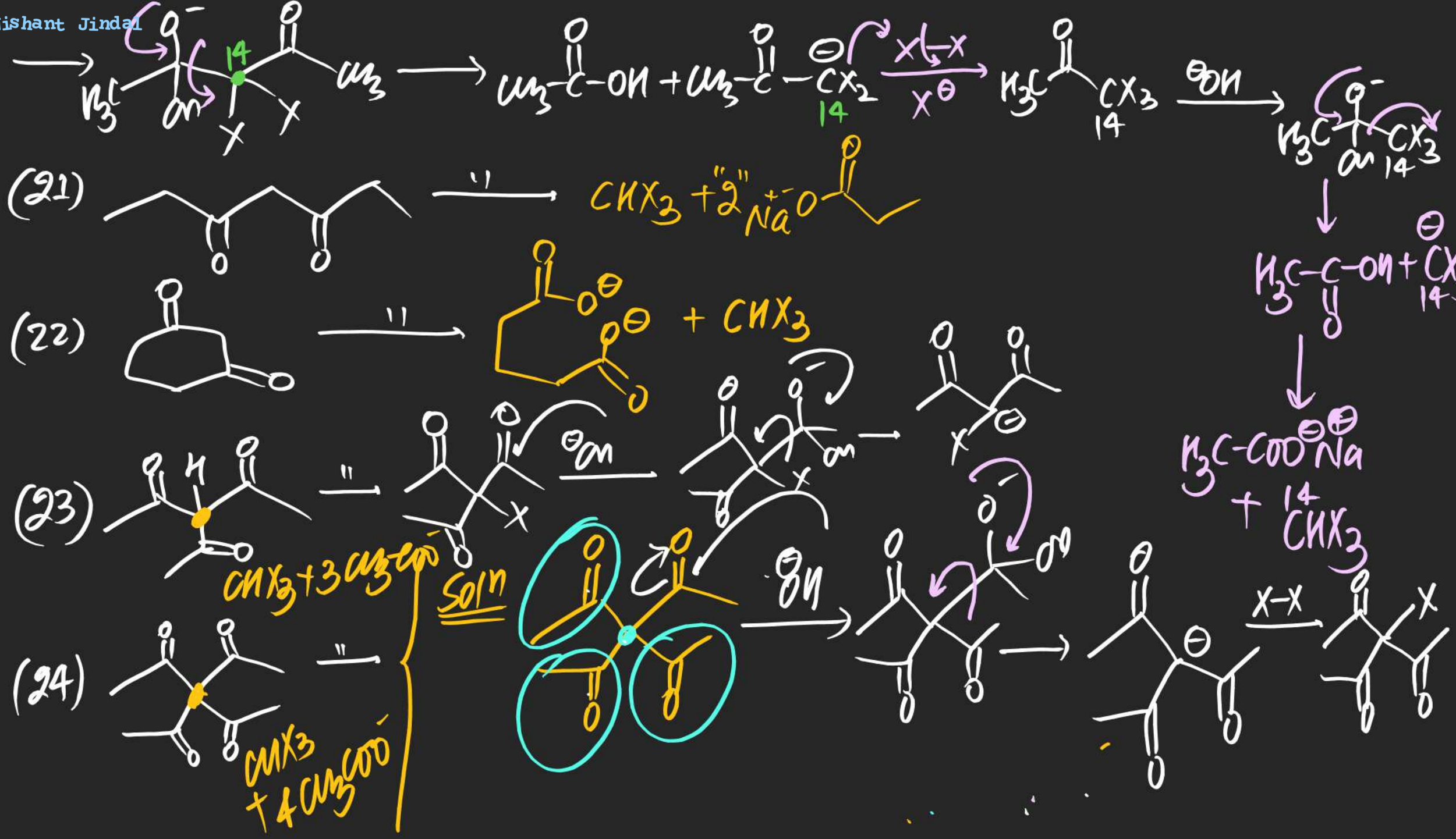
Nishant Jindal



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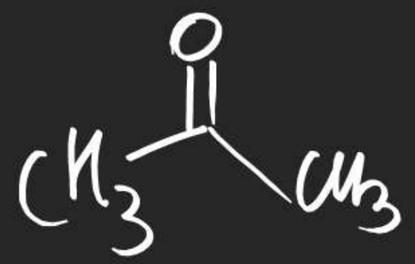
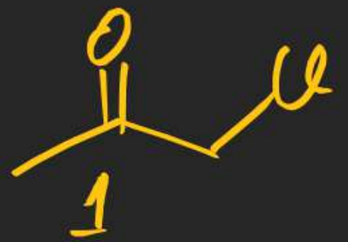
(iii) Rate exp:

$$r = k[\text{Acetone}]^1[X_2]^0$$

$$\Rightarrow r = k[\text{Acetone}]$$

(iv) rate of halogenation

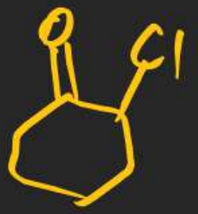
(33)  $+Cl_2 \xrightarrow{Acon}$

(a) $t=0$ 1 $\quad \frac{1}{0}$ 

$t=t$ 0

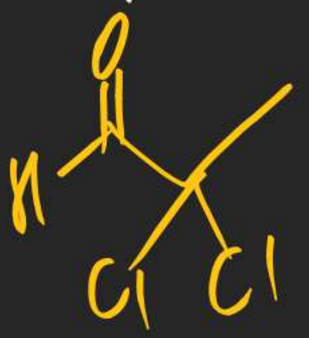
(b) $t=0$ 1 $\quad \frac{2}{0}$

$t=t$ 0

(34) $+Cl_2 \xrightarrow{Acon}$ 

(35) $+Cl_2 \xrightarrow{NaOH}$

1 : 1



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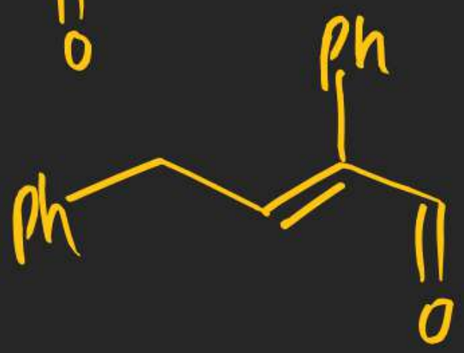
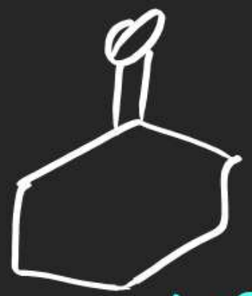
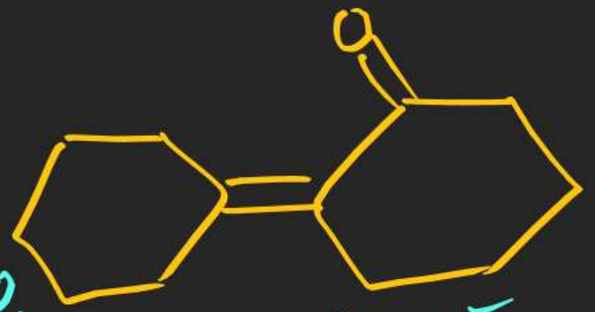
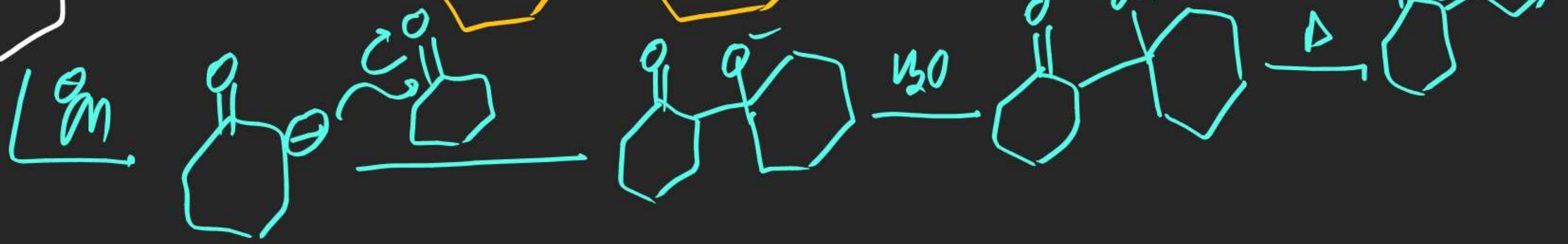
(3) $CH_3-CH_2-C(=O)-H \xrightarrow[NaOH]{dil} P \xrightarrow[\Delta]{NaOH} Q$

(4) $\xrightarrow[Na_2CO_3,\ \Delta]{Aq.}$ 

(5)  $\xrightarrow[\Delta]{Ba(OH)_2}$ 



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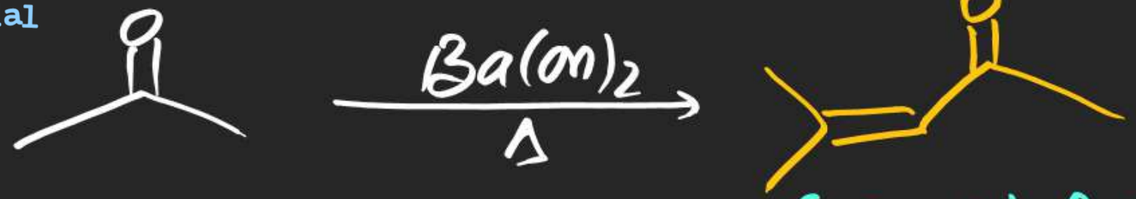
(6)

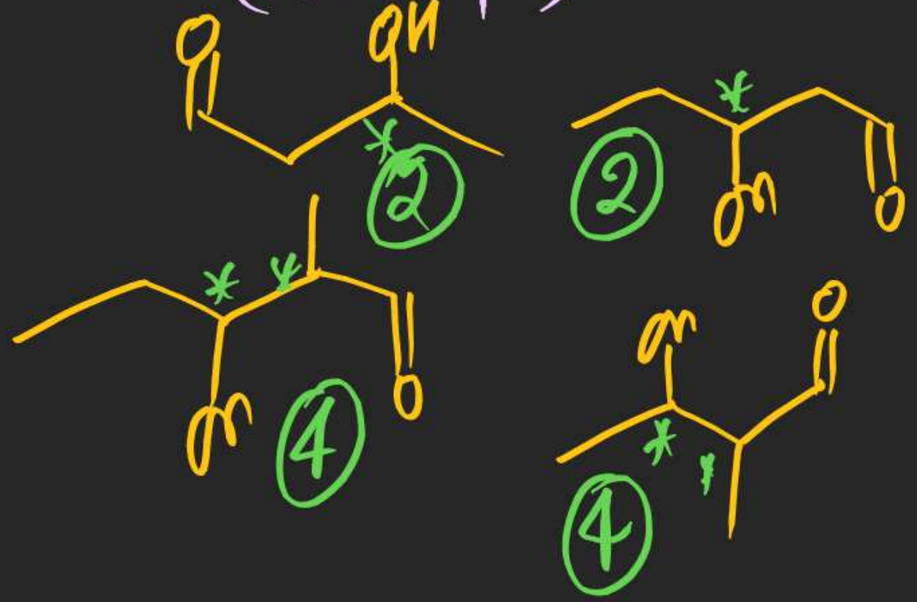


(Mesityl oxide)

Cross Aldol Reaction:

(7) $CH_3-\underset{\underset{O}{\|}}{C}-H + CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H \xrightarrow{NaOH}$ Total possible Aldol

(Aldehyde) (Aldehyde)



Total possible Aldol

- without stereoisomerism (4)
- with stereo-Isomerism (12)

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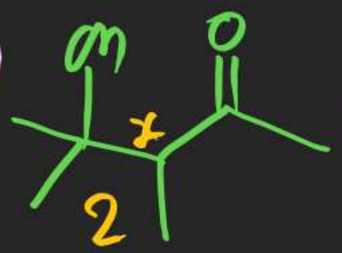
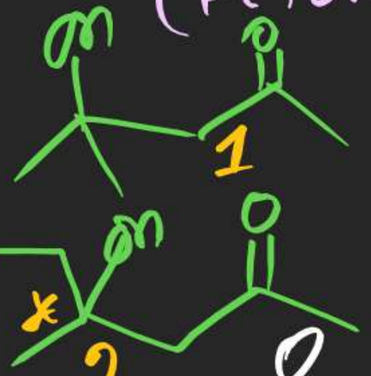
(8) + $\xrightarrow{Ba(OH)_2}$

