Aldehydes & Ketones - 06
Chemical properties - 5

Haloform Reaction

Chloroform
$CHCl_3$
Colourless liquid
with pleasant odour

Bromoform
$CHBr_3$
Light Yellow Liquid
with sweet smell

Todoform
CHI_3
Yellow crystalline solid
Pale Yellow ppt
Hosptial like smell (antiseptic smell)

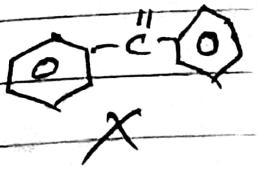
$$CH_3-\overset{O}{\overset{\|}{C}}-H + 3X_2 + 4NaOH \longrightarrow CHX_3 + HCOO^-Na^+ + 3NaX + 3H_2O$$

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

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

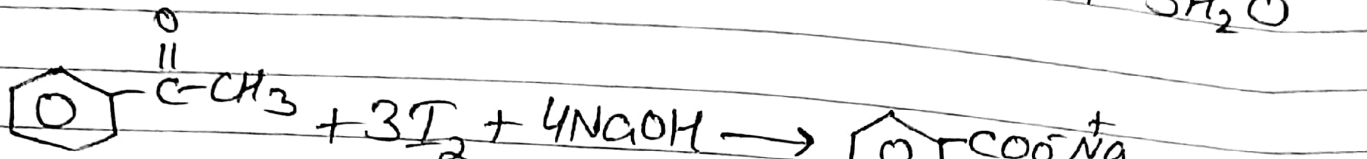
→ Ketones → $R-\overset{O}{\overset{\|}{C}}-CH_3$ all α-Methyl or Methyl alkyl ketones give Haloform Reaction.

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

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

$CH_3-\overset{O}{\overset{\|}{C}}-H + 3Cl_2 + 4NaOH \longrightarrow CHCl_3 + HCOO^-Na^+ + 3NaCl + 3H_2O$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COO^-Na^+ + 3NaI + 3H_2O$



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)

