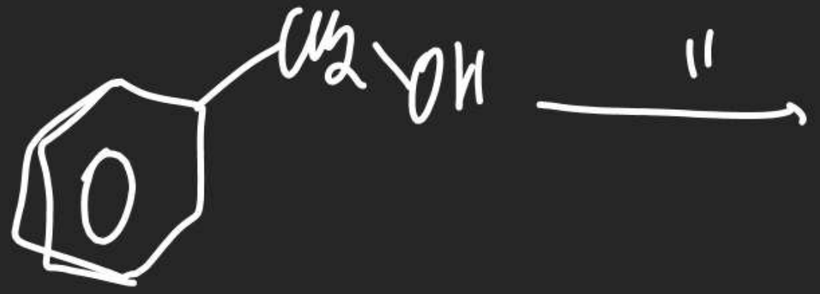
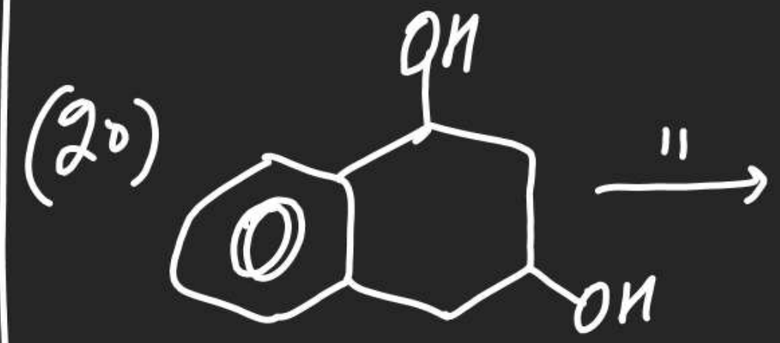
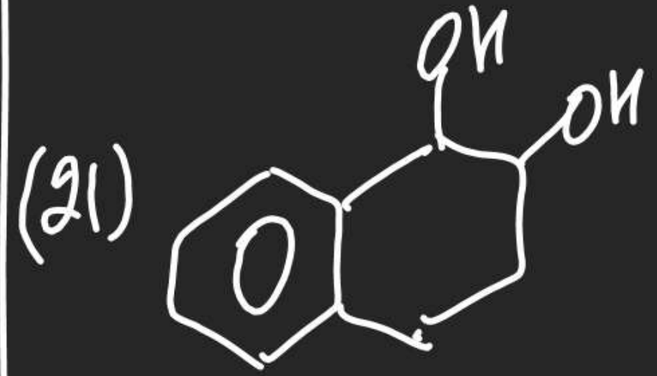
(16) 

(17) 

(18) 

(19) 

(20) 

(21) 

