Aldehydes & Ketones - 1

Introduction : Preparation of Aldehydes & Ketones (Common Method to both)

$$-\overset{O}{\overset{\|}{C}}-$$

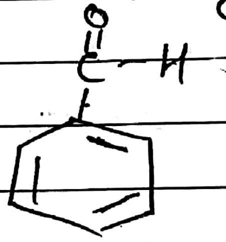
Carbonyl group

Aldehyde	Ketone
$R-\overset{O}{\overset{\|}{C}}-H$	$R-\overset{O}{\overset{\|}{C}}-R'$
Aldehyde	Ketone
Secondary suffix → 'al'	secondary suffix → 'one'

Aldehydes

1) $H-\overset{O}{\overset{\|}{C}}-H$
   methanal
   Formaldehyde

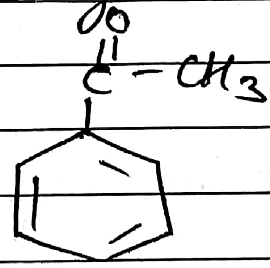
2) $CH_3-\overset{O}{\overset{\|}{C}}-H$
   ethanal
   Acetaldehyde

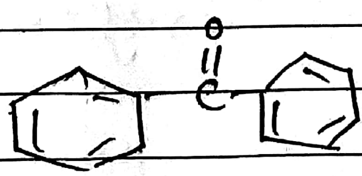
3) 
   Benzaldehyde

Ketones

1) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$
   propanone or (-2one)
   Acetone
   Dimethyl ketone

2) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
   butan-2-one
   Ethyl methyl ketone

3) 
   Acetophenone
   Methyl phenyl Ketone

4) 
   Benzophenone
   Diphenyl Ketone

1 & 4 → Symmetrical Ketone

Preparation of Aldehydes & Ketones

① By oxidation of Alcohols → with :-

i) with acidic $K_2Cr_2O_7$ OR acidic $KMnO_4$ (only Secondary Alcohols)

2° Alcohols ⟶ Ketones

$$CH_3-\underset{}{\overset{OH}{\overset{|}{C}}}H-CH_3 \xrightarrow[\text{OR } KMnO_4/H^+]{K_2Cr_2O_7/H^+} CH_3-\overset{O}{\overset{||}{C}}-CH_3$$

1° Alcohol ⟶ Carboxylic Acid

3° Alcohol ⟶ NO effect

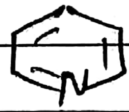
ii) ① P.C.C. (Pyridinium Chlorochromate)

 : CrO_3 : HCl

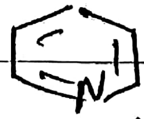
1 : 1 : 2

② Jone's Reagant [$H_2Cr_2O_4$ in aq Acetone]

CrO_3/H_2SO_4, Acetone

③ Collin's Reagant  : CrO_3 : CH_2Cl_2

2 : 1 : 1

④ Sarret's Reagant  : CrO_3 : HCl : CH_2Cl_2

1 : 1 : 1 : 1

⑤ NBS

All ① to ⑤ oxidises

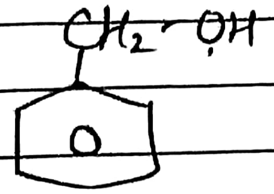
1° Alcohol $\longrightarrow$ Aldehyde

2° Alcohol $\longrightarrow$ Ketones.

$$CH_3-\overset{OH}{\overset{|}{CH_2}} \xrightarrow{PCC} CH_3-\overset{O}{\overset{||}{C}}-H$$

$$CH_3-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{PCC} CH_3-\overset{O}{\overset{||}{C}}-CH_3$$

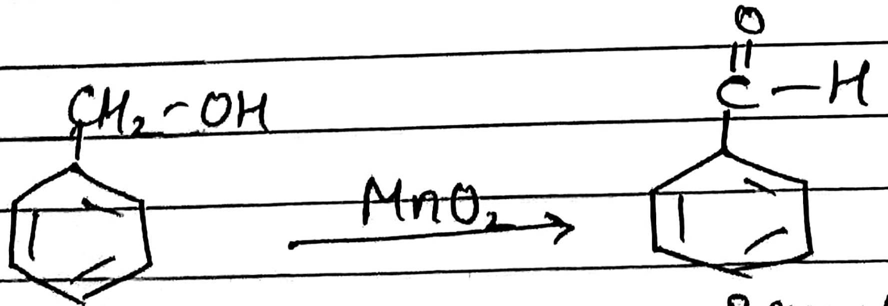
iii) with MnO_2 : oxidises benzylic or allylic alcohols



benzylic alcohols

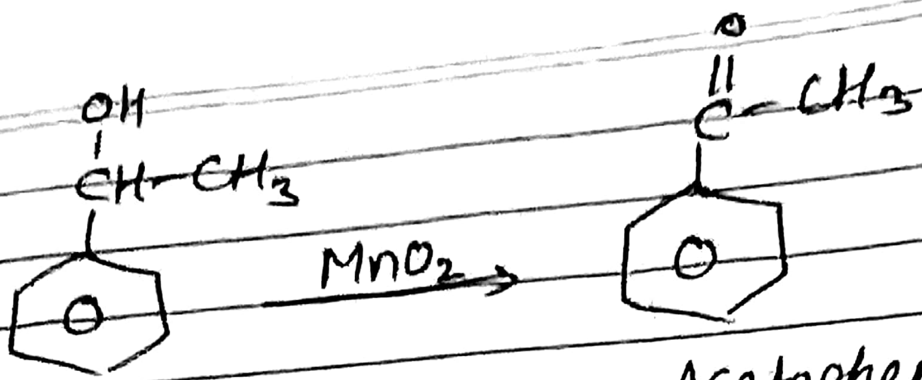
$CH_2=CH-CH_2-OH$
allylic alcohols

1° Alcohol $\longrightarrow$ Aldehyde
2° Alcohol $\longrightarrow$ Ketone



Benzaldehyde

$$CH_2=CH-CH_2-OH \xrightarrow{MnO_2} CH_2=CH-\overset{O}{\overset{||}{C}}-H$$



2° benzylic alcohol

Acetophenone

② By dehydrogenation of Alcohols :-

with Red hot Copper tube (passing vapours of alcohols)

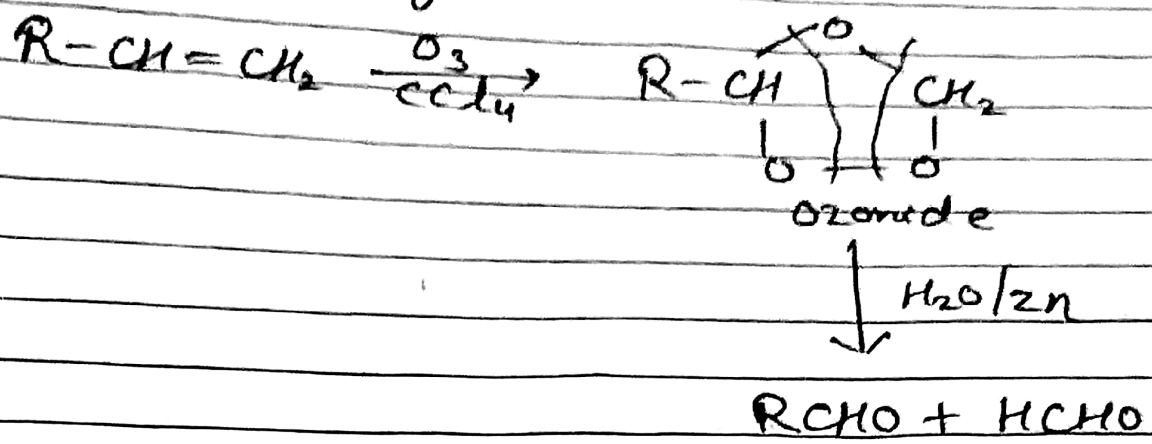
1° Alcohol ⟶ Aldehyde

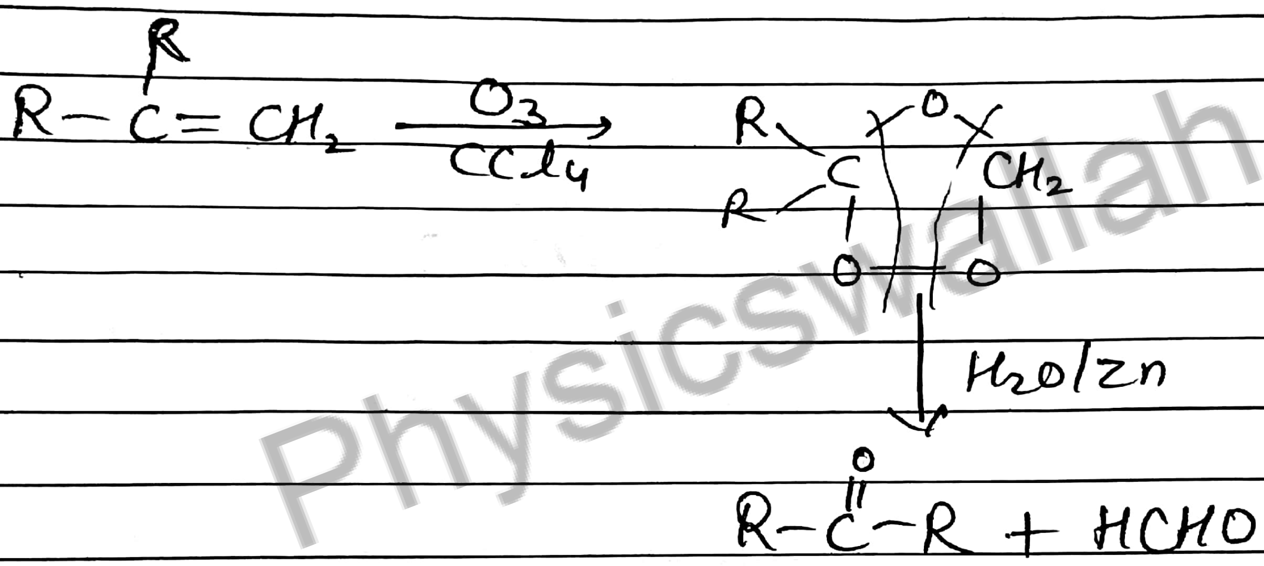
2° Alcohol ⟶ Ketone

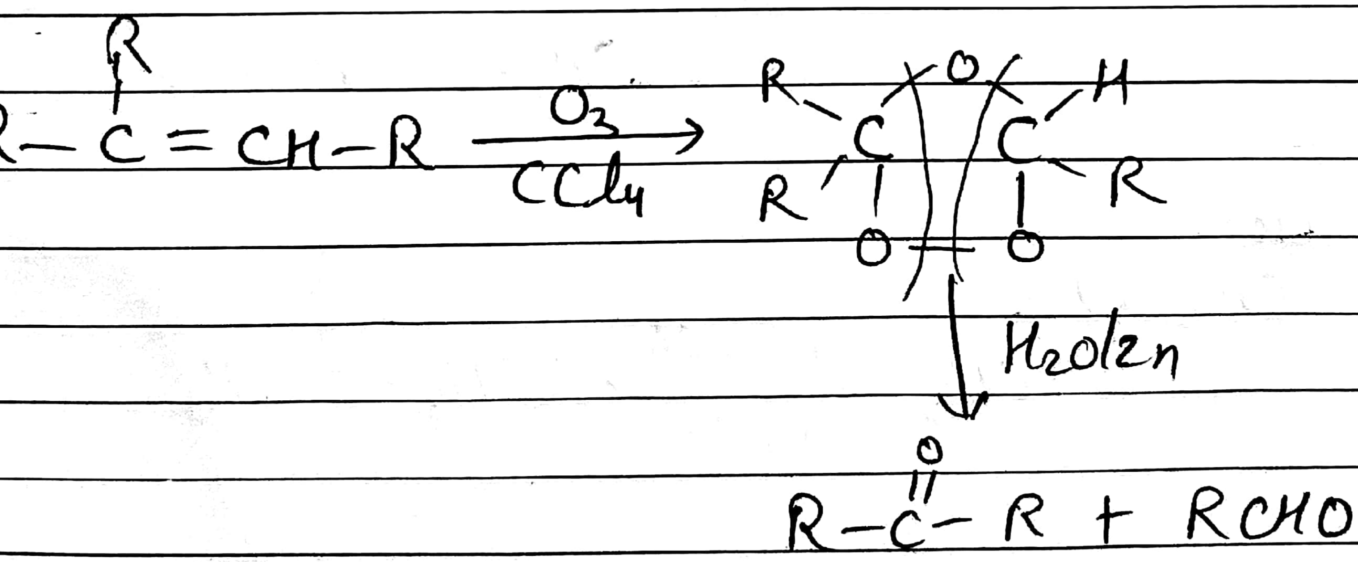
$$CH_3-\underset{}{\overset{OH}{\overset{|}{C}}}H_2 \xrightarrow[\Delta]{Cu} CH_3-\overset{O}{\overset{||}{C}}-H$$

$$CH_3-\overset{OH}{\overset{|}{C}}H-CH_3 \xrightarrow[\Delta]{Cu} CH_3-\overset{O}{\overset{||}{C}}-CH_3$$

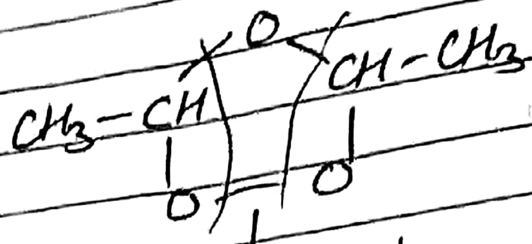
(3) By ozonolysis of alkene:







example:

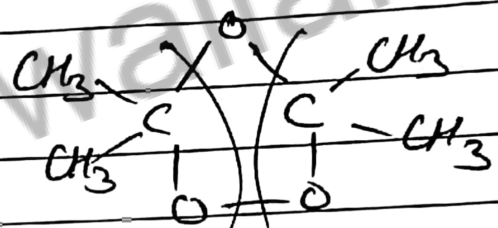
i) $CH_3CH=CH-CH_3 \xrightarrow[CCl_4]{O_3}$ 

$\downarrow H_2O/Zn$

$CH_3CHO + CH_3CHO$

Short trick: double Bond तोड़ दो , O को जोड़ दो

$CH_3-\overset{O}{C}H \neq \overset{O}{C}H-CH_3 \xrightarrow[ii)\,H_2O/Zn]{i)\,O_3/CCl_4} CH_3CHO + CH_3CHO$

ii) $CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow[CCl_4]{O_3}$ 

$\downarrow H_2O/Zn$

$CH_3-\overset{O}{\overset{||}{C}}-CH_3 + CH_3-\overset{O}{\overset{||}{C}}-CH_3$

Short trick:

$CH_3-\underset{O}{\overset{CH_3}{\overset{|}{C}}} \neq \underset{O}{\overset{CH_3}{\overset{|}{C}}}-CH_3 \xrightarrow[ii)\,H_2O/Zn]{i)\,O_3/CCl_4} 2CH_3-\overset{O}{\overset{||}{C}}-CH_3$