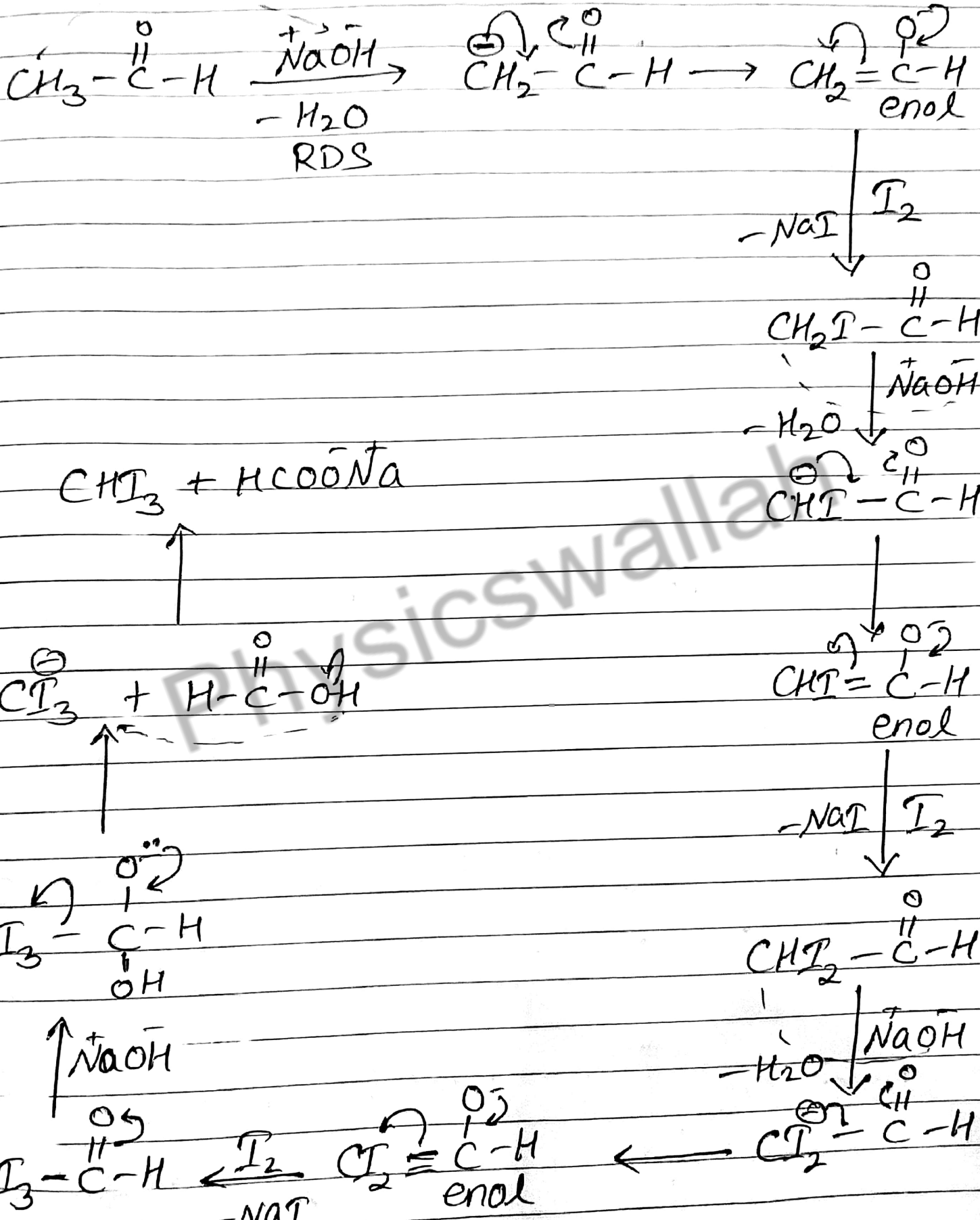
Q1) Give a chemical test to distinguish

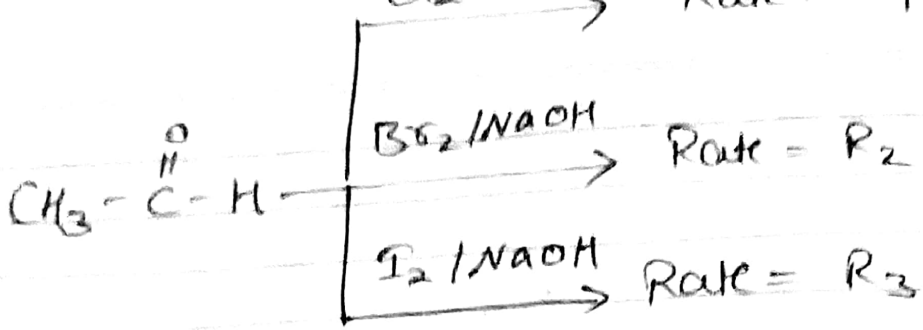
a) HCHO & CH_3CHO : HCHO do not give yellow ppt on treatment with $I_2/NaOH$ whereas CH_3CHO gives yellow ppt on treatment with $I_2/NaOH$

b) $H-\overset{O}{\overset{\|}{C}}-H$ & $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ → HCO → X
CH_3COCH_3 → ✓

c) $C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$ & $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$
X ✓

Mechanism of Iodoform





$R_1 = R_2 = R_3$

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 :-

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

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

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

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

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

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

$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ $\xrightarrow{①}$ $CHCl_3 + CH_3COO-Ca-OOCCH_3$ $\xrightarrow[-CaCO_3]{\Delta}$ dry distillation of Calcium salt of fatty acid to give Ketone

Some Alcohols also give Haloform Reaction or Iodoform Test.