#) By Periodic Acid : [Mala Parade Oxidation] / Per-Iodat cleave :-

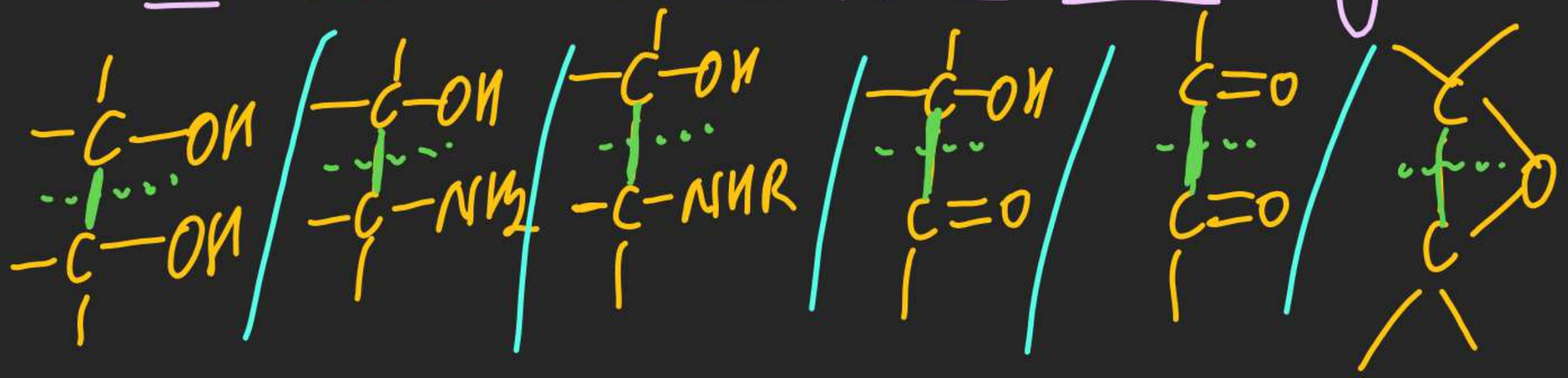
⇒ It's strong oxidising agent

⇒ H_5IO_6

$\downarrow \Delta$

⇒ $HIO_4 + 2H_2O$

⇒ It oxidises vicinal functional groups along with cleavage of C–C Bond.



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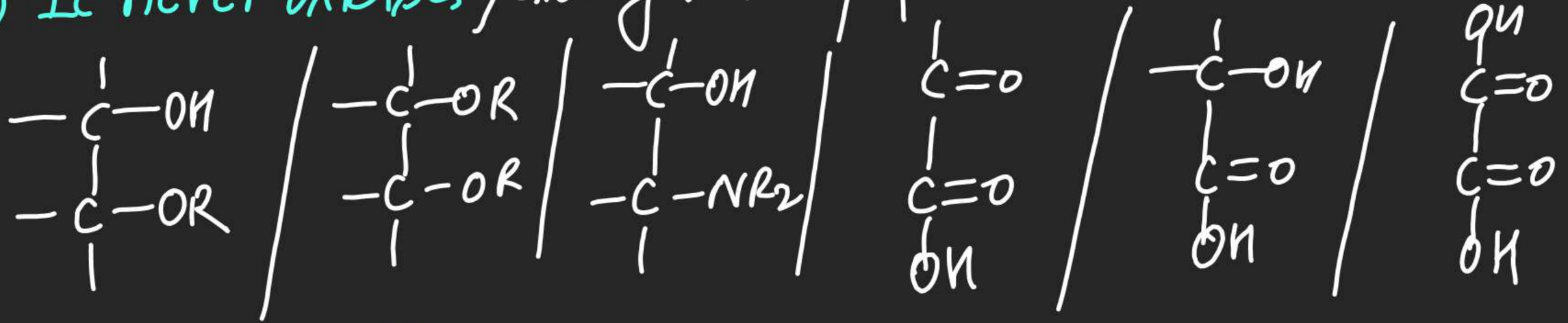
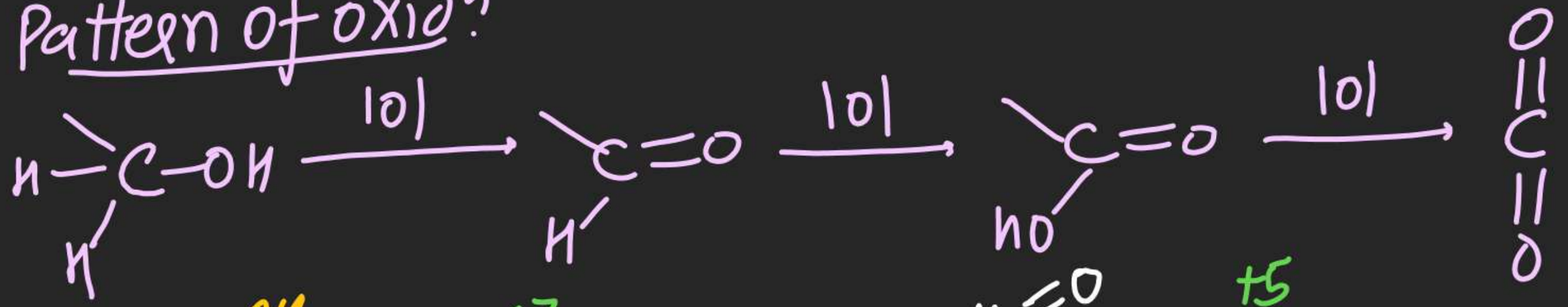
⟹ It never oxidises following vicinal groups.