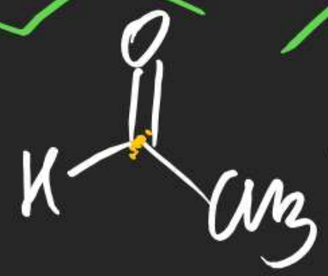
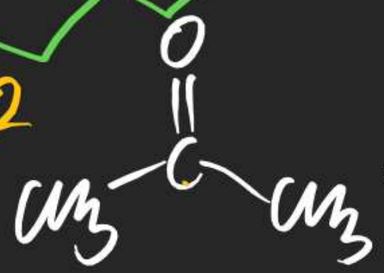
(Ketone) (Ketone)



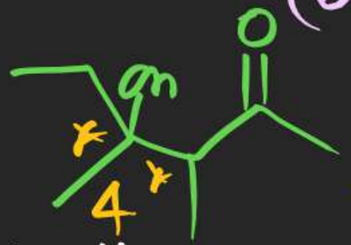
Total possible Aldol

- without stereo (6)
- with stereo (12)



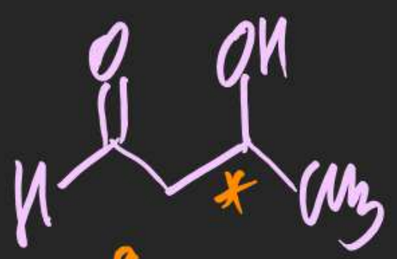
(9)  + 

$\xrightarrow{NaOH}$



Total possible Aldol

- without stereo (4)
- with stereo (6)



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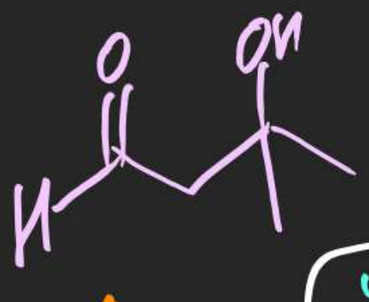
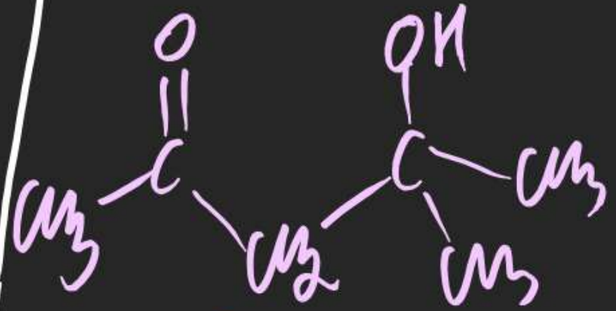


1

Major Product

Enolate 2 Acceptor



1

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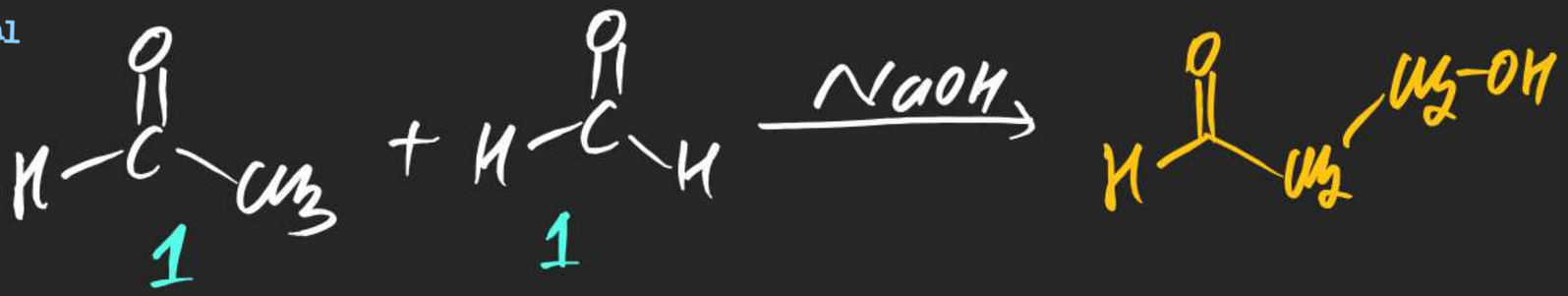
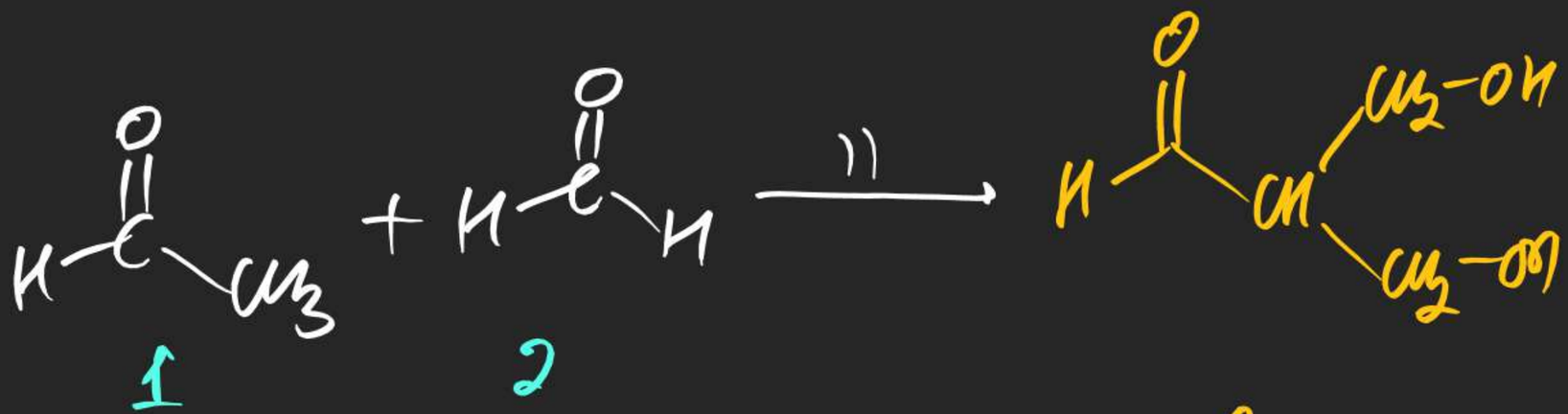
(10) 