(4) By hydration of alkynes: in presence of dil H_2SO_4 & $HgSO_4$

Ethyne ⟶ Acetaldehyde

Any other alkyne ⟶ Ketone

$$CH\equiv CH \xrightarrow[\text{dil } H_2SO_4,\ HgSO_4,\ \Delta]{H-OH} \underset{(3)}{\overset{H}{\overset{|}{H-C}}}=\underset{(2)}{\overset{OH}{\overset{|}{C}}}-H \xrightarrow[\text{1,3 H Migration}]{\text{Tautomerism}} CH_3-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3-C\equiv CH \xrightarrow[\text{dil } H_2SO_4,\ HgSO_4,\ \Delta]{H-OH} CH_3-\underset{(2)}{\overset{OH}{\overset{|}{C}}}=\underset{(3)}{\overset{H}{\overset{|}{C}}}-H$$

$$\downarrow \text{Tautomerism, 1,3 H Migration}$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

$$CH_3-C\equiv C-CH_3 \xrightarrow{''} CH_3-\overset{OH}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_3$$

$$\downarrow ''$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

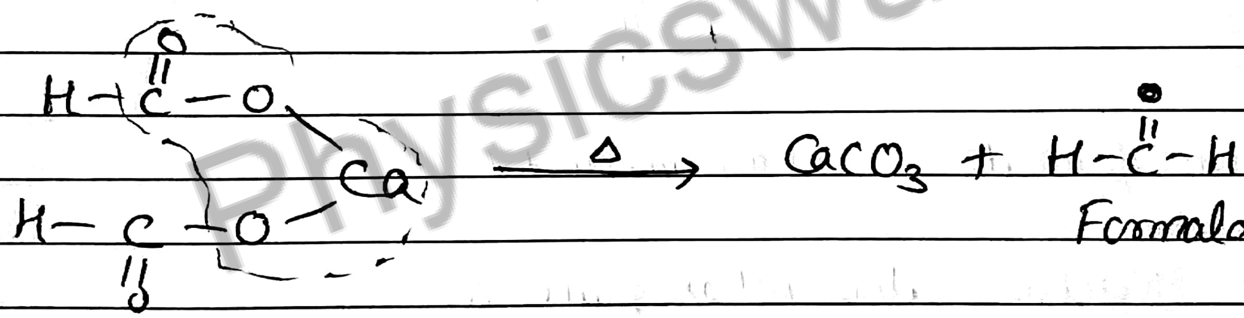
Aldehydes & Ketones—02

Preparation of Aldehydes & Ketones

1) From Carboxylic Acids:

i) By dry distillation of Calcium Salts of Carboxylic Acids : Pyrolysis

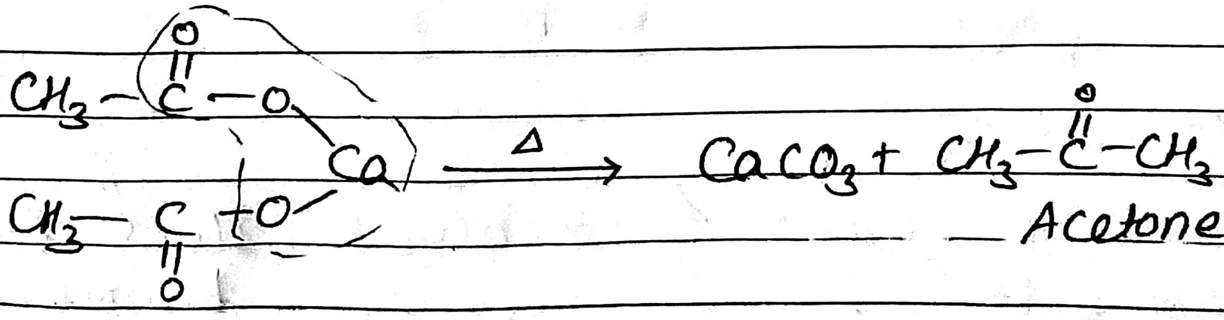
$$\underset{\text{Formic Acid}}{2HCOOH} \xrightarrow[-2H_2O]{Ca(OH)_2} \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$



Formaldehyde

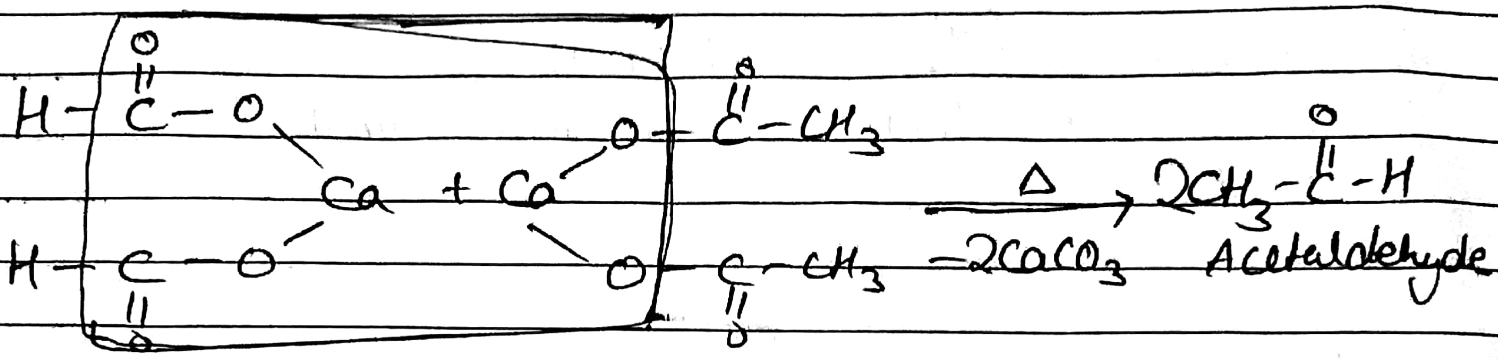
Calcium Formate

$$\underset{\text{Acetic Acid}}{2CH_3COOH} \xrightarrow[-2H_2O]{Ca(OH)_2} \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}$$



Acetone

Calcium Acetate

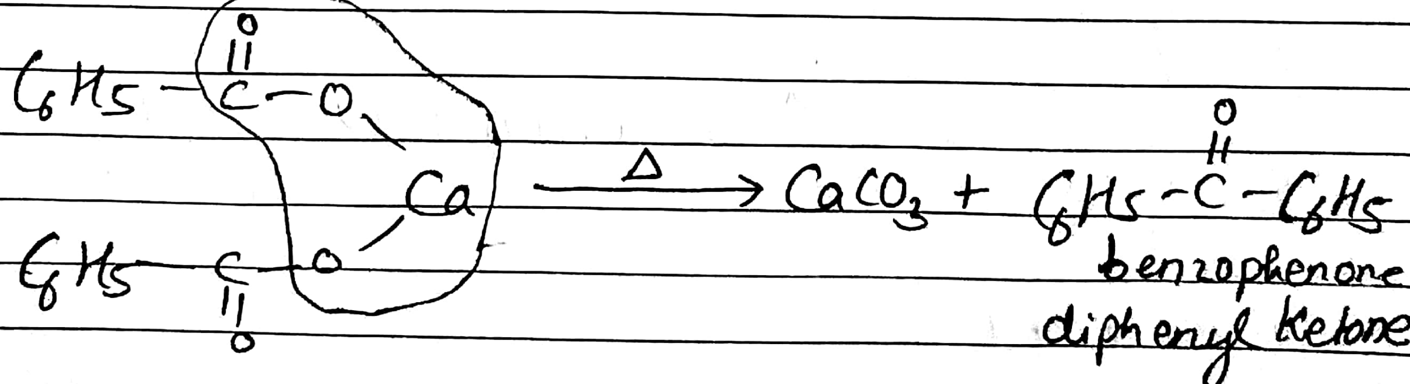


Calcium formate   Calcium acetate

Side reactions also takes place & formaldehyde & acetone are also formed.
So yield of Acetaldehyde is not good

$$C_6H_5COOH \xrightarrow{Ca(OH)_2} (C_6H_5COO)_2Ca$$

Benzoic acid   Calcium benzoate



Calcium benzoate

$$\boxed{(C_6H_5COO)_2Ca + Ca(OOCH)_2} \xrightarrow[-2CaCO_3]{\Delta} 2C_6H_5-\overset{O}{\overset{\|}{C}}-H$$

Benzaldehyde

Calcium benzoate   Calcium formate

side reactions also takes place & formaldehyde & benzophenone are also formed So yield of benzaldehyde is not good.

Q) $CH_3COOH \xrightarrow{Ca(OH)_2} A \xrightarrow[\text{dry distillation}]{\Delta} B$

$A \rightarrow (CH_3COO)_2Ca$

$B \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

ii) Catalytic decomposition of Carboxylic Acids:

By passing vapours of carboxylic acid over Manganous oxide at 575 K

a) $HCOOH + HCOOH \xrightarrow[575K]{MnO} H_2O + CO_2 + H-\overset{\overset{O}{||}}{C}-H$

Formic Acid. formaldehyde

$HCOOH \xrightarrow[575K]{MnO} HCHO$

b) $CH_3COOH + HOOC-CH_3 \xrightarrow[575K]{MnO} H_2O + CO_2 + CH_3-\overset{\overset{O}{||}}{C}-CH_3$

acetic Acid. Acetone

$CH_3COOH \xrightarrow[575K]{MnO} CH_3-\overset{\overset{O}{||}}{C}-CH_3$

c) $CH_3COOH + HCOOH \xrightarrow[575K]{MnO} H_2O + CO_2 + CH_3-\overset{\overset{O}{||}}{C}-H$

Acetaldehyde

side reactions also takes place & formaldehyde & Acetone are also formed

2) From Grignard's Reagant:

i) with nitriles (cyanides)

a) $$\underset{\substack{\text{Hydrogen}\\\text{Cyanide}\\\text{(methanenitrile)}}}{H-C\equiv N} + \overset{\delta-}{CH_3}\overset{\delta+}{Mg}Br \xrightarrow[\text{ether}]{\text{dry}} H-\underset{\substack{|\\CH_3}}{C}=\overset{\ominus}{N}\,\overset{\oplus}{Mg}Br$$

$$\xrightarrow[H^+]{\overset{+}{H}-\overset{-}{OH}} H-\underset{\substack{|\\CH_3}}{C}=NH \quad Mg\begin{matrix}OH\\Br\end{matrix}$$

$$H-\underset{\substack{|\\CH_3}}{\overset{\substack{O-H\\|}}{C}}-NH_2 \xleftarrow[H^+]{\overset{+}{H}-\overset{-}{OH}} H-\underset{\substack{|\\CH_3}}{C}=NH$$

$$\downarrow$$

$$\underset{\text{Acetaldehyde}}{H-\overset{\substack{O\\\|}}{C}-CH_3} + NH_3$$

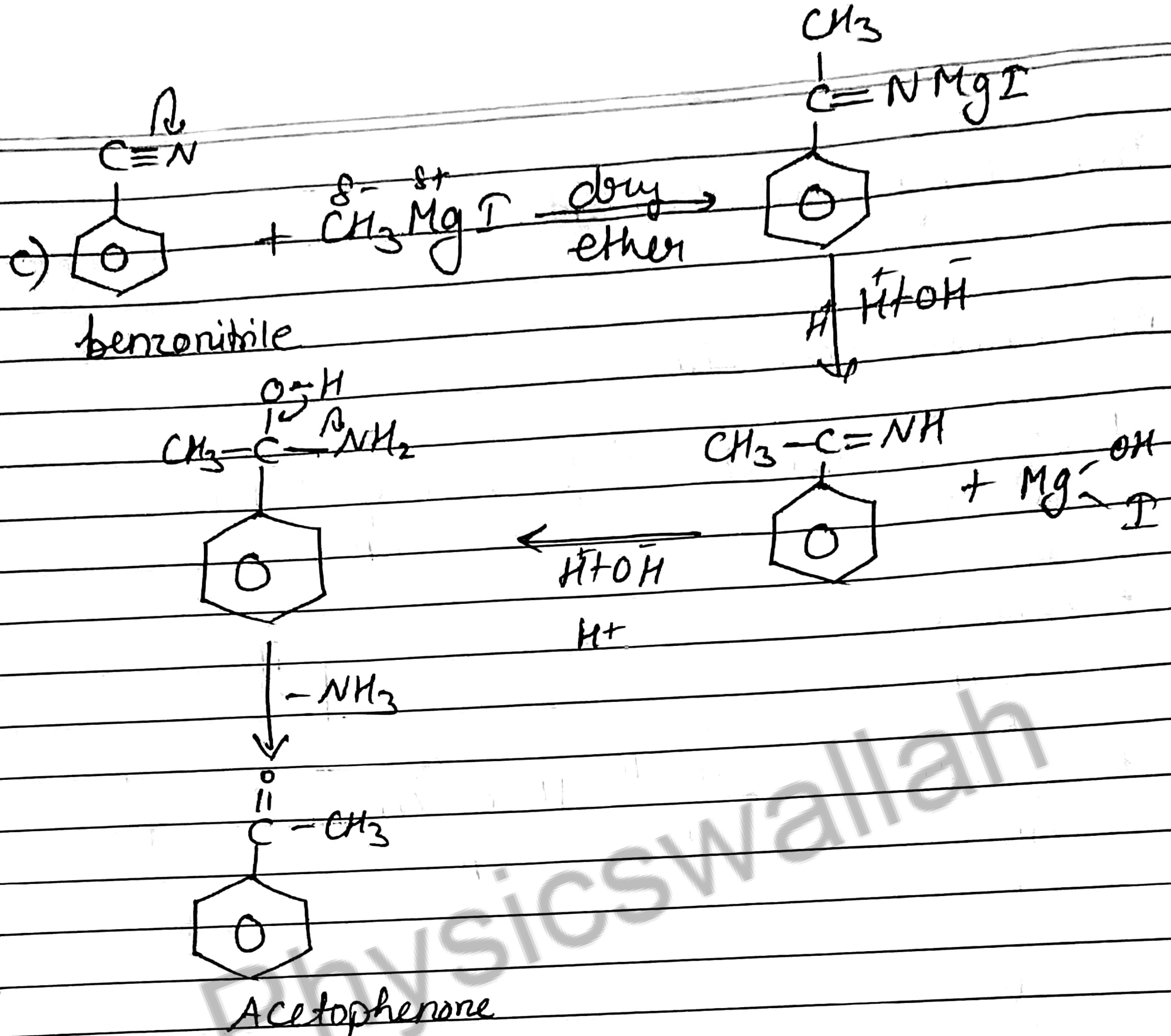
b) $$\underset{\substack{\text{ethanenitrile}\\\text{Methyl cyanide}\\\text{Acetonitrile}}}{CH_3-C\equiv N} + \overset{\delta-}{CH_3}\overset{\delta+}{Mg}Br \xrightarrow[\text{ether}]{\text{dry}} CH_3-\underset{\substack{|\\CH_3}}{C}=\overset{\delta-}{N}\,\overset{\delta+}{Mg}Br$$

$$\xrightarrow[H^+]{\overset{+}{H}-\overset{-}{OH}} CH_3-\underset{\substack{|\\CH_3}}{C}=NH + Mg\begin{matrix}Br\\OH\end{matrix}$$

$$CH_3-\underset{\substack{|\\CH_3}}{\overset{\substack{O-H\\|}}{C}}-NH_2 \xleftarrow[H^+]{\overset{+}{H}-\overset{-}{OH}} CH_3-\underset{\substack{|\\CH_3}}{C}=NH$$

$$\downarrow -NH_3$$

$$\underset{\text{Acetone}}{CH_3-\overset{\substack{O\\\|}}{C}-CH_3}$$



ii) with esters:

a) $CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + \overset{\delta-}{CH_3}\overset{\delta+}{MgBr} \xrightarrow[\text{ether}]{\text{dry}}$

ethyl ethanoate

ethyl acetate

$CH_3-\overset{OMgBr}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OC_2H_5$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (Acetone) $+ Mg\begin{matrix} Br \\ OC_2H_5 \end{matrix}$

b) $\overset{\delta-\ \ \delta+}{} \quad CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_6H_5MgBr$

ethyl ethanoate

ethyl acetate

$\downarrow$ dry ether

$$CH_3-\underset{C_6H_5}{\underset{|}{\overset{O-MgBr}{\overset{|}{C}}}}-OC_2H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5$$