⟹ Pattern of oxidn:



(1) $CH_2(OH)-CH_2(OH) + HIO_4 \longrightarrow CH_2=O + CH_2=O + HIO_3$

(+7 in HIO_4; +5 in HIO_3)

$HIO_3 \xrightarrow{AgNO_3}$ ∴ $AgIO_3$ (white ppt)

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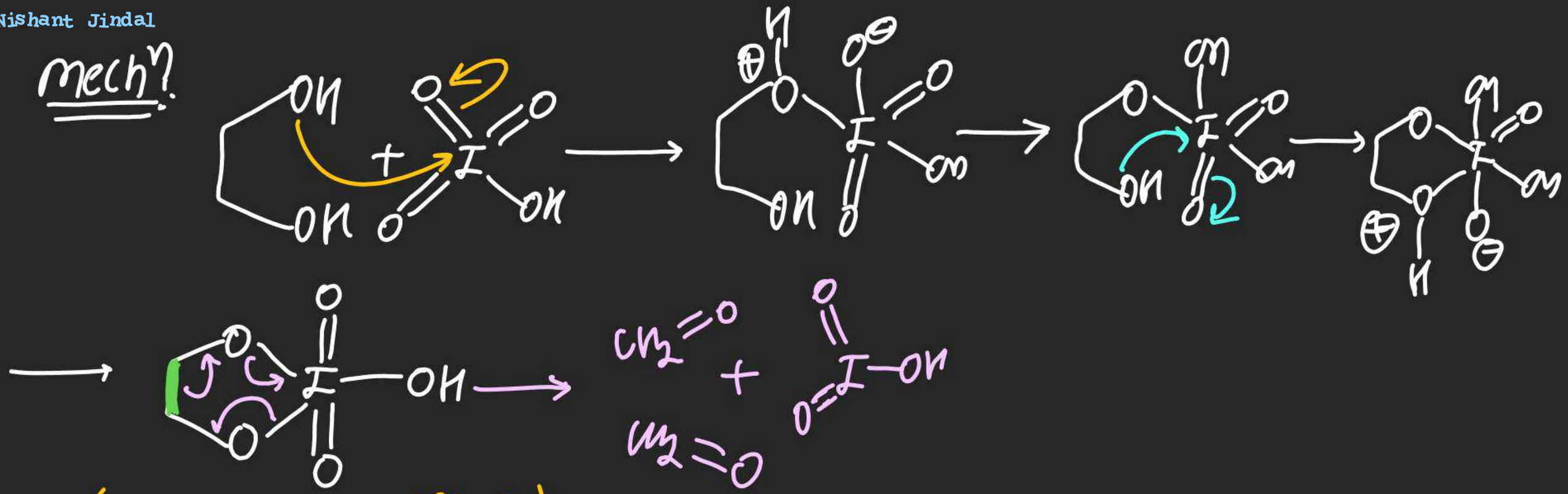
Mech?



(Cyclic Intermidiate)

Note (i) Cyclic Intermidiate

(ii) One vicinal System Consumes 1 mole of HIO_4

(2) $CH_2(OH)-CH(OH)-CH_2(OH)$ + "x" HIO_4 ⟶ "y" $CH_2=O$ + "z" $H-COOH$ + "w" CO_2

(x=2) (y=2) (z=1) (w=0)

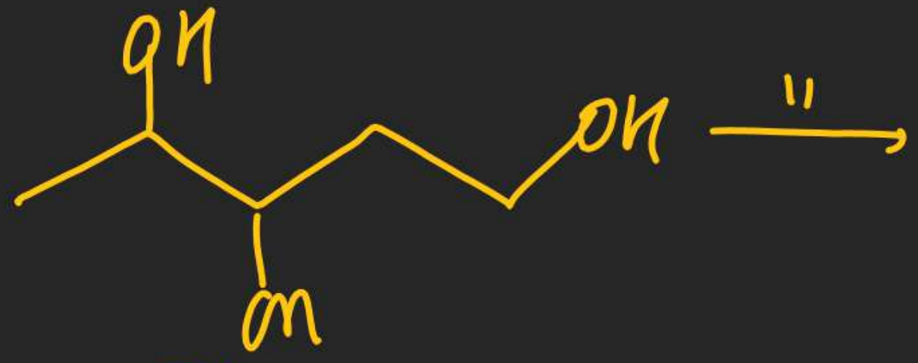
(3) $CH(=O)-CH(OH)-CH_2(OH)$ + "x" HIO_4 ⟶ $CH_2=O$ + $2HCOOH$