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

Primary alcohol
↳ only Methyl alcohol

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

Secondary Alcohols
↳ having 2-ol

Balanced Reaction for Alcohols

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

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOO^-Na^+ + 5NaI + 5H_2O$$

$$CH_3-\underset{OH}{CH}-CH_3 + 4I_2 + 6NaOH \longrightarrow CHI_3 + CH_3COO^-Na^+ + 5NaI + 5H_2O$$

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

Alcohols $\longrightarrow 4I_2 + 6NaOH$

Q2) Give a chemical test to distinguish:-

a) CH_3OH & C_2H_5OH → 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 & $CH_3-CH_2-CH_2-OH$
✓ ✗

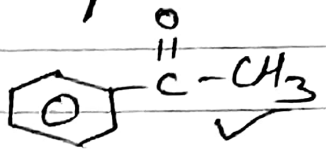
oxidise करके aldehyde/ketone बना लो. फिर check करलो $\alpha-CH_3$ group है या नहीं

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

Cannot be distinguished with Iodoform test

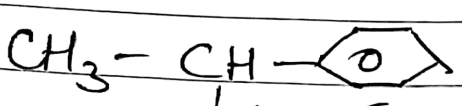
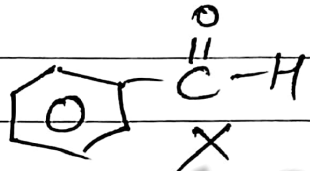
d) $CH_3-\underset{OH}{CH}-CH_3$ ✓ & $CH_3-CH_2-\underset{OH}{CH}-CH_2-CH_3$ ✗

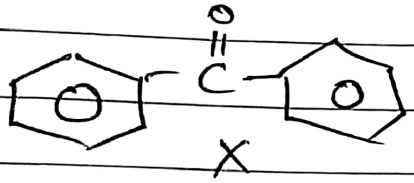
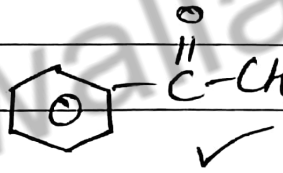
Will the following Compound Show Iodoform Test

(1) $CH_3-\overset{O}{\overset{\|}{C}}-H$ ✓ (2) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ ✓ (3)  ✓

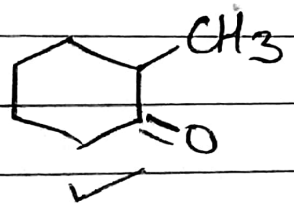
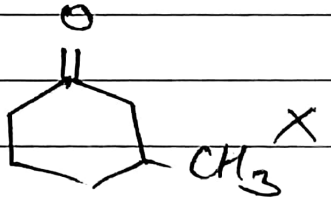
(4) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ ✓ (5) CH_3-CH_2-OH ✓ (6) $CH_3-\underset{OH}{CH}-CH_3$ ✓

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

(9)  ✓ (10)  ✗

(11)  ✗ (12)  ✓

(13) $CH_3-\overset{O}{\overset{\|}{C}}-CHI_2$ ✓ (14) $CI_3-\overset{O}{\overset{\|}{C}}-H$ ✓

(15)  ✓ (16)  ✗

(17) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-NO_2$ ✗ ($-I, -M$)

$\downarrow OH^-$

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

(18) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CN$ ✗ ($-I, -M$)

Strong $-M$ group Stronger EWG than C Not give

$\downarrow OH^-$

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

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

$\downarrow OH^-, I_2$

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

$\downarrow OH^-, I_2$

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

$\downarrow OH^-$

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

$\downarrow$

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

$\downarrow I_2$

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

$\downarrow OH^-$

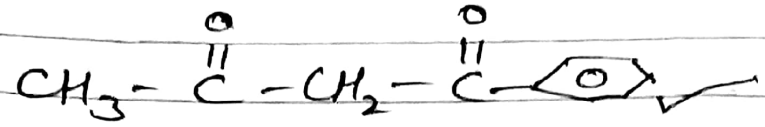
$CI_3-\underset{OH}{\overset{O}{\overset{\|}{C}}}-CH_3$