(11) 

(12)

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Claisen Reaction :-

(13) CH_3-CHO + $Ph-CHO$ $\xrightarrow[\Delta]{NaOH}$ $Ph-CH=CH-CHO$

Aliphatic aldehyde — Aromatic aldehyde — (Cinnamaldehyde)

Nitro Aldol :-

(14) CH_3-NO_2 + $HCHO$ $\xrightarrow{NaOH}$ $O_2N-CH_2-CH_2-OH$

Cyno Aldol

(15) $CH_3-C\equiv N$ + $HCHO$ $\xrightarrow{NaOH}$ $N\equiv C-CH_2-CH_2-OH$

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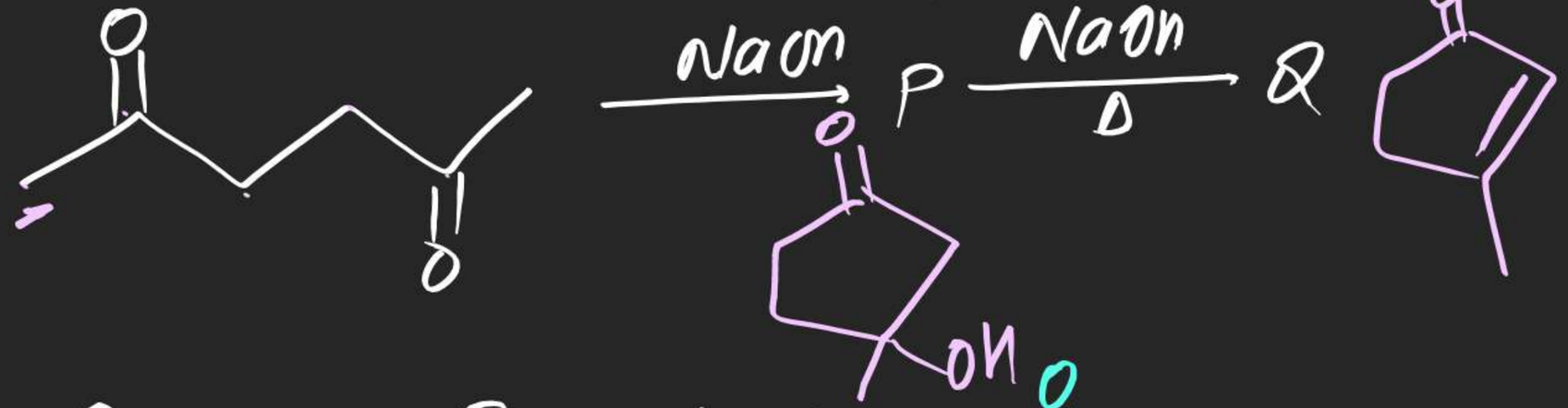
Intramolecular Aldol :

⇒ di Carbonyl compound may undergo Intramolecular Aldol only when 5 & 6 membered Ring is formed

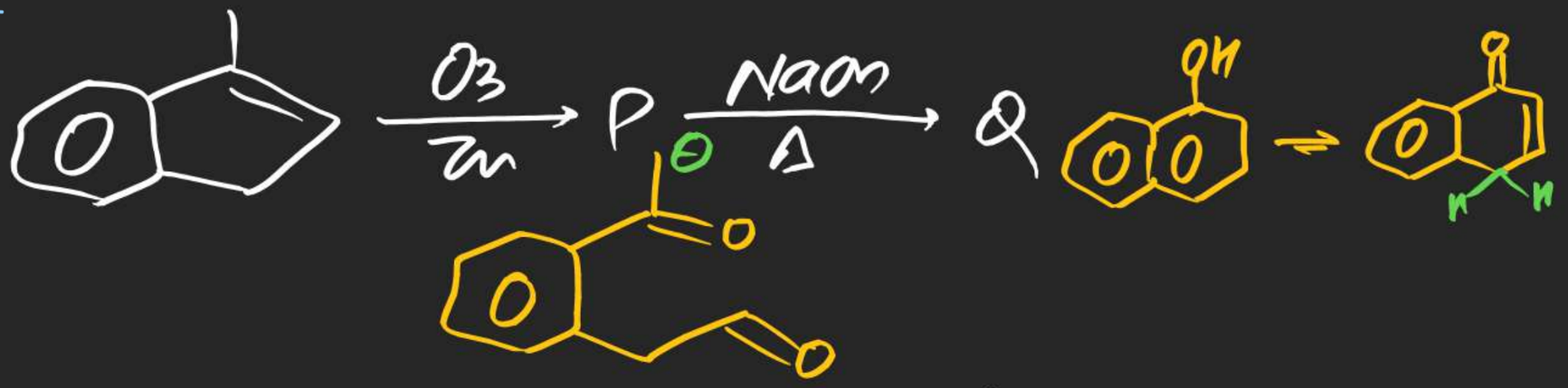
(16)



(17)

Nishant Jindal

(18)