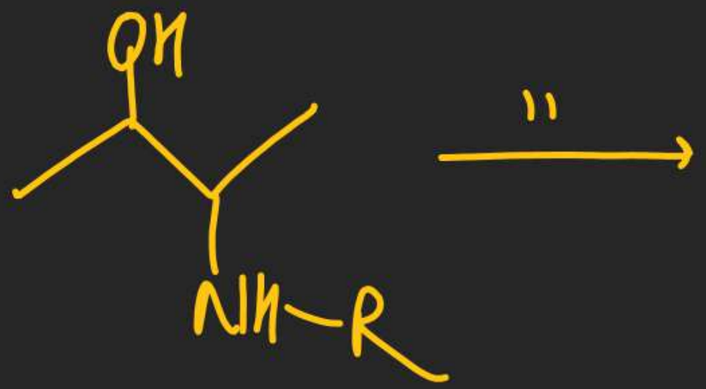
(Acid)

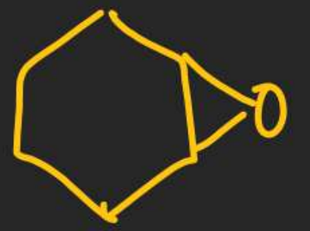
(x=2) (y=1) (z=2) w=0

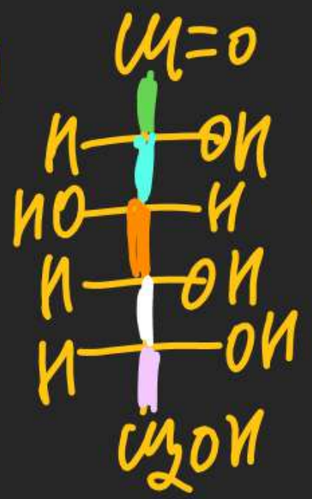
(4) $CH_2(OH)-C(=O)-CH_2(OH)$ + "x" HIO_4 ⟶

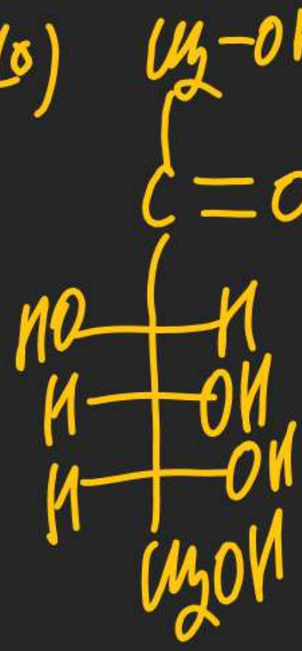
(5) CH_2-OH / $C=O$ / CH_2-OH $\xrightarrow{HIO_4}$

(6)  $\xrightarrow{''}$

(7)  $\xrightarrow{''}$

(8)  $\xrightarrow{''}$

(9)  $\xrightarrow{\text{"x" } HIO_4}$

(10)  $\xrightarrow{\text{"x" } HIO_4}$

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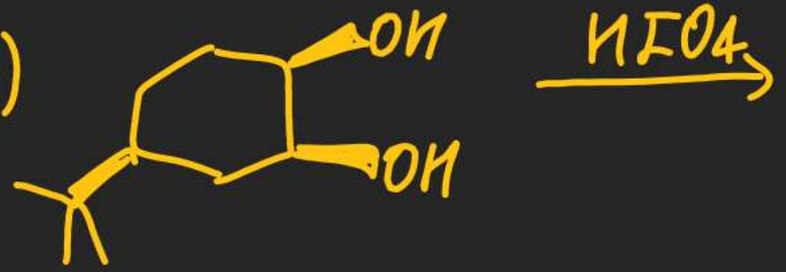
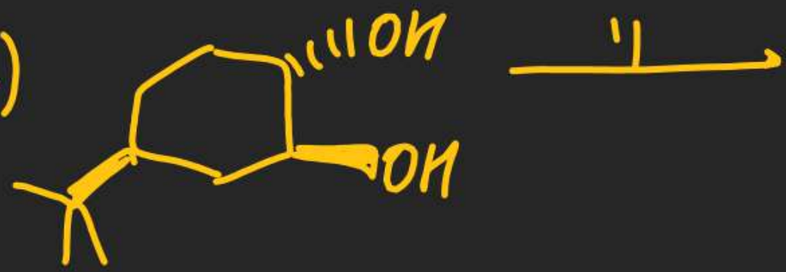
(11) 