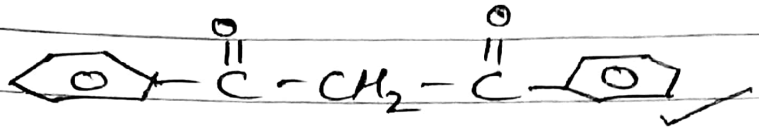
$\downarrow$

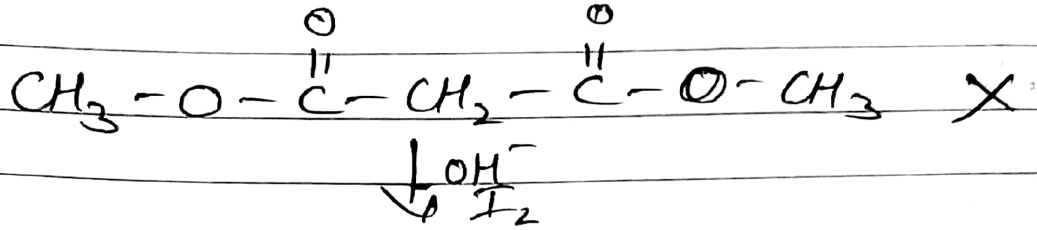
$\overset{\ominus}{C}I_3 + CH_3-\overset{O}{\overset{\|}{C}}-OH$

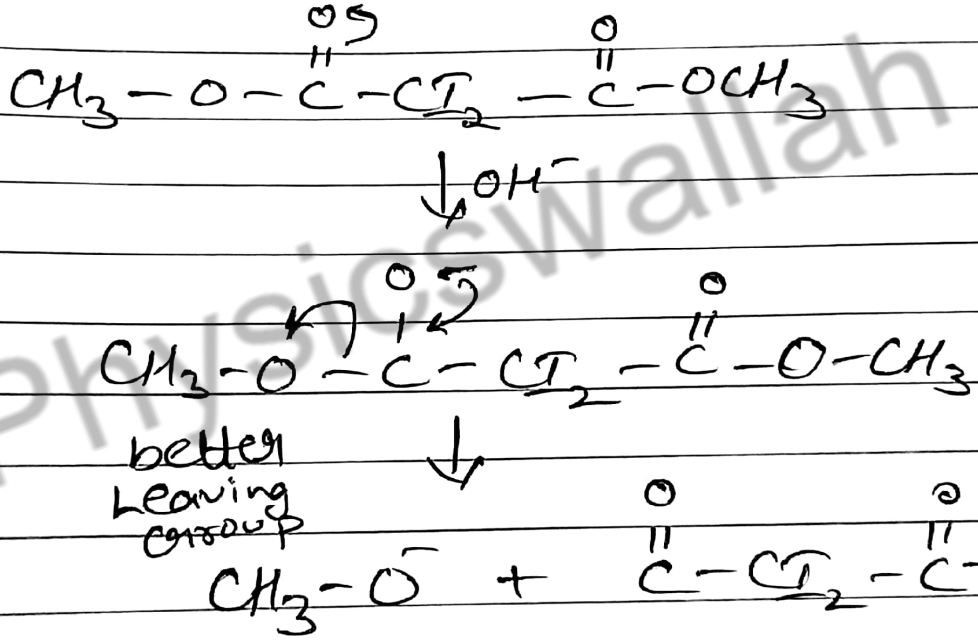
$\rightarrow CHI_3 \downarrow$

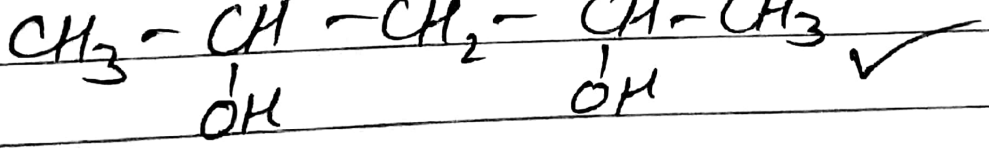
Yellow ppt

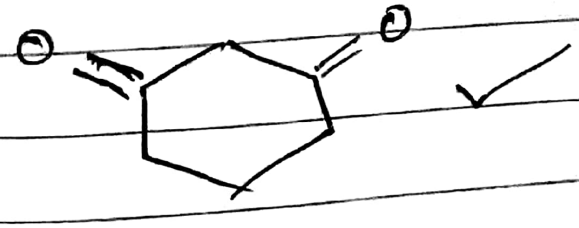
(20)  ✓

(21)  ✓

(22)  ✗



(23)  ✓

(24)  ✓