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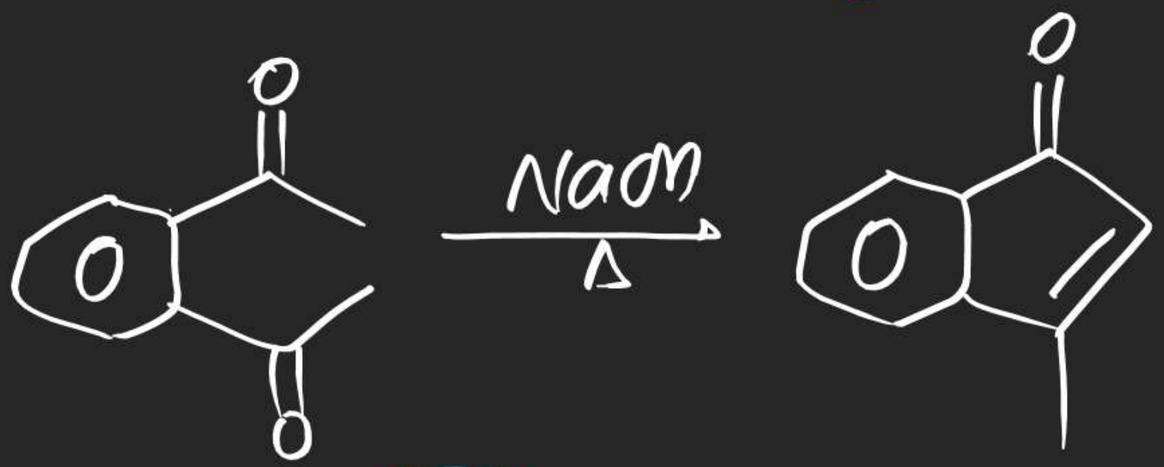
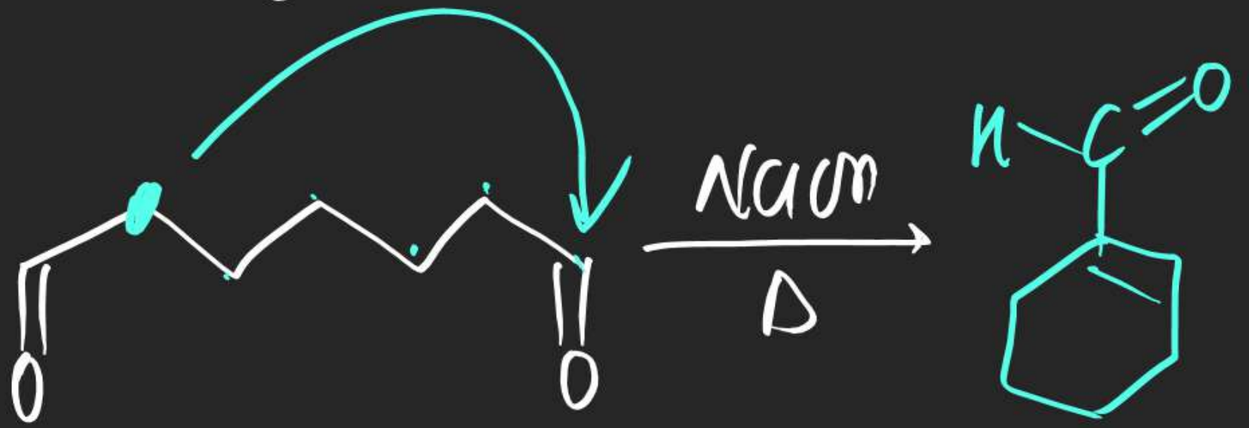


(20)



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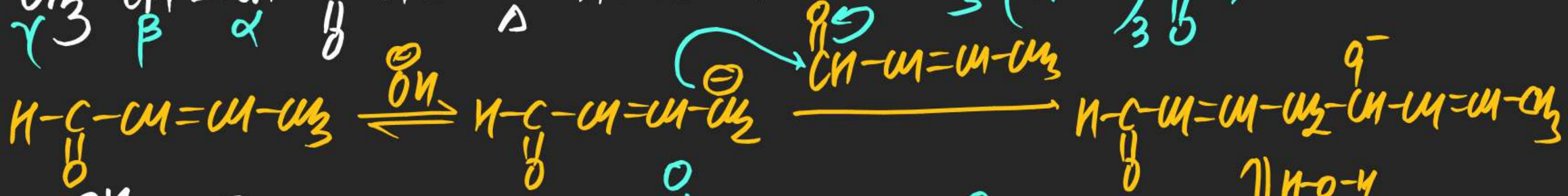
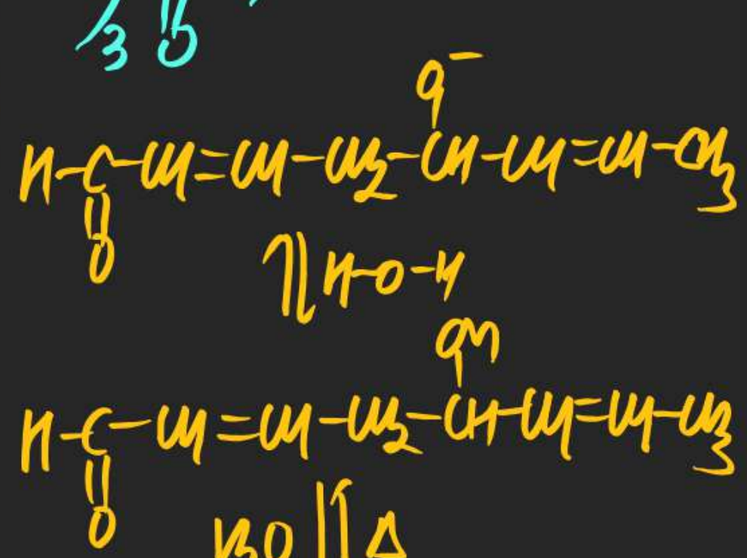
(21) $CH_3-\overset{\gamma}{CH}=\overset{\beta}{CH}-\overset{\alpha}{\underset{O}{\overset{\|}{C}}}-H \xrightarrow[\Delta]{NaOH}$ Linear Product $CH_3-(CH=CH)_3-\underset{O}{\overset{\|}{C}}-H$

Soln:



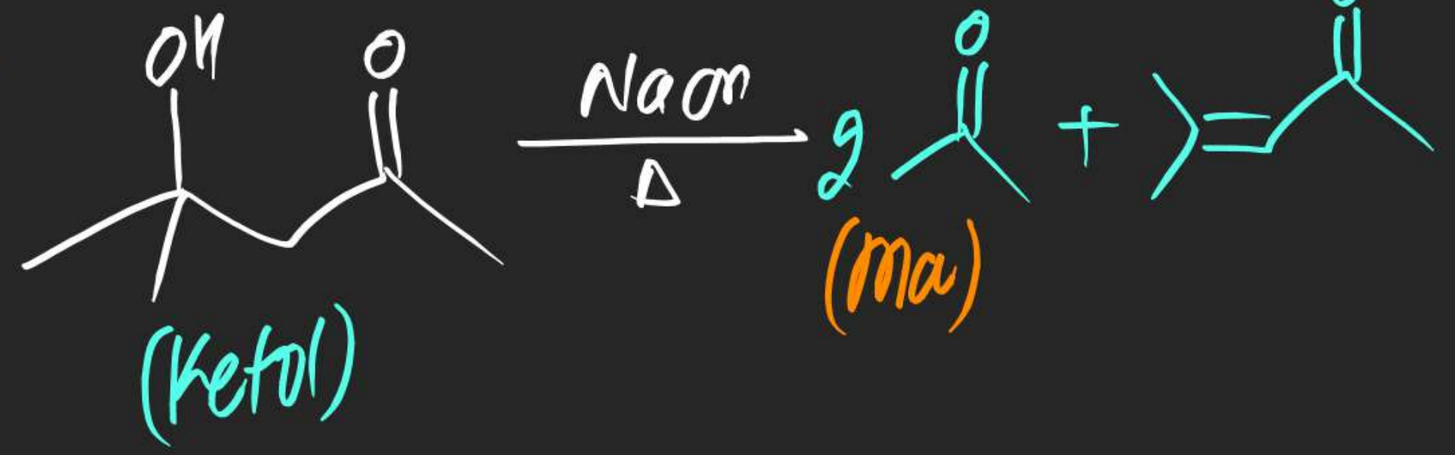


Imp

(22)