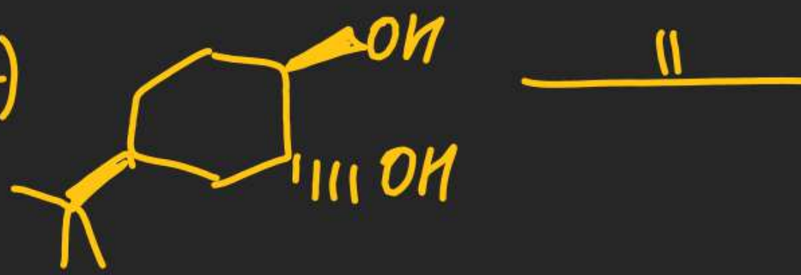
HIO_4 →

(12) 

‖ →

(13) 

‖ →

(14) 

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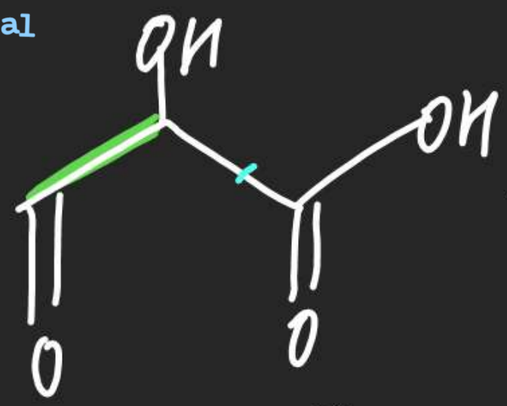
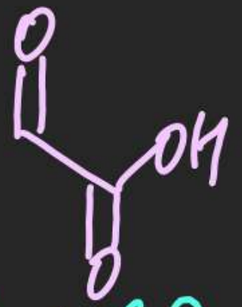
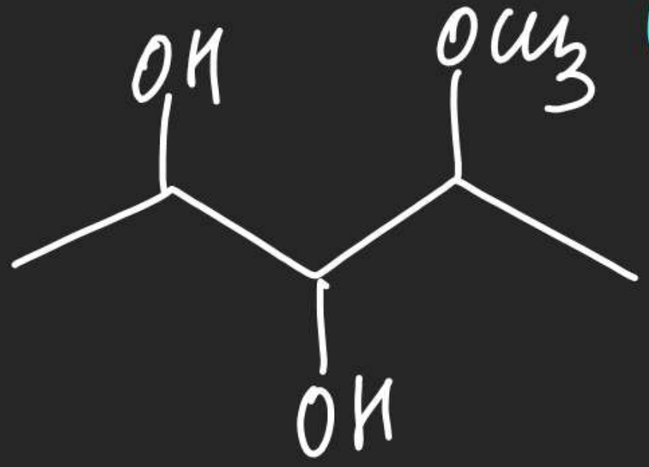
(15)



HIO_4 → H-COOH + 

$Pb(OAc)_4$ (Strong O. Agent) → $2\,H\text{-}COOH + CO_2$

(16)



HIO_4 →

Note: This Reaction is used in POC for distinguishion of Vicinal Functional groups.