Acetophenone

$+ \ Mg\begin{matrix}-Br \\ -OC_2H_5\end{matrix}$

c) $H-\overset{O}{\overset{\|}{C}}-OC_2H_5 \quad + \quad C_6H_5MgBr$

ethyl methanoate

ethyl formate

$\downarrow$ dry ether

$$H-\underset{C_6H_5}{\underset{|}{\overset{O-MgBr}{\overset{|}{C}}}}-OC_2H_5$$

$\downarrow$

$$H-\overset{O}{\overset{\|}{C}}-C_6H_5 \quad + \quad Mg\begin{matrix}-Br \\ -OC_2H_5\end{matrix}$$

Benzaldehyde

Aldehydes & Ketones – 02

Preparation of Aldehyde

① Rosenmund Reduction:

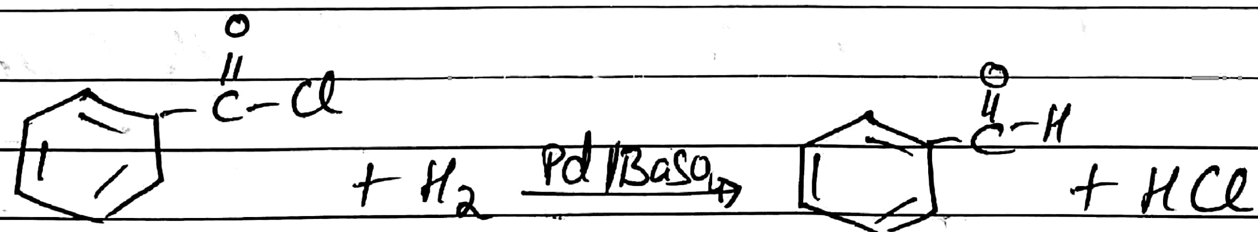
Acid Chloride $\xrightarrow[\text{Catalyst} / H_2]{\text{Lindlar's}}$ Aldehyde

Lindlar's Catalyst → $Pd/BaSO_4$
poisoned by Sulphur or Quinoline
⇓
partial reduction

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Pd/BaSO_4]{H_2} R-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Pd/BaSO_4]{H_2} CH_3-\overset{O}{\overset{\|}{C}}-Cl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H + HCl$$



Benzoyl chloride   Benzaldehyde

** Formaldehyde can't be prepared as $H-\overset{O}{\overset{\|}{C}}-Cl$ is unstable

(2) Stephen's Reduction

$$\underset{\text{(nitrile)}}{\text{Alkyl cyanide}} \xrightarrow[\text{ii) } H_2O/H^+]{\text{i) } SnCl_2/HCl} \text{Aldehyde}$$

$$\underset{\substack{\text{cyanide}\\\text{(nitrile)}}}{R-C\equiv N} \xrightarrow[HCl]{SnCl_2} \underset{\text{imine}}{R-CH=NH} \xrightarrow[H^+]{H_2O} \underset{\text{aldehyde}}{R-CHO}$$

$$\underset{\text{ethanenitrile}}{CH_3-C\equiv N} \xrightarrow[HCl]{SnCl_2} \underset{\text{ethanimine}}{CH_3-CH=NH} \xrightarrow[H^+]{H_2O} \underset{\text{ethanal}}{CH_3-CHO}$$

Mechanism:

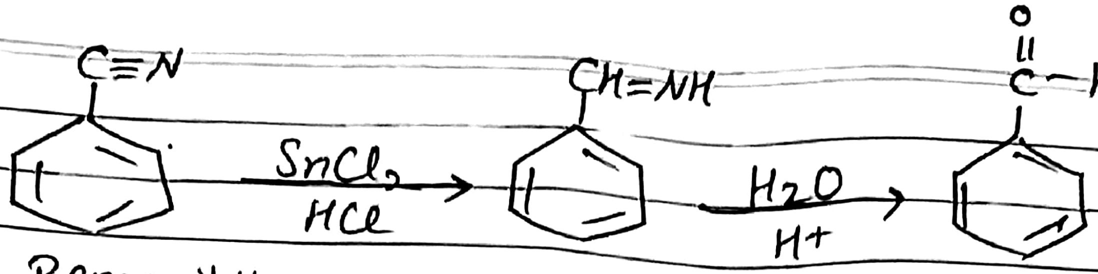
$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2H^+$$

$$\overset{+2}{SnCl_2} \longrightarrow \overset{+4}{SnCl_4}$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

$$CH_3-C\equiv N \xrightarrow{2e^-} CH_3-\overset{\ominus}{C}=N^{\ominus} \xrightarrow{2H^+} CH_3-\underset{\substack{|\\H}}{C}=NH$$

$$CH_3-\underset{\substack{|\\H}}{C}=\boxed{NH} \xrightarrow[-NH_3]{H_2O} CH_3-\overset{\substack{O\\||}}{C}-H$$



Benzonitrile $\qquad -NH_3 \qquad$ Benzaldehyde

③ Using DiBAL-H :

diisobutyl Aluminium Hydride

$$\left(\underset{\displaystyle CH_3}{CH_3-\overset{}{CH}}-CH_2\right)_2 Al-H \quad OR \quad AlH(i\text{-}Bu)_2$$

$$\underset{\text{nitrile}}{R-C\equiv N} \xrightarrow[\text{ii) } H_2O/H^+]{\text{i) DiBAL-H}} R-CHO$$

$$\underset{\text{acid halide}}{R-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow[\text{ii) } H_2O/H^+]{\text{i) DiBAL-H}} R-CHO$$

$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[\text{ii) } H_2O/H^+]{\text{i) DiBAL-H}} R-CHO + R'OH$$

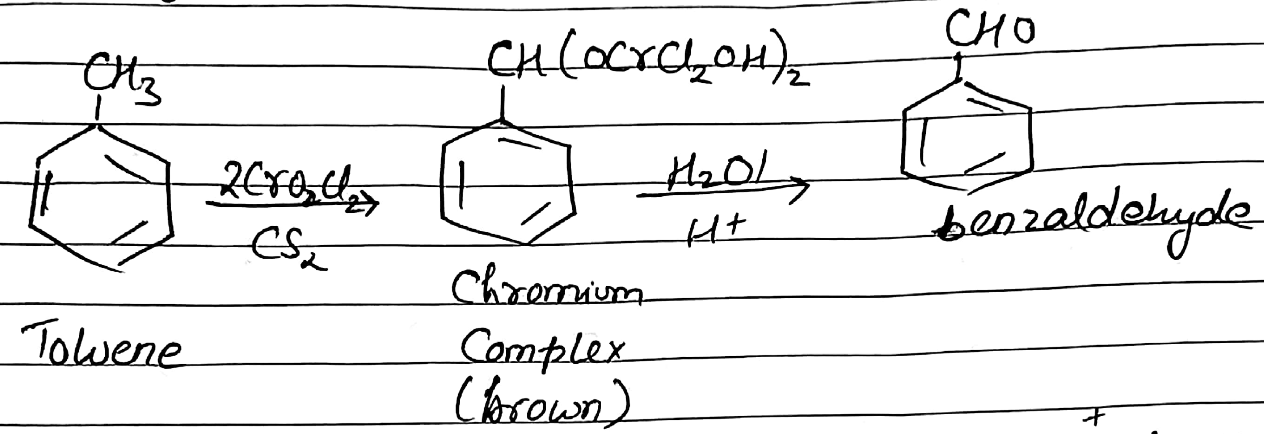
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\text{ii) } H_2O/H^+]{\text{i) DiBAL-H}} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + C_2H_5OH$$

Aldehydes & Ketones – 04

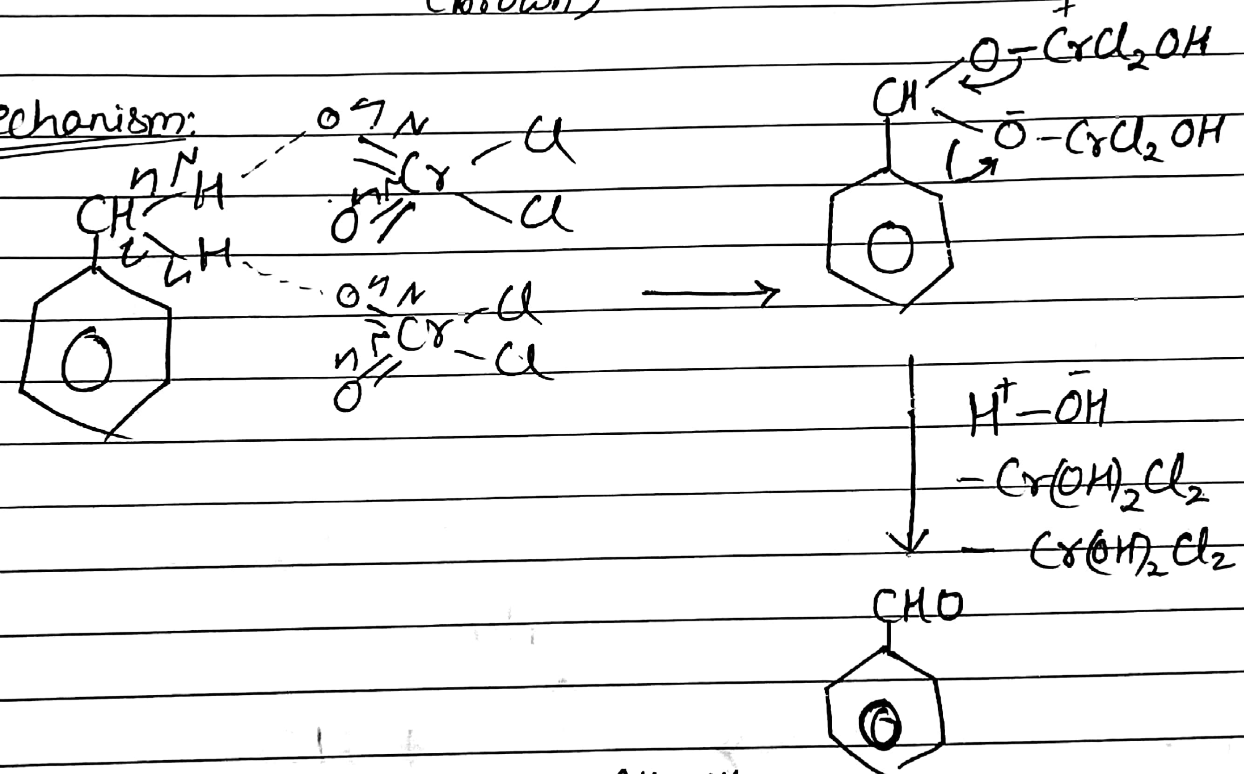
Preparation of Aldehydes – 2
(Benzaldehyde)

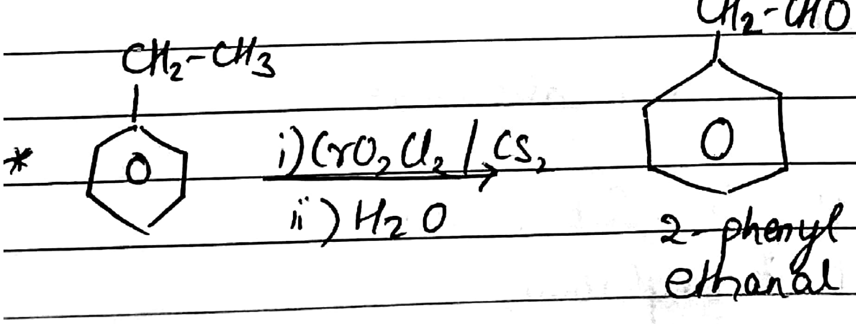
① From Methylbenene ÷ By controlled oxidation (partial)

a) Using chromyl chloride (CrO_2Cl_2): Etard's Reaction



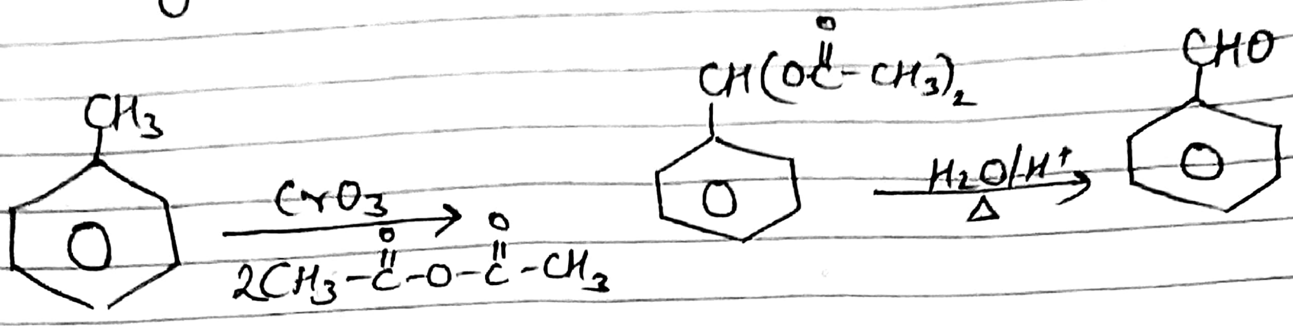
Mechanism:



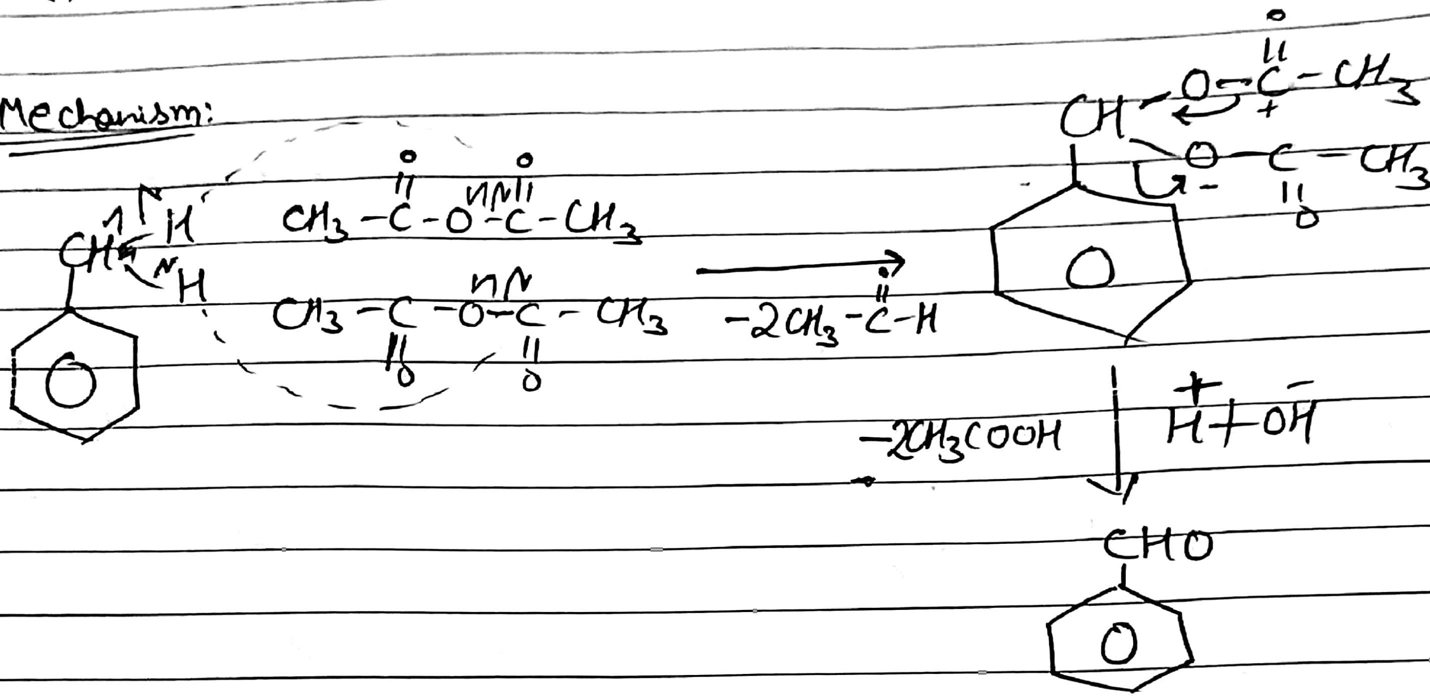


in case side chain contains group higher than $-CH_3$ group, the end carbon atom is oxidised to CHO

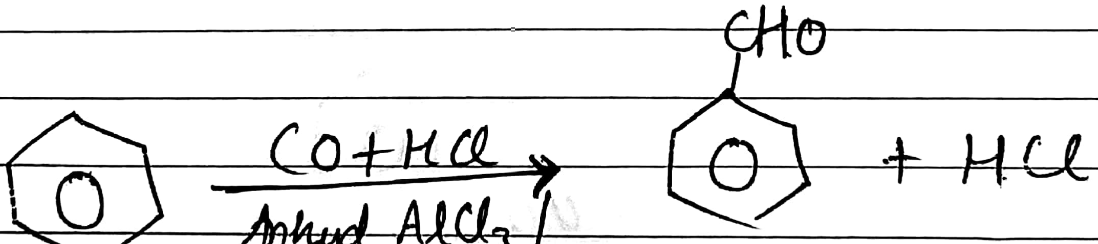
b) Using Chromic oxide CrO_3 in presence of acetic anhydride



Mechanism:



ii) From Benzene → Gatterman-Koch Reaction



Benzene

Benzaldehyde

(Electrophilic Substitution)

Friedel Craft Formylation

$H-\overset{O}{\overset{\|}{C}}-$

(formyl)

Mechanism:

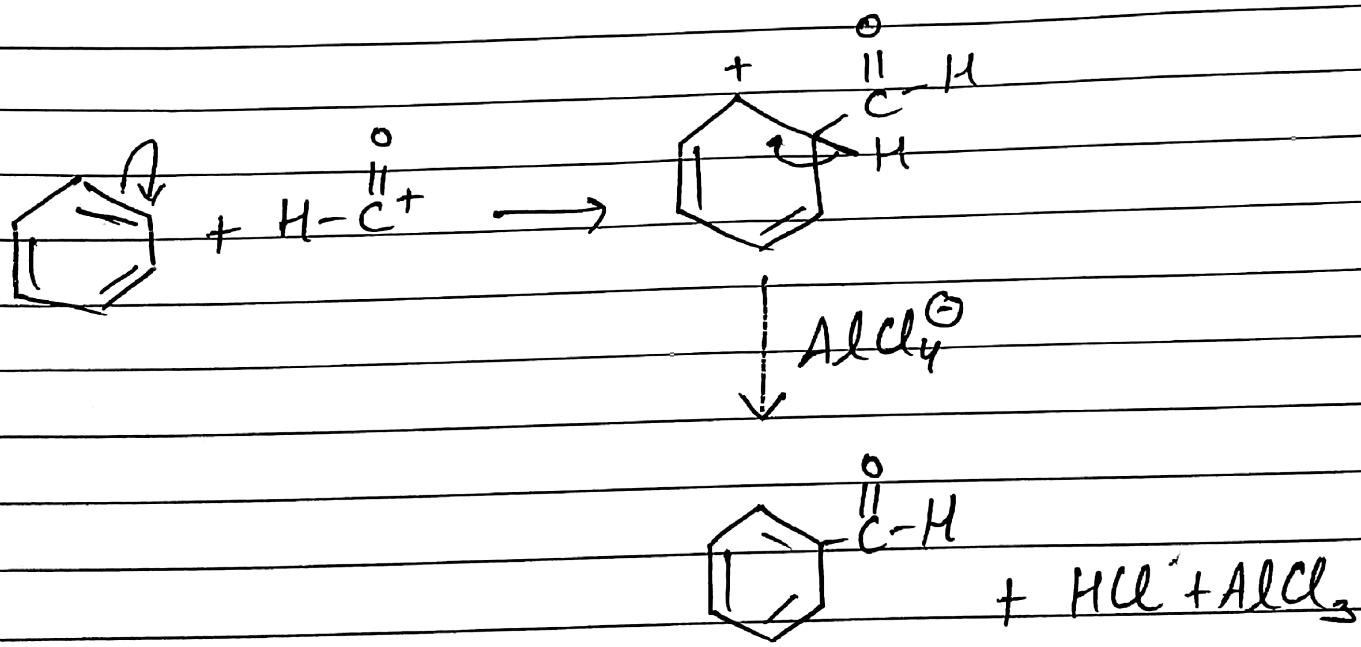
$$\ddot{C} \equiv O^{+}\colon + \overset{+}{H}-\overset{-}{Cl} \xrightarrow[H^+]{} H-C\equiv\overset{+}{O}$$

$$\big\downarrow Cl^-$$

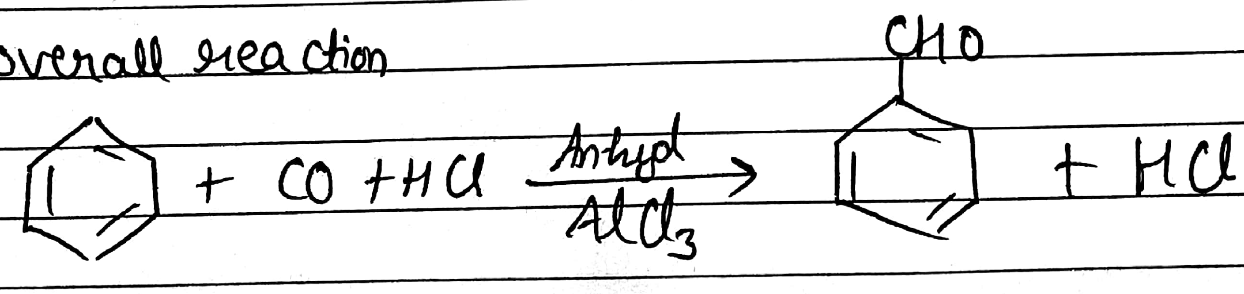
$$H-\overset{O}{\overset{\|}{C}}-Cl$$

methanoyl chloride
(formyl chloride)

$$H-\overset{O}{\overset{\|}{C}}-Cl + \underset{\substack{L.A. \\ \text{or } CuCl}}{AlCl_3} \longrightarrow \overset{-}{AlCl_4} + \underset{\text{Electrophile}}{H-\overset{O}{\overset{\|}{C}}{}^{+}}$$



overall reaction



Aldehydes & Ketones - 05

Preparation of Ketones

1) From Acid chlorides / Acyl chlorides:

Ketones can be prepared by the action of dialkyl cadmium on acid chlorides

$$2R'-\overset{O}{\overset{\|}{C}}-Cl + R_2Cd \longrightarrow 2R'-\overset{O}{\overset{\|}{C}}-R + CdCl_2$$

Acid chloride   dialkyl cadmium

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl,\ CH_3-\overset{O}{\overset{\|}{C}}-Cl + Cd\begin{matrix} CH_3 \\ CH_3 \end{matrix} \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CdCl_2$$

Acetyl chloride   dimethyl cadmium   Acetone

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl,\ CH_3-\overset{O}{\overset{\|}{C}}-Cl + Cd\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5 + CdCl_2$$

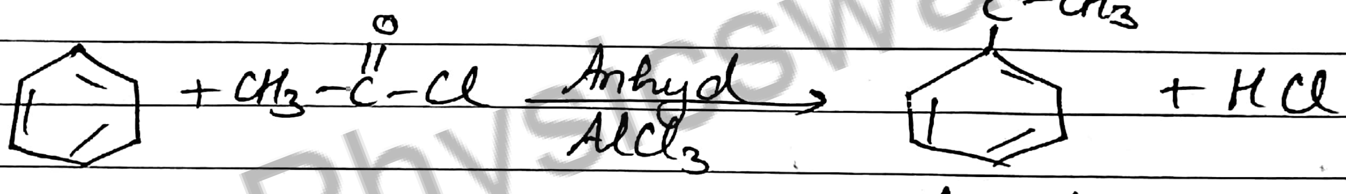
Acetyl chloride   diethyl Cadmium   butanone

$$C_6H_5-\overset{O}{\overset{\|}{C}}-Cl,\ C_6H_5-\overset{O}{\overset{\|}{C}}-Cl + Cd\begin{matrix} CH_3 \\ CH_3 \end{matrix} \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 + CdCl_2$$

Benzoyl Chloride   dimethyl Cadmium   Acetophenone dialkyl cadmium is prepared by reaction of anhydrous $CdCl_2$ with Grignard's Reagent

$$2R-Mg-X + CdCl_2 \xrightarrow[\text{ether}]{\text{dry}} R_2Cd + 2Mg(X)Cl$$

② From Benzene : Friedel Craft Acylation

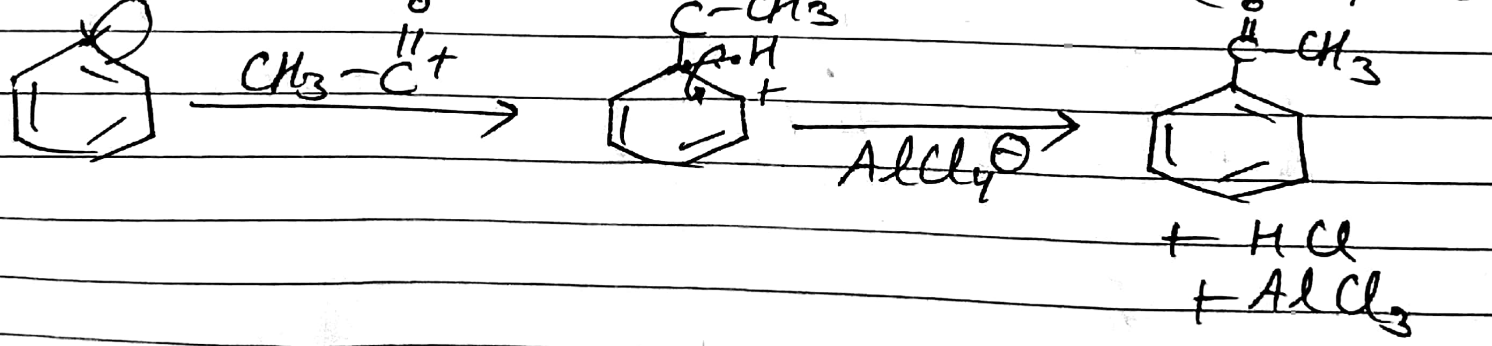


Acetophenone

Mechanism: $E^{\oplus}$ Substitution

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow AlCl_4^{\ominus} + CH_3-\overset{O}{\overset{\|}{C}}{}^{+}$$

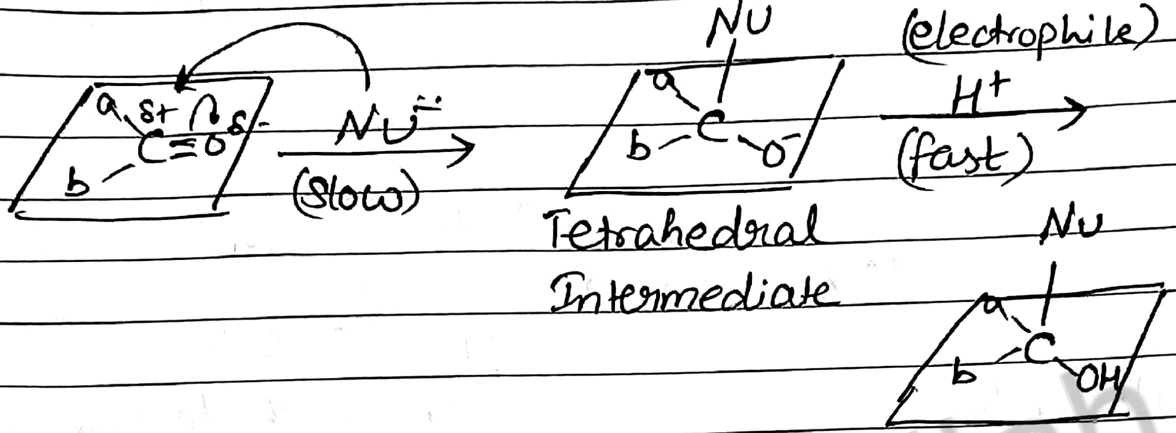
(Electrophile)



Aldehydes & Ketones – 06

Properties: Nucleophilic Addition Reaction

Both Aldehydes & Ketones contain $-\overset{O}{\overset{\|}{C}}-$ carbonyl group, which gives Nucleophilic Addition Product.