Imp

(23)



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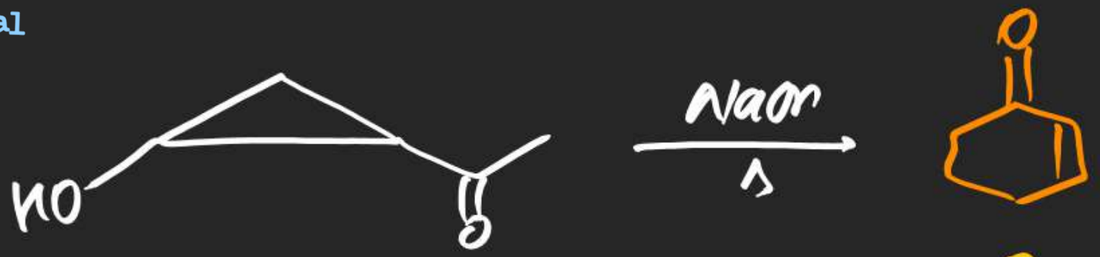
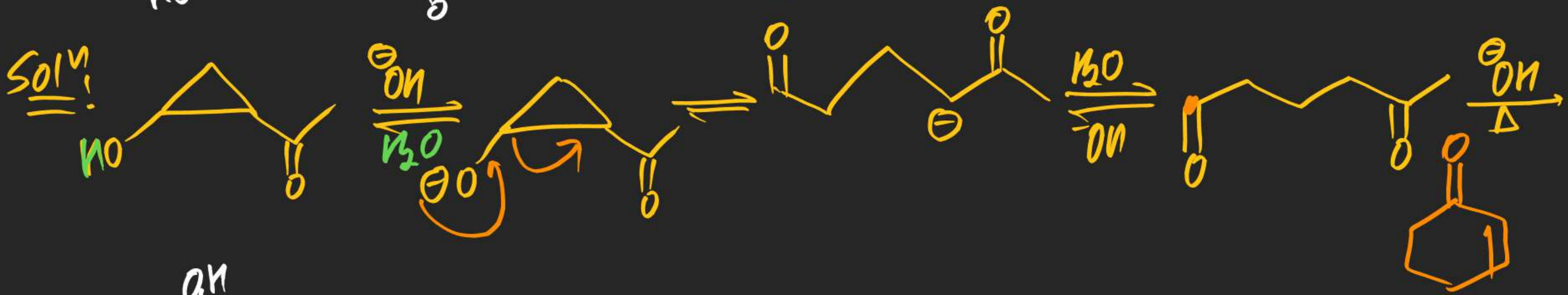
(24)



Soln:



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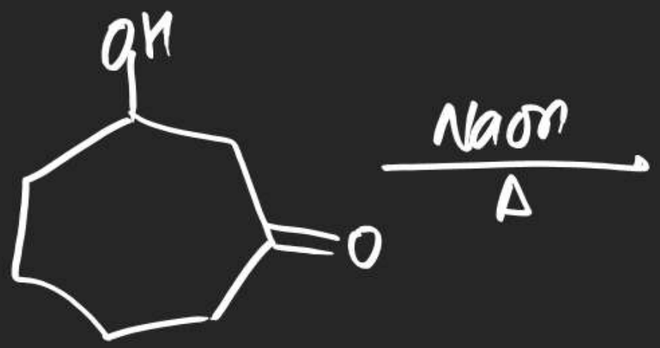

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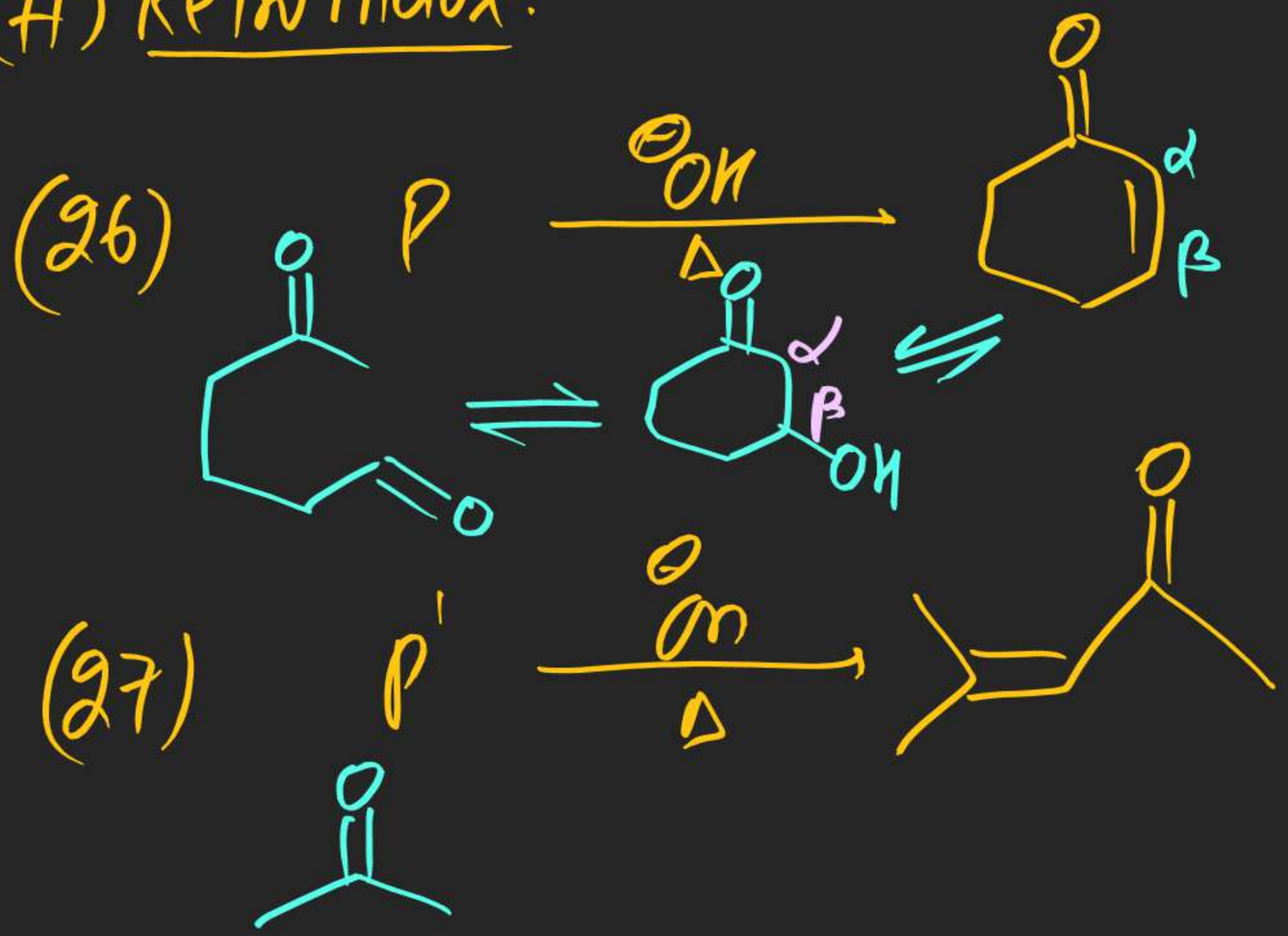
(#) Retro Aldol :-