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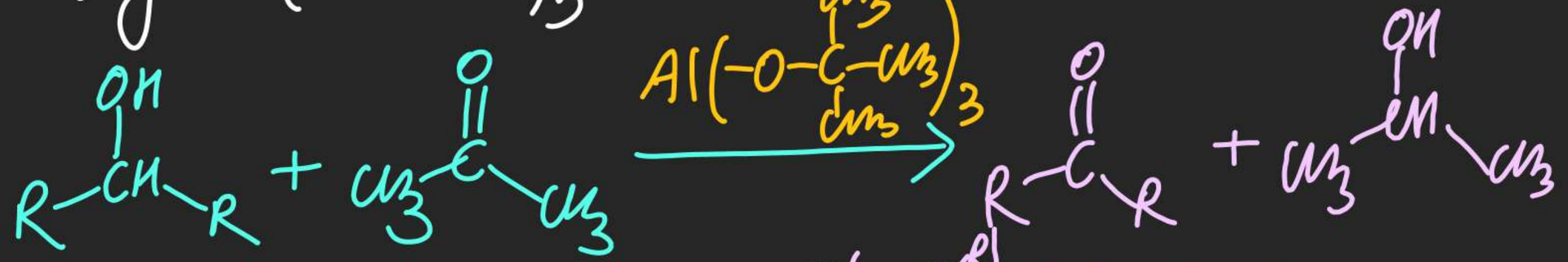
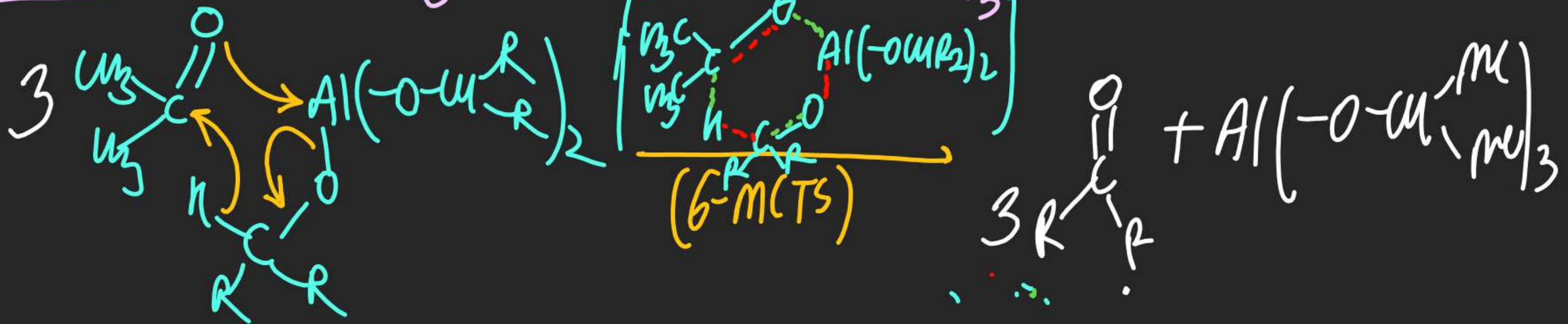
(#) Oppenauer Oxidation:-

⟹ In this oxidation alcohol gets oxidised into Carbonyl compound By using $Al(-O-CMe_3)_3$ in Acetone Solution

(1) 

Mechn:- $Al(-OCMe_3)_3 + 3HO-CHR_2 \longrightarrow Al(-O-CHR_2)_3 + 3Me_3C-OH$



Oxidation of $>C=O$ Compound

Oxidation of Aldehyde only:

(1) By Acidic $K_2Cr_2O_7$

(1) $R-CH=O \xrightarrow[H_2SO_4]{K_2Cr_2O_7} R-COOH + Cr_2(SO_4)_3$

(Orange to Green)

(2) By $KMnO_4$:

(2) $R-C(=O)-H \xrightarrow[Hot]{KMnO_4} R-COOH$

(3) $R-C(=O)-H \xrightarrow[Cold]{KMnO_4} R-COOH$

(Purple to Brown)

(3) By Jone's Reagent:-

(4) $R-CH=O \xrightarrow[H_2SO_4]{CrO_3} R-COOH$ (Orange to Green)

M.M.I.M

(4) By Ammonical Silver Nitrate Solution:- (By Tollen's Reagent)

(Silver mirror Test)