Tetrahedral Intermediate

Addition Product
R/S due to chiral centre

i) Addition of HCN:– with Base Catalyst

$$\underset{\text{from base}}{OH^-} + H\text{-}CN \longrightarrow \overset{\ominus}{C}N + H_2O$$

$$\underset{H}{\overset{R}{>}}C\overset{\delta+\ \ \delta-}{=}O + \overset{\ominus}{C}N \longrightarrow R(H)C(O^-)(CN) \xrightarrow{H^+} R(H)C(OH)(CN)$$

Cyanohydr

$$\underset{\text{Acetaldehyde}}{CH_3(H)C=O} + HCN \xrightarrow[\text{(Base)}]{pH\ 9\text{-}10} \underset{\text{Acetaldehyde Cyanohydrin}}{CH_3(H)C(OH)(CN)}$$

$$(CH_3)_2C{=}O + HCN \xrightarrow[\text{(Base)}]{pH\ 9\text{-}10} (CH_3)_2C(OH)(CN)$$

Acetone → Acetone cyanohydrin

$$C_6H_5(H)C{=}O + HCN \xrightarrow{\text{''}} C_6H_5(H)C(OH)(CN)$$

Benzaldehyde → Benzaldehyde cyanohydrin

$$C_6H_5(CH_3)C{=}O + HCN \xrightarrow{\text{''}} C_6H_5(CH_3)C(OH)(CN)$$

Acetophenone → Acetophenone cyanohydrin

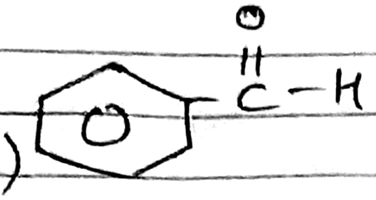
Rate of Reaction $\propto \dfrac{1}{\text{sterric hinderance}}$

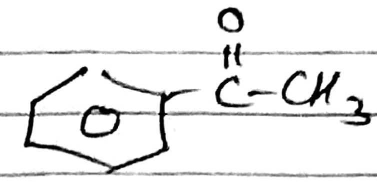
Q) Arrange in decreasing order of reactivity towards HCN.

① a) $CH_3-\overset{O}{\overset{\|}{C}}-H$ b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ d) $H-\overset{O}{\overset{\|}{C}}-H$

Solution: d > a > b > c

(2) a) 

b) 

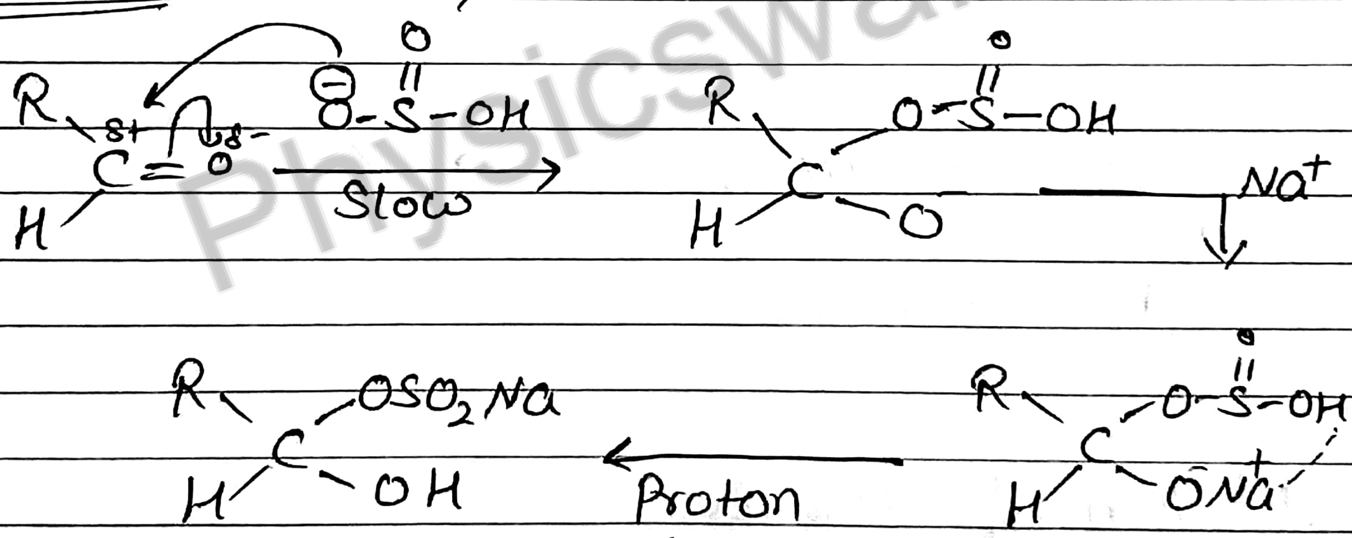
Solution: a > b

ii) Addition of $NaHSO_3$ (sodium hydrogensulphite)

$R-\overset{O}{\overset{\|}{C}}-H + NaHSO_3 \longrightarrow$ R(H)C(OH)(OSO_2Na)

white crystalline solid

Mechanism: $\overset{+}{Na}\overset{-}{O}-\overset{O}{\overset{\|}{S}}-OH$



Bisulphite
Addition Product
white crystalline solid

For Ketones: lower Ketones (Methyl Ketones) gives Addition product while higher Ketones don't due to sterric crowding

$$\begin{matrix} CH_3 \\ H \end{matrix} \rangle C=O + NaHSO_3 \longrightarrow \begin{matrix} CH_3 \\ H \end{matrix} \rangle C \langle \begin{matrix} OSO_2Na \\ OH \end{matrix}$$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \rangle C=O + NaHSO_3 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix} \rangle C \langle \begin{matrix} OSO_2Na \\ OH \end{matrix}$$

$$\begin{matrix} C_6H_5 \\ H \end{matrix} \rangle C=O + NaHSO_3 \longrightarrow \begin{matrix} C_6H_5 \\ H \end{matrix} \rangle C \langle \begin{matrix} OSO_2Na \\ OH \end{matrix}$$

$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} \rangle C=O + NaHSO_3 \longrightarrow \times$$

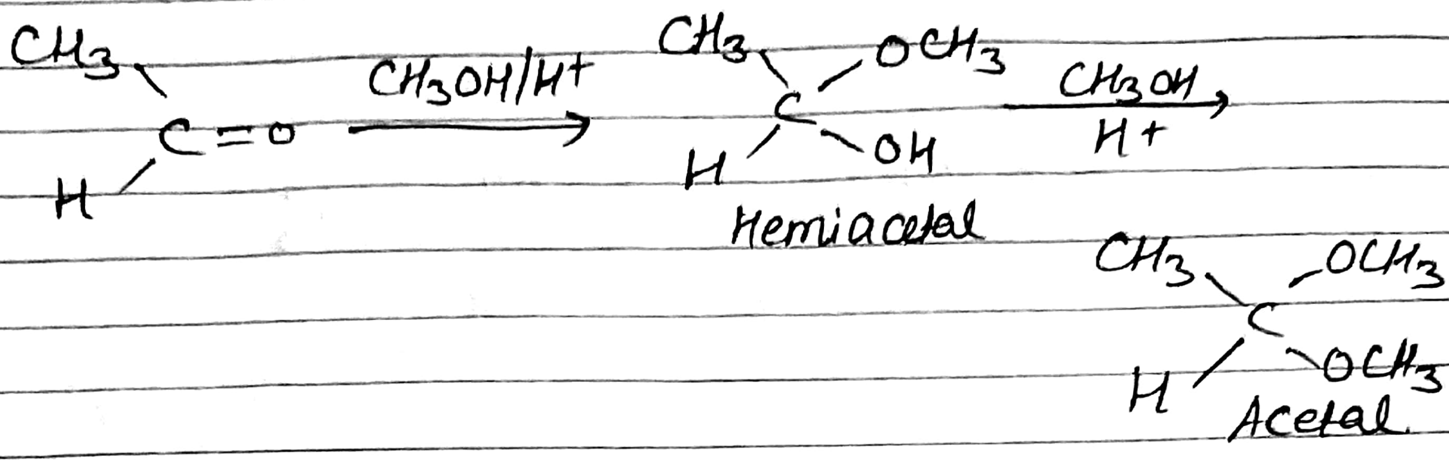
(Higher ketone)

iii) Addition of alcohols:

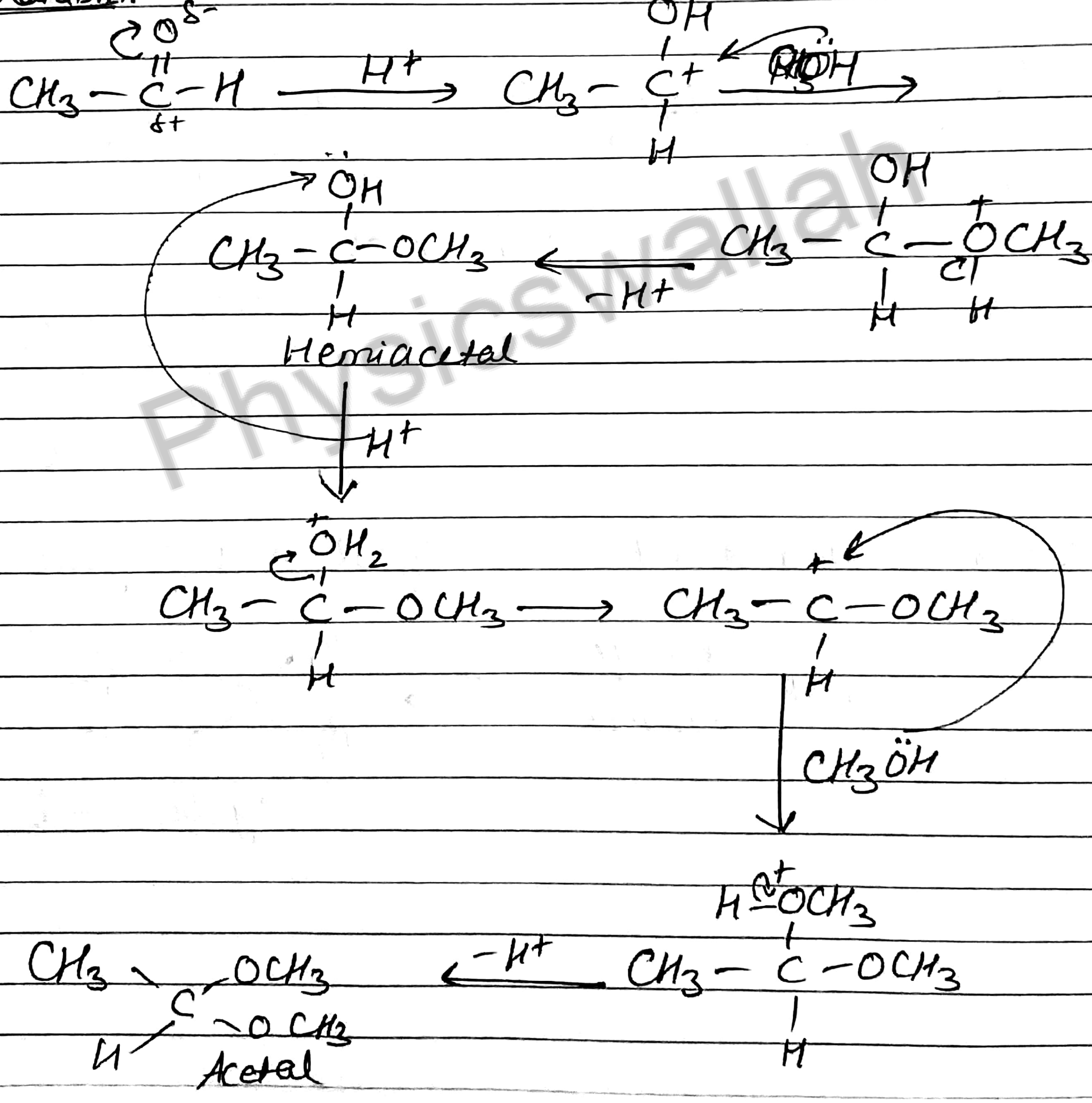
<u>Aldehyde:</u>

$$\begin{matrix} R \\ H \end{matrix} \rangle C=O \xrightarrow{R'OH/H^+} \begin{matrix} R \\ H \end{matrix} \rangle C \langle \begin{matrix} OH \\ OR' \end{matrix} \xrightarrow{R'OH/H^+} \begin{matrix} R \\ H \end{matrix} \rangle C \langle \begin{matrix} OR' \\ OR' \end{matrix}$$

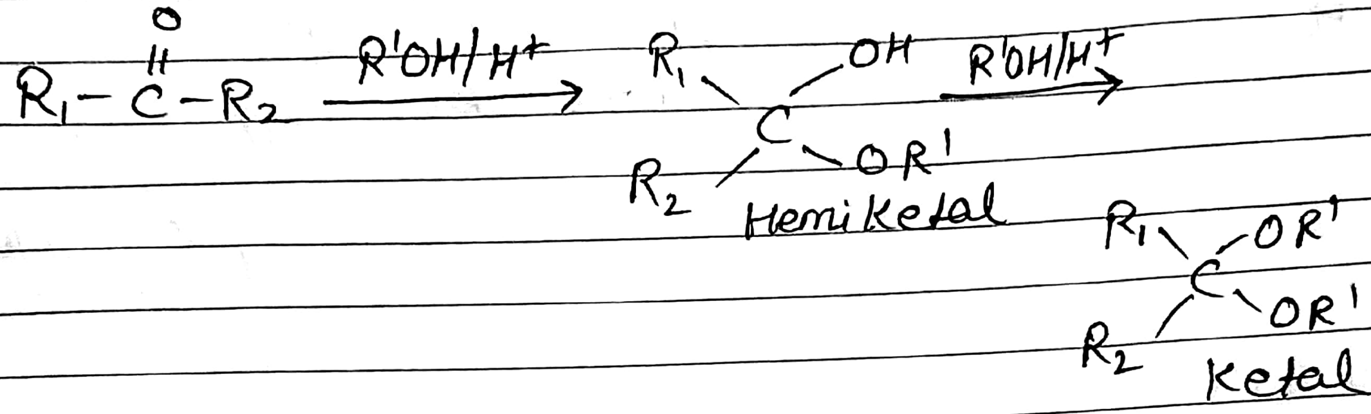
Hemi Acetal ... Acetal

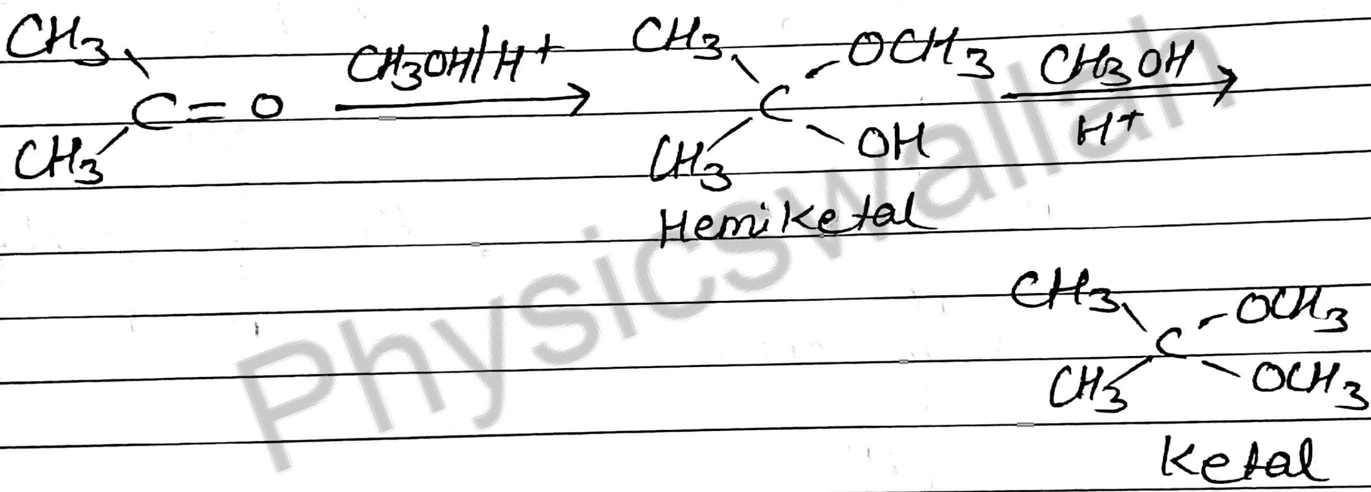

CH3OH/H+
Hemiacetal
CH3OH
H+
Acetal

Mechanism:

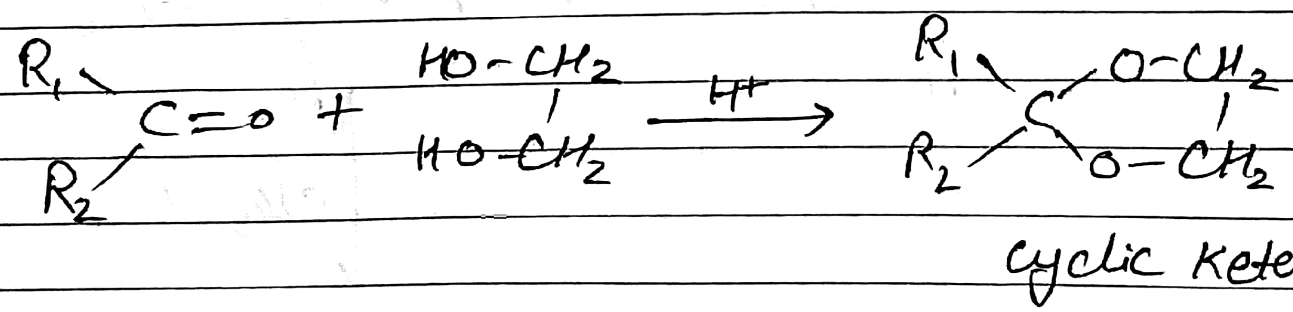

H+
-H+
Hemiacetal
H+
CH3ÖH
-H+
Acetal

Ketones:

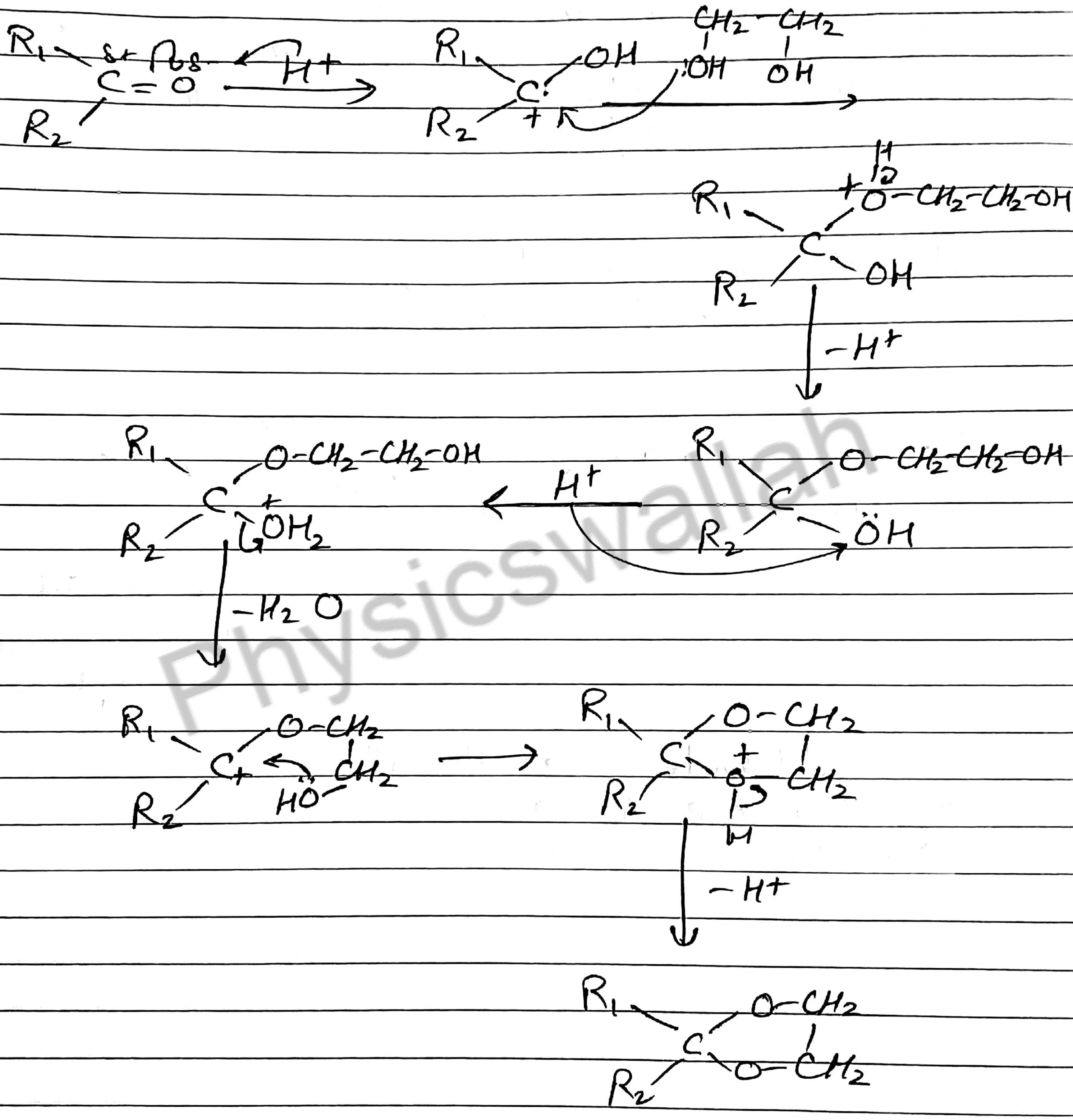




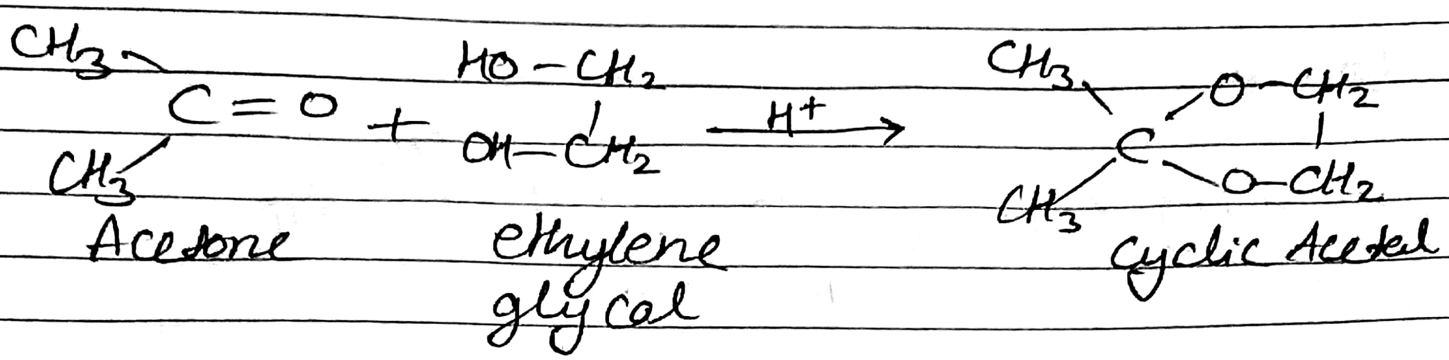
Ketones also react with glycol to give cyclic Ketal



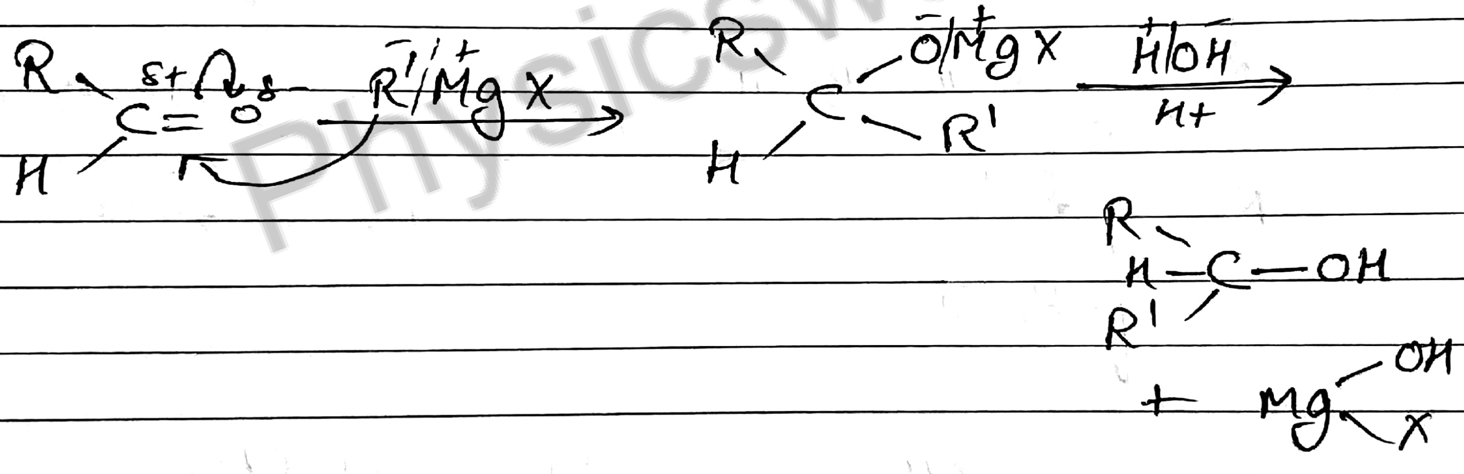
Mechanism:



R1
R2
δ+
δ-
C=O
H+
OH
C
+
CH2-CH2
OH OH
O-CH2-CH2-OH
-H+
O-CH2-CH2-OH
OH2
-H2O
O-CH2
CH2
HO
H



iv) Addition of Grignard's Reagant: RMgX
— Preparation of alcohol



Formaldehyde $\longrightarrow$ 1° Alcohol
Any other aldehyde $\longrightarrow$ 2° "
Ketone $\longrightarrow$ 3° "

Aldehydes & Ketones - 07

Properties 3: Nucleophilic Addition - elimination

Addition of Ammonia & it's derivatives:

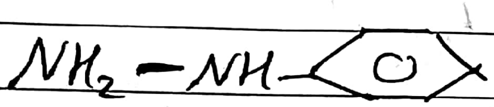
Ammonia : NH_3

Ammonia derivatives:

$NH_2 - Z$

$NH_2 - OH$ Hydroxyl amine

$NH_2 - NH_2$ Hydrazine


Phenyl hydrazine

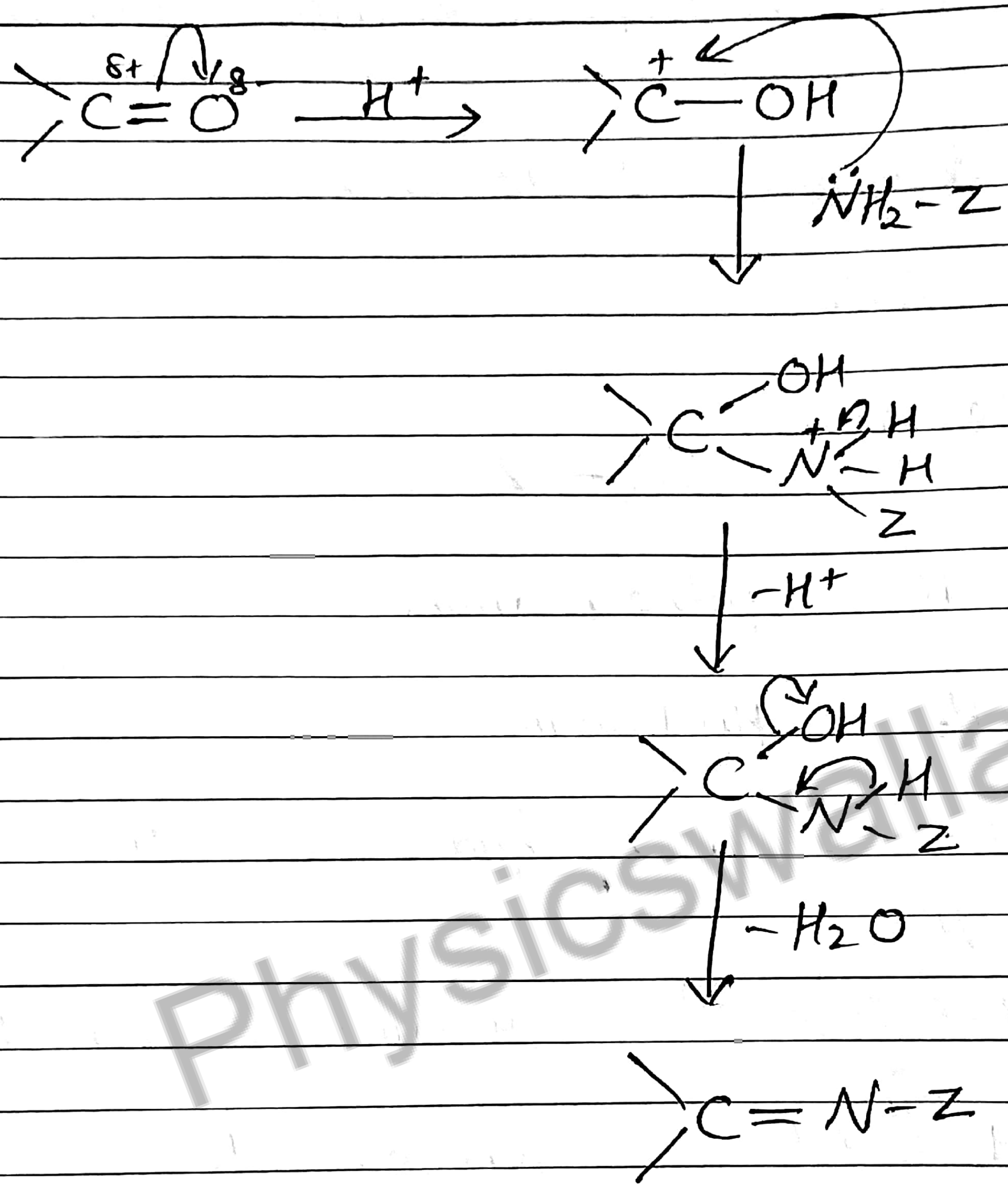

2,4-dinitrophenyl hydrazine

$NH_2 - NH - \overset{O}{\overset{\|}{C}} - NH_2$ Semicarbazide

$$>C=O + NH_2-Z \xrightarrow{H^+} >C=N-Z + H_2O$$

The reaction is acid catalysted.