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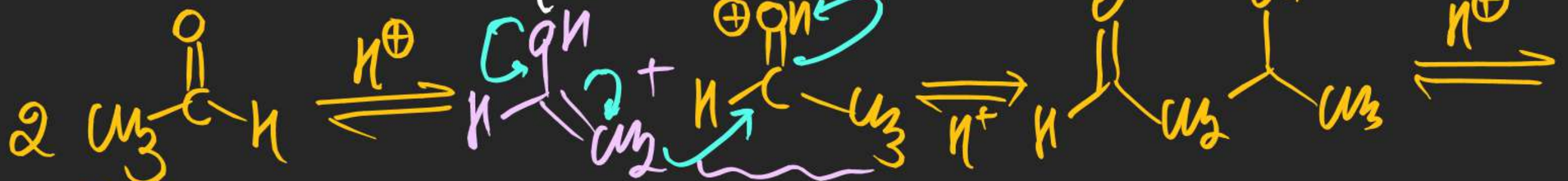
(#) Acid-Catalysed Aldol :

⇒ Carbonyl Compound in Acid Catalysed condⁿ gives dehydrated Aldol

⇒ Aldol is not stable in Acidic condⁿ

(28)

Mechⁿ: 

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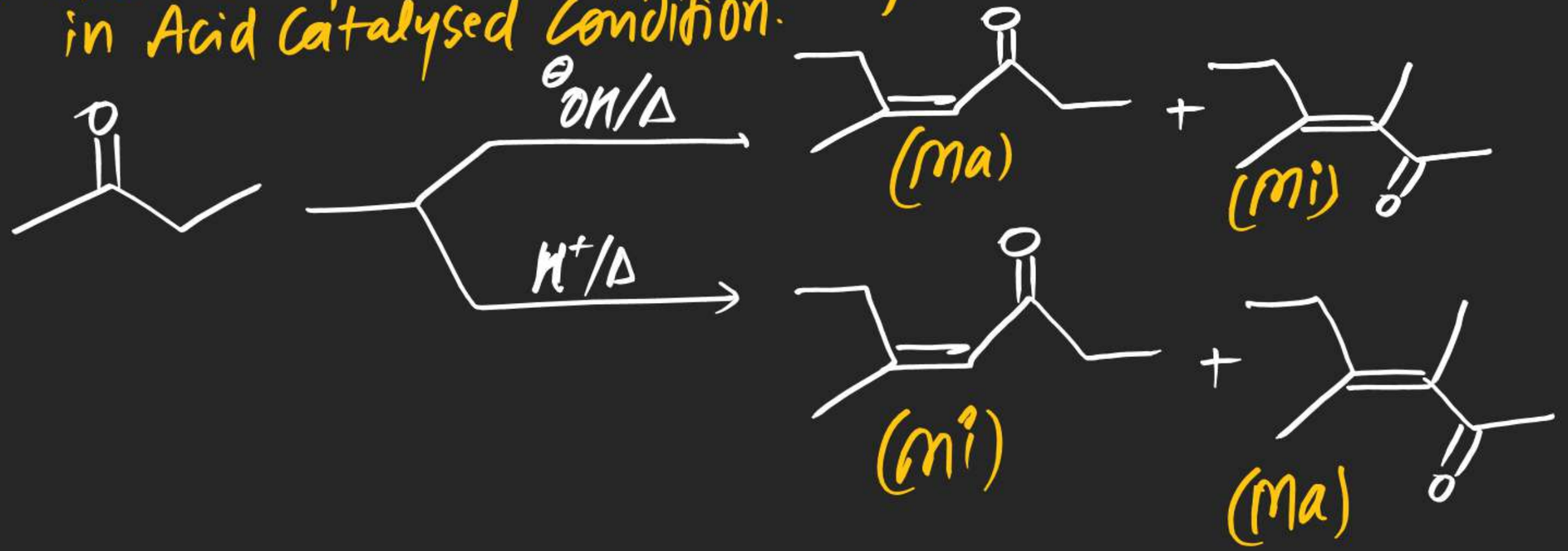
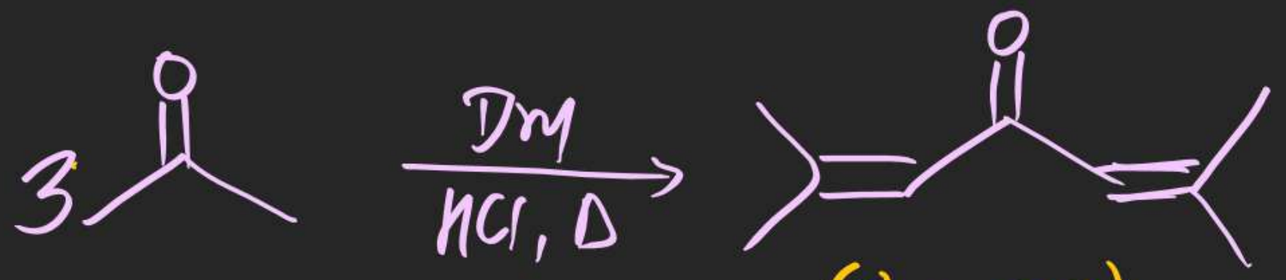
Note (i) Aldol dehydration takes place By E^1 mechanism in Acid Catalysed Condition.