Whenever Silver nitrate solution is taken in alkaline condition ppt of Ag_2O is obtained, which gets dissolved on passing Excess Ammonia

$$2AgNO_3 + 2NaOH \longrightarrow \underset{(ppt)}{Ag_2O} + 2NaNO_3 + H_2O$$

$$Ag_2O + 4NH_3 + H_2O \longrightarrow 2[Ag(NH_3)_2]OH$$

Tollen's Reagent

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Whenever Aldehyde is treated with Tollen's Reagent a Black substance is obtained which on heating becomes shiny & looks like a mirror, deposited on inner wall of glass tube. It is Silver & Test is known as Silver mirror Test

$$R-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}} + 3\overset{\ominus}{O}H \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} + 2H_2O + 2e^{\ominus}$$

$$2\left[Ag(NH_3)_2\right]OH + 2e^{\ominus} \longrightarrow 2Ag + 4NH_3 + 2\overset{\ominus}{O}H \qquad \left(E^{\circ}_{Ag^+/Ag} = +0.80\right)$$

$$R-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-H + 2\left[Ag(NH_3)_2\right]OH + \overset{\ominus}{O}H \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{O} + 2Ag + 2H_2O + 4NH_3$$

(Silver Mirror)

∴

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(5) By Fehling Solution :-

$$R-CH=O + 3OH^{\ominus} \longrightarrow R-COO^{\ominus} + 2e^{\ominus}$$
$$2Cu^{+2} + 2OH^{\ominus} + 2e^{\ominus} \longrightarrow Cu_2O + H_2O$$
$$R-CH=O + 2Cu^{+2}_{Comp} + 5OH^{\ominus} \longrightarrow RCOO^{\ominus} + Cu_2O + H_2O$$

(Blue) (Red)

⟹ Fehling Soln is store in form of two diff-soln

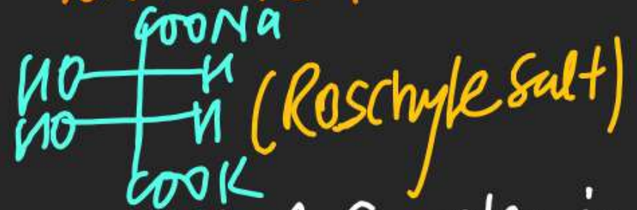
- Fehling Soln-I
- Fehling Soln-II

Fehling Soln-I

Aq. soln of $CuSO_4$

Fehling Soln-II

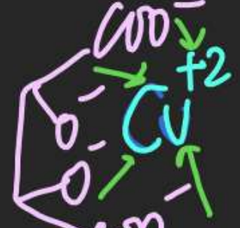
Sodium potassium Tartarate + NaOH



(Rosehyle salt)

When F.S I & II is mixed A Complex is obtained which oxidises R-CHO & Red ppt is obtained.

$$CuSO_4 + \begin{matrix} HO & | & H \\ HO & | & H \\ COOK & | & COONa \end{matrix} + 2NaOH \longrightarrow$$



$$Na_2SO_4 + 2H_2O$$

(Blue colour)

$\therefore$

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(6) By Benedict solution :-

$$R-CH=O + 3OH^{\ominus} \longrightarrow R-COO^{\ominus} + 2e^{\ominus}$$

$$2Cu^{+2}_{Complex} + 2OH^{\ominus} + 2e^{\ominus} \longrightarrow Cu_2O + H_2O$$

$$R-CH=O + 2Cu^{+2}_{Comp} + 5OH^{\ominus} \longrightarrow RCOO^{\ominus} + Cu_2O + H_2O$$

(Blue) (Red)

⟹ Benedict Soln is store in form of two diff-soln

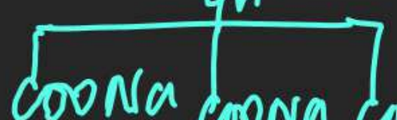
- Benedict Soln-I
- Benedict Soln-II

Benedict Soln-I

Aq. soln of $CuSO_4$

Sodium Citrate + NaOH

or



When B.S I & II is mixed A Complex is obtained which oxidises R-CHO & Red ppt is obtained.

$$CuSO_4 + \text{(COONa, COONa, COONa)} + 2NaOH \longrightarrow \text{(Blue colour)} + Na_2SO_4 + 2H_2O$$

(7) By Schiff's Reagent :-

∴