Mechanism:



Control of pH during Reaction:

If medium is highly acidic → Ammonia derivatives react with medium & form ammonium salts

If medium is basic → Protonation of $>C=O$ won't happen

so optimum pH 3.5 is set.

(i) Reaction with Ammonia → Formation of Imine

$$\underset{H}{\overset{R}{>}}C=O + NH_2-H \xrightarrow[pH\ 3.5]{H^+} \underset{H}{\overset{R}{>}}C=NH + H_2O$$

Imine

$$\underset{H}{\overset{CH_3}{>}}C=O + NH_2-H \xrightarrow[pH\ 3.5]{H^+} \underset{H}{\overset{CH_3}{>}}C=NH + H_2O$$

Acetaldehyde → Acetaldimine

$$\underset{CH_3}{\overset{CH_3}{>}}C=O + NH_2-H \xrightarrow[pH\ 3.5]{H^+} \underset{CH_3}{\overset{CH_3}{>}}C=NH + H_2O$$

Acetone → Acetone imine

$$\underset{H}{\overset{C_6H_5}{>}}C=O + NH_2-H \xrightarrow[pH\ 3.5]{H^+} \underset{H}{\overset{C_6H_5}{>}}C=NH + H_2O$$

Benzaldehyde → Benzaldimine

(ii) Reaction with Hydroxyl Amine → Formation of Oxime

$$\underset{H}{\overset{R}{>}}C=O + NH_2-OH \xrightarrow[pH\ 3.5]{H^+} \underset{H}{\overset{R}{>}}C=N-OH + H_2O$$

hydroxyl Amine → Oxime

$$\underset{\text{Formaldehyde}}{H_2C=O} + NH_2-OH \xrightarrow[pH\ 3.5]{H^+} \underset{\text{Formaldoxime}}{H_2C=N-OH} + H_2O$$

$$\underset{\text{Acetaldehyde}}{CH_3(H)C=O} + NH_2-OH \xrightarrow[pH\ 3.5]{H^+} \underset{\text{Acetaldoxime}}{CH_3(H)C=N-OH} + H_2O$$

$$\underset{\text{Acetone}}{(CH_3)_2C=O} + NH_2-OH \xrightarrow{''} \underset{\text{Acetoxime / Acetone oxime}}{(CH_3)_2C=N-OH} + H_2O$$

$$\underset{\text{Benzaldehyde}}{C_6H_5(H)C=O} + NH_2-OH \xrightarrow{''} \underset{\text{Benzaldoxime}}{C_6H_5(H)C=N-OH} + H_2O$$

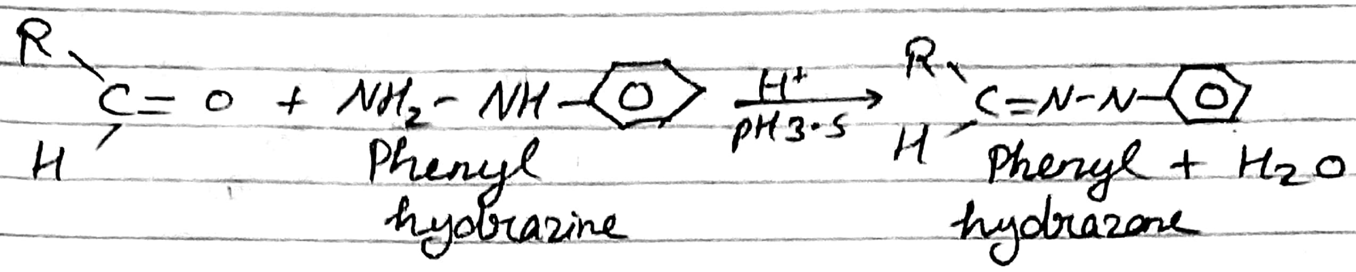
ii) Reaction with hydrazine → Formation of hydrazone

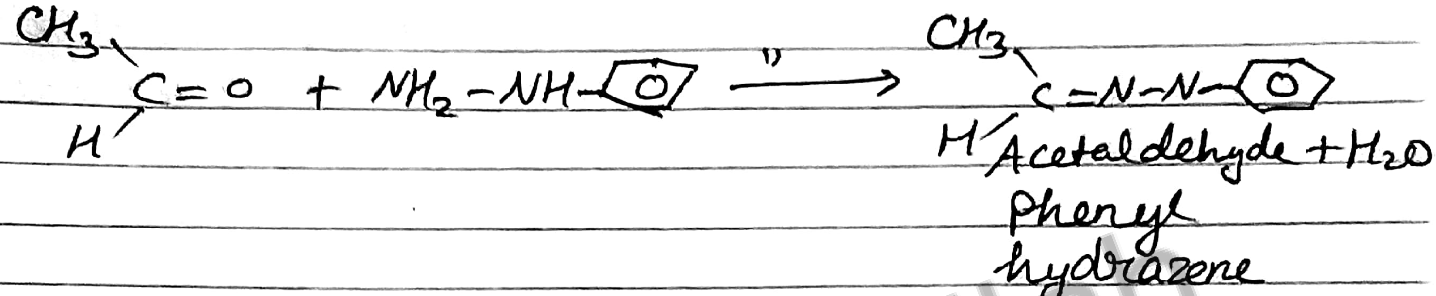
$$R(H)C=O + \underset{\text{hydrazine}}{NH_2-NH_2} \xrightarrow[pH\ 3.5]{H^+} \underset{\text{hydrazone}}{R(H)C=N-NH_2} + H_2O$$

$$H_2C=O + NH_2-NH_2 \xrightarrow{''} \underset{\text{Formaldehyde hydrazone}}{H_2C=N-NH_2} + H_2O$$

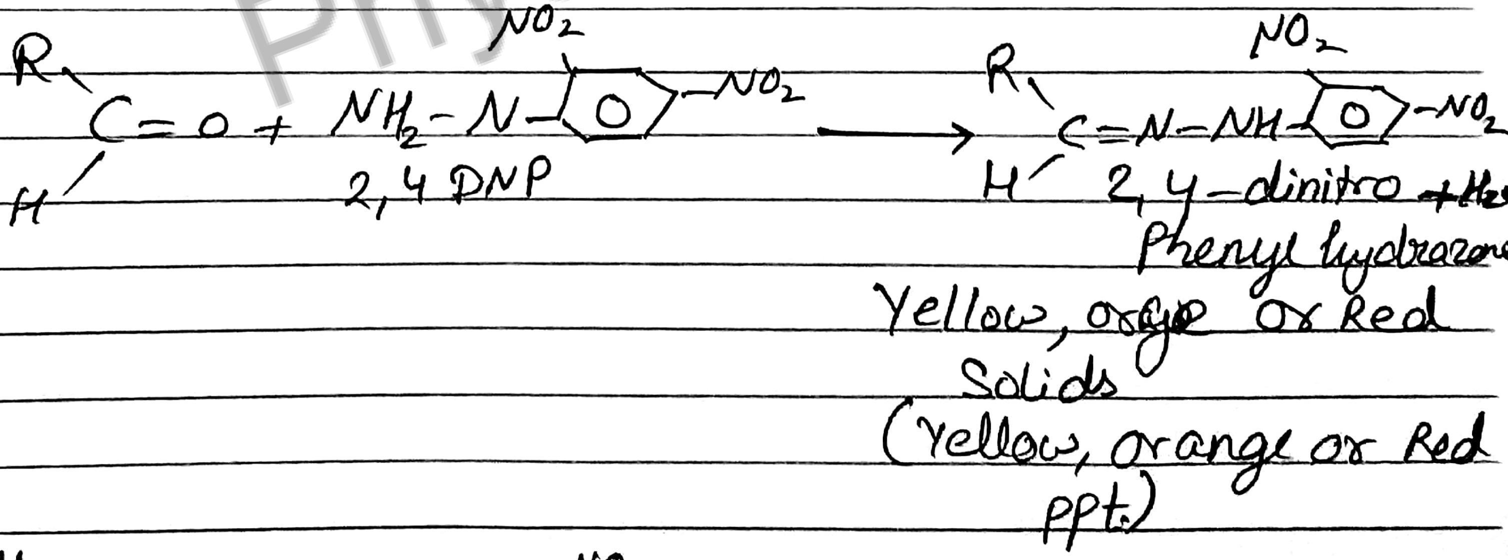
$$(CH_3)_2C=O + NH_2-NH_2 \xrightarrow{''} \underset{\text{Acetone hydrazone}}{(CH_3)_2C=N-NH_2} + H_2O$$

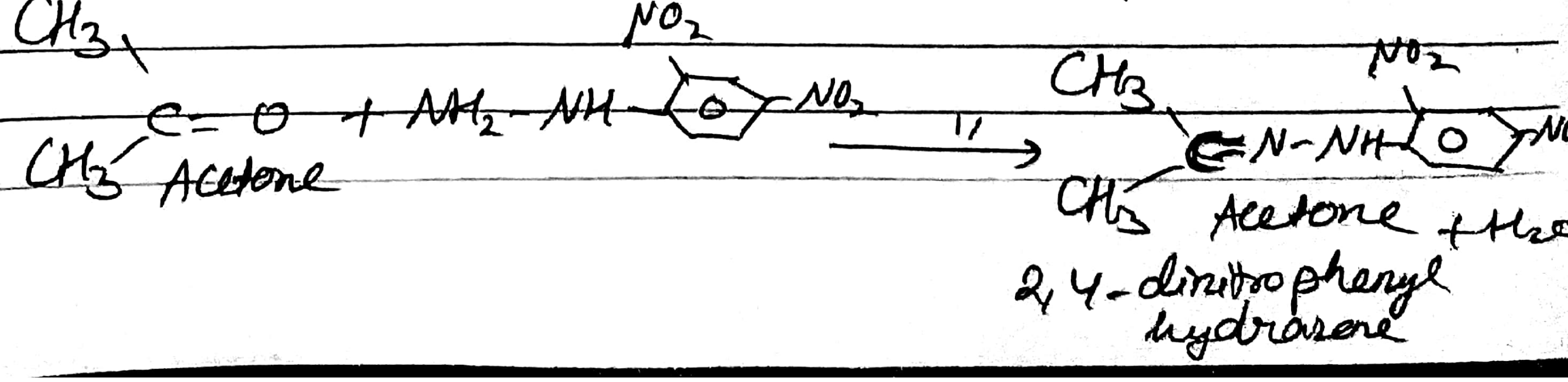
iv) Reaction with phenyl hydrazine → Formation of Phenyl hydrazone





v) Reaction with 2,4 dinitro Phenyl hydrazine (2,4-DNP)
→ Formation of 2,4 dinitro Phenyl hydrazone





vi) Reaction with Semicarbazide ⟶ Formation of Semicarbazone

$$\begin{matrix} R \\ H \end{matrix}\!\!>C=O + NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[pH\,3.5]{H^+} \begin{matrix} R \\ H \end{matrix}\!\!>C=N-NH-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

Semi Carbazone

$$\begin{matrix} CH_3 \\ H \end{matrix}\!\!>C=O \longrightarrow \begin{matrix} CH_3 \\ H \end{matrix}\!\!>C=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$$

Acetaldehyde Semicarbazone

Aldehydes & Ketones - 09

chemical properties - 4

i) Tollen's Test
ii) Fehling's Test

Aldehydes are easily oxidised to corresponding Carboxylic Acids with strong as well as mild oxidising agents

$$R-CHO \xrightarrow{[O]} R-COOH$$

Strong oxidising agent → HNO_3, acidified $K_2Cr_2O_7$, acidified $KMnO_4$, etc

Mild oxidising agent → Tollen's Reagent, Fehling's Reagent

Ketones are oxidised at high temperature only by strong oxidising agent and not by mild oxidising agents.

i) Tollen's Test: (Silver Mirror Test)

Tollen's Reagent: Ammoniacal Silver Nitrate

$$AgNO_3 \xrightarrow{NH_4OH} \underset{\text{ppt forms \& redissolves}}{Ag_2O} \xrightarrow{NH_4OH} \underset{\text{Tollen's Reagent}}{[Ag(NH_3)_2]^+OH^-}$$

freshly prepared

$$R-CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$$

(Basic medium)

$\boxed{Ag^+ \longrightarrow Ag \text{ (Reduction)}}$

ppt of metallic silver formed deposist as a mirror

⇒ Silver Mirror Test

$$CH_3-CHO \xrightarrow{T.R} CH_3COO^- + Ag \checkmark$$
$$C_6H_5-CHO \xrightarrow{T.R} C_6H_5COO^- + Ag \checkmark$$

This test is shown by aliphatic as well as Aromatic aldehydes

*** Ketones do not show this Silver Mirror Test or Tollen's Test

But α-hydroxy ketones do

$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\alpha}{\underset{OH}{CH}}-CH_3 \xrightarrow[-H_2O]{T.R\ [O]} CH_3-\overset{O}{\overset{\|}{C}}-\underset{O}{\underset{\|}{C}}-CH_3$$ diketo

Formic acid also gives Positive Tollen's Test

$$HCOOH \xrightarrow{T.R\ [O]} CO_2 + H_2O + \underset{\text{Silver Mirror}}{Ag}$$

Terminal alkynes also show Tollen's Test But do not form silver mirror Test

$$CH_3-C\equiv C-H \xrightarrow{T.R} CH_3-C\equiv \bar{C}Ag^+$$
$$CH\equiv CH \xrightarrow{T.R} CH\equiv \bar{C}Ag^+ \text{ (white ppt)}$$

ii) Fehling's Solution Test: equal mixture of Fehling Solution A + Fehling Solution B

Fehling Solution A → aq Copper sulphate $CuSO_4.5H_2O$ (Blue)

Fehling Solution B → Sodium potassium salt of tartaric acid (Rochelle Salt)

$$KOOC-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-COONa$$

- $R-CHO + 2Cu^{2+} + 5OH^{-} \longrightarrow RCOO^{-} + Cu_2O + 3H_2O$

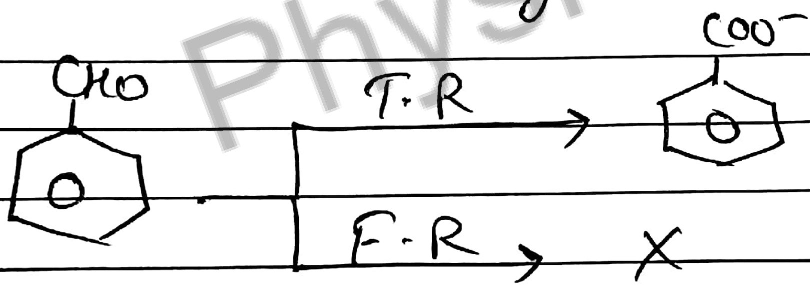
aldehyde — Cu_2O: Reddish brown ppt

$Cu^{2+} \longrightarrow Cu^{+1}$

Cupric blue $\longrightarrow$ Cuprous Reddish brown

Note: Aromatic aldehydes do not give positive Fehling's Solution test as

Fehling solution is very weak oxidising agent



Haloform Reaction

Chloroform
$CHCl_3$
Colourless liquid
with pleasant odour

Bromoform
$CHBr_3$
Light Yellow Liquid
with sweet smell

$\boxed{\text{Iodoform}}$
CHI_3
Yellow crystalline solid
Pale Yellow ppt
Hosptial like smell (antiseptic smell)

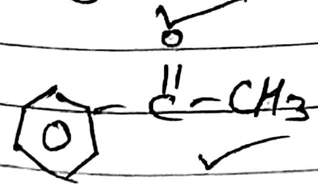
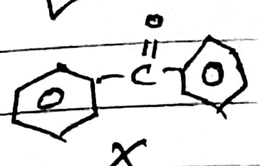
$$CH_3-\overset{O}{\overset{\|}{C}}-H + 3X_2 + 4NaOH \longrightarrow CHX_3 + HCO\overset{-}{O}\overset{+}{Na} + 3NaX + 3H_2O$$

→ Haloform Reaction is a property of carbonyl Compounds - Aldehydes & Ketones having α-Methyl (Not always)

→ Aldehyde → only Acetaldehyde gives Haloform Reaction $\underset{\alpha}{CH_3}-\overset{O}{\overset{\|}{C}}$ (α-Methyl)

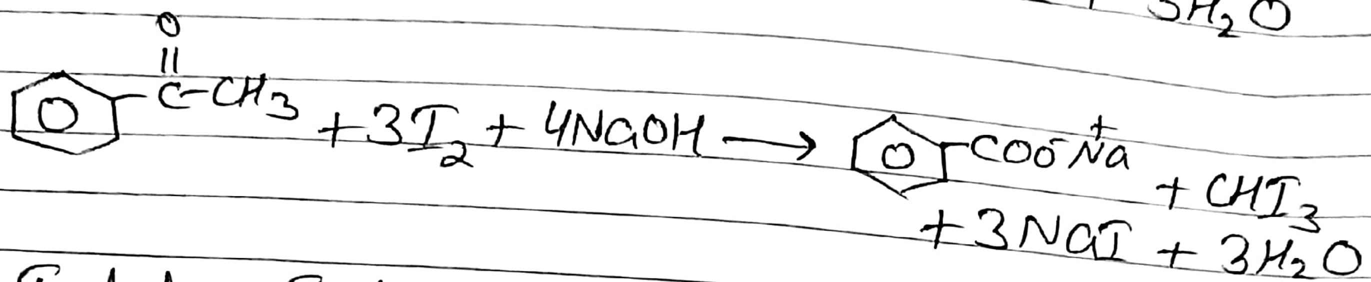
→ Ketones → $R-\overset{O}{\overset{\|}{C}}-CH_3$ all α-Methyl or Methyl alkyl ketones give Haloform Reaction.

⇒ $CH_3-\overset{O}{\overset{\|}{C}}-H$ ✓, $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ ✓, $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ ✓,

 ✓, $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ ✗,  ✗

$$CH_3-\overset{O}{\overset{\parallel}{C}}-H + 3Cl_2 + 4NaOH \longrightarrow CHCl_3 + HCO\bar{O}\overset{+}{Na} + 3NaCl + 3H_2O$$

$$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3CO\bar{O}\overset{+}{Na} + 3NaI + 3H_2O$$



__Iodoform Test:__ Aldehydes & Ketones having α-Methyl group gives yellow ppt with antiseptic smell on treatment with I_2/ NaOH.

(Not Always)

(Some exceptions are there → will study later)

Q1) Give a chemical test to distinguish

a) HCHO & CH_3CHO : HCHO do not give yellow ppt on treatment with I_2/NaOH whereas CH_3CHO gives yellow ppt on treatment with I_2/NaOH

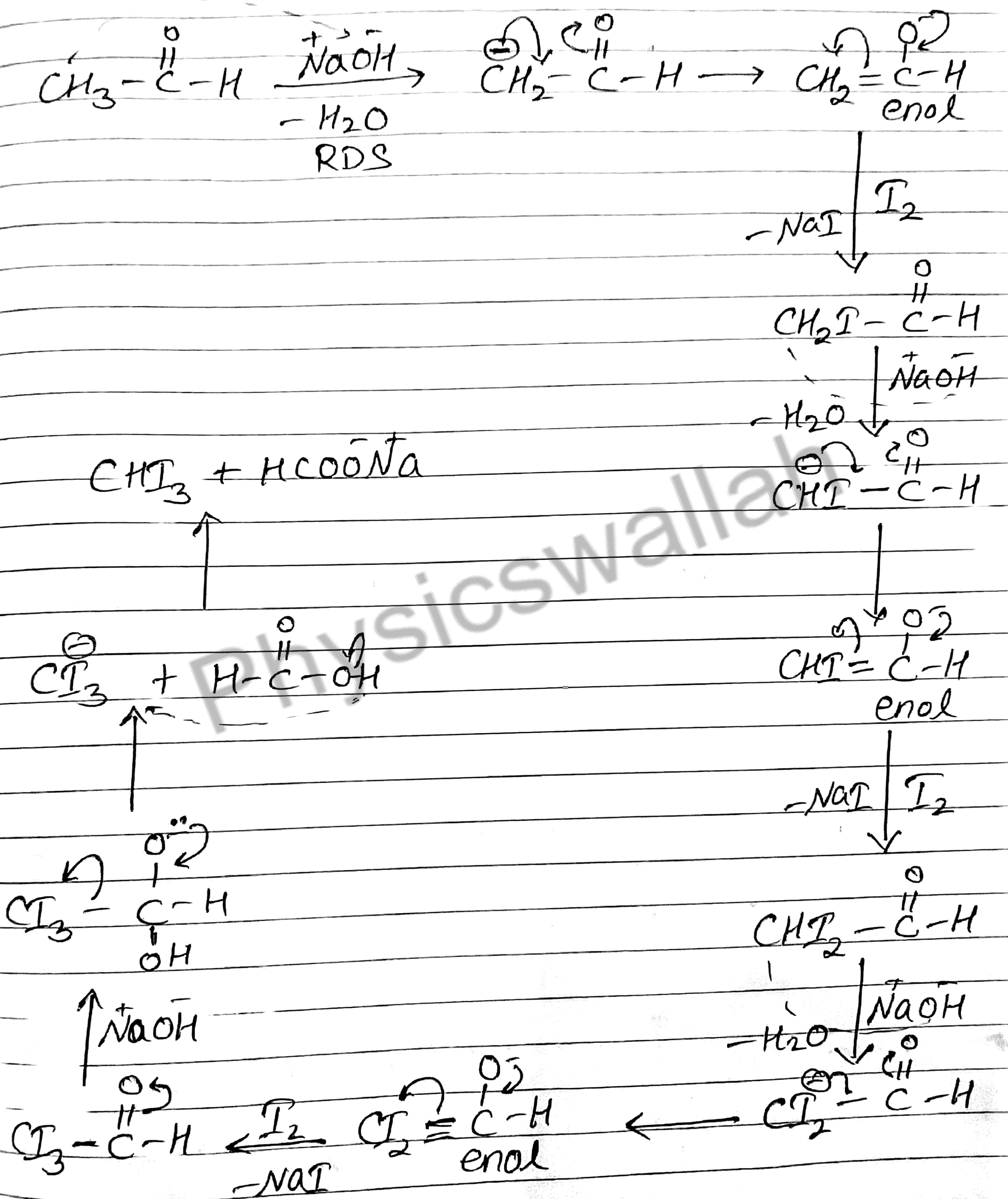
b) $H-\overset{O}{\overset{\parallel}{C}}-H$ & $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3$ → HCHO → X

CH_3COCH_3 → ✓

c) $C_6H_5-\overset{O}{\overset{\parallel}{C}}-C_6H_5$ & $CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3$

X ✓

Mechanism of Iodoform



$$CH_3-\overset{O}{\overset{\|}{C}}-H \begin{cases} \xrightarrow{Cl_2/NaOH} & \text{Rate} = R_1 \\ \xrightarrow{Br_2/NaOH} & \text{Rate} = R_2 \\ \xrightarrow{I_2/NaOH} & \text{Rate} = R_3 \end{cases}$$

$$R_1 = R_2 = R_3$$

because in RDS only NaOH is present which is same here in 1, 2 & 3.

Sometimes inplace of $X_2 + NaOH$ some other agents are given :-

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaOI} CHI_3\downarrow + CH_3COO^-\overset{+}{Na}$$

$$(2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O)$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NaOCl} CHCl_3 + CH_3COO^-\overset{+}{Na}$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CaOCl_2} CHCl_3 + (CH_3COO)_2Ca$$

$$(Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2)$$

Note: $$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CaOCl_2/\Delta} CHCl_3 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

$\downarrow$ (1)

$$CHCl_3 + \begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\!\!>Ca \xrightarrow[-CaCO_3]{\Delta}$$

dry distillation of calcium salt of fatty acid to give ketone

Some Alcohols also give Haloform Reaction OR Iodoform Test.

$$CH_3-CH_2-OH \xrightarrow[\text{Oxidising agent}]{NaOI} CH_3-\overset{\overset{O}{\parallel}}{C}-H \xrightarrow{NaOI} CHI_3\downarrow$$

Primary alcohol

↳ only Methyl alcohol

$CHI_3\downarrow$ yellow ppt

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{NaOI} CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3 \xrightarrow{NaOI} CHI_3\downarrow$$

Secondary Alcohols

↳ having 2-ol

$CHI_3\downarrow$ yellow ppt

<u>Balanced Reaction for Alcohols</u>

$$2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$$

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCO\bar{O}\overset{+}{Na} + 5NaI + 5H_2O$$

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + 4I_2 + 6NaOH \longrightarrow CHI_3 + CH_3CO\bar{O}\overset{+}{Na} + 5NaI + 5H_2O$$

Aldehyde | Ketone $\longrightarrow 3I_2 + 4NaOH$

Alcohols $\longrightarrow 4I_2 + 6NaOH$

Q2) Give a chemical test to distinguish:-

a) CH_3OH & C_2H_5OH $\longrightarrow$ C_2H_5OH on treatment with $I_2/NaOH$ gives yellow ppt with antiseptic smell whereas CH_3OH do not.

b) CH_3-CH_2-OH ✓ & $CH_3-CH_2-CH_2-OH$ ✗

oxidise करके aldehyde/ketone बना लो. फिर check करलो $\alpha-CH_3$ group है या नहीं

c) $CH_3-\underset{OH}{CH}-CH_3$ ✓ & $CH_3-\underset{OH}{CH}-CH_2-CH_3$ ✓

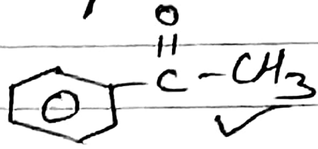
Cannot be distinguished with Iodoform test

d) $CH_3-\underset{OH}{CH}-CH_3$ ✓ & $CH_3-CH_2-\underset{OH}{CH}-CH_2-CH_3$ ✗

Will the following Compound Show Iodoform Test

(1) $CH_3-\overset{O}{\overset{\|}{C}}-H$ ✓

(2) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ ✓

(3)  ✓

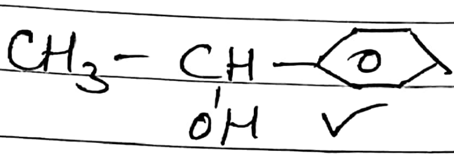
(4) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ ✓

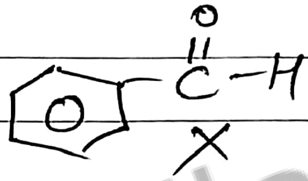
(5) CH_3-CH_2-OH ✓

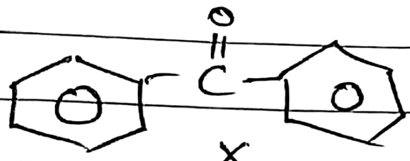
(6) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$ ✓

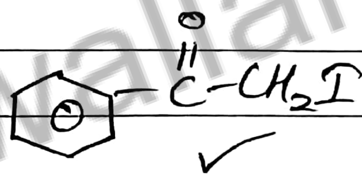
(7) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$ ✓

(8) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_2-CH_3$ ✓

(9)  ✓

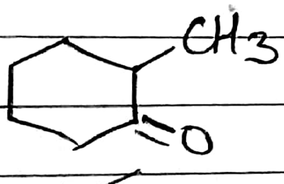
(10)  ×

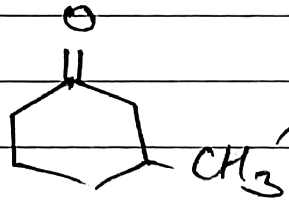
(11)  ×

(12)  ✓

(13) $CH_3-\overset{O}{\overset{\|}{C}}-CHI_2$ ✓

(14) $CI_3-\overset{O}{\overset{\|}{C}}-H$ ✓

(15)  ✓

(16)  ×

(17) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-NO_2$ ×

$-I, -M$

$\downarrow OH^-$

$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{CH}-CN$

Strong -M group
Strong EWG than $\overset{O}{\overset{\|}{C}}$
than Not give

(18) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CN$ ×

$-I, -M$

$\downarrow OH^-$

$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{CH}-CN$

(19) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ ✓

$$\Big\downarrow \; OH^-, \; I_2$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CHI-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\Big\downarrow \; OH^-, \; I_2$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CI_2-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\Big\downarrow \; OH^-$$

$$CH_3-\underset{OH}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-CI_2-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\Big\downarrow$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + \overset{\ominus}{C}I_2-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\Big\downarrow \; I_2$$

$$CI_3-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\Big\downarrow \; OH^-$$

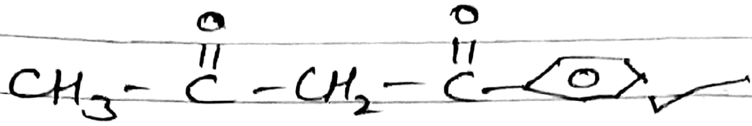
$$CI_3-\underset{OH}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-CH_3$$

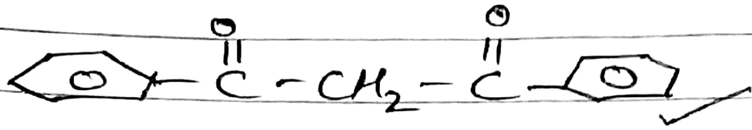
$$\Big\downarrow$$

$$\overset{\ominus}{C}I_3 + CH_3-\overset{O}{\overset{\|}{C}}-O-H$$

$$CHI_3 \downarrow$$

yellow ppt

(20) 

(21) 

(22) $CH_3-O-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$ ✗

$$\downarrow OH^-, I_2$$

$$CH_3-O-\overset{O}{\overset{\|}{C}}-CI_2-\overset{O}{\overset{\|}{C}}-OCH_3$$

$$\downarrow OH^-$$

$$CH_3-O-\overset{O^-}{\overset{|}{C}}-CI_2-\overset{O}{\overset{\|}{C}}-O-CH_3$$

better Leaving group

$$\downarrow$$

$$CH_3-O^- + \overset{O}{\overset{\|}{C}}-CI_2-\overset{O}{\overset{\|}{C}}-O-CH_3$$

(23) $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$ ✓

(24)