(29)



(30)



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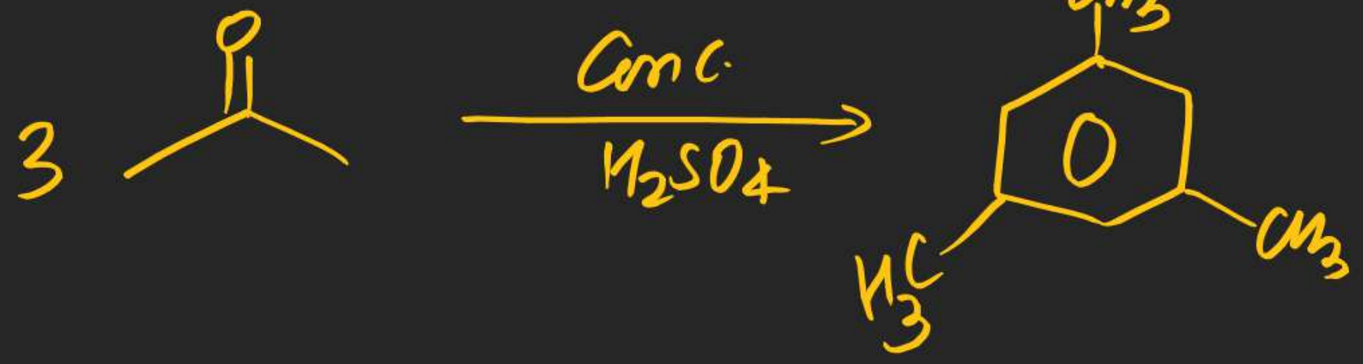
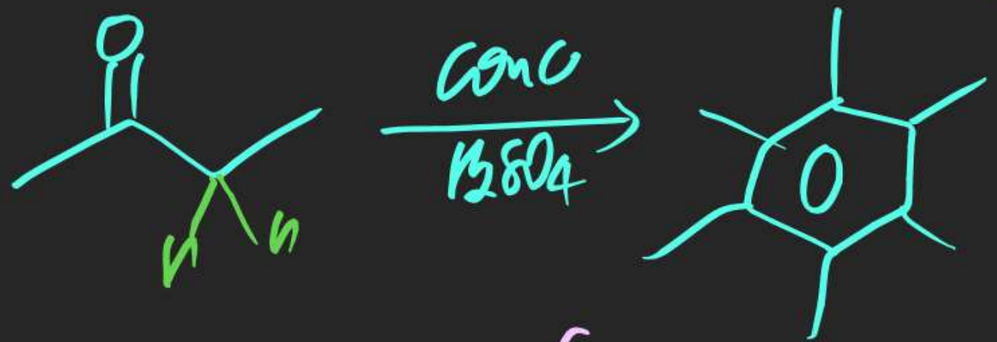
(31)



(1) 1,3,5-Tri methyl Benzene
(Mesitylene)

(32)



(Hexa methyl Benzene)

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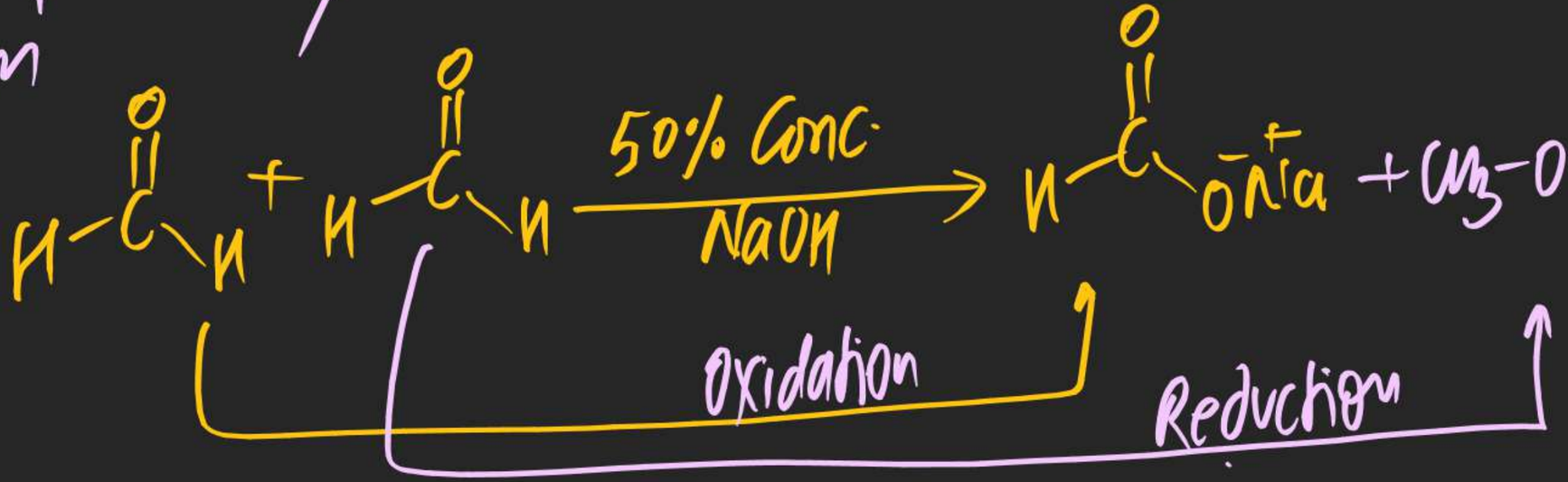
(#) Cannizaro's Reaction:

⇒ This Reaction is shown By Carbonyl compound without "α" H

⇒ In this Reaction Carbonyl compound without "α" H gets disproportionate / Oxidised & Reduced in 50% conc NaOH or KOH Solution

(1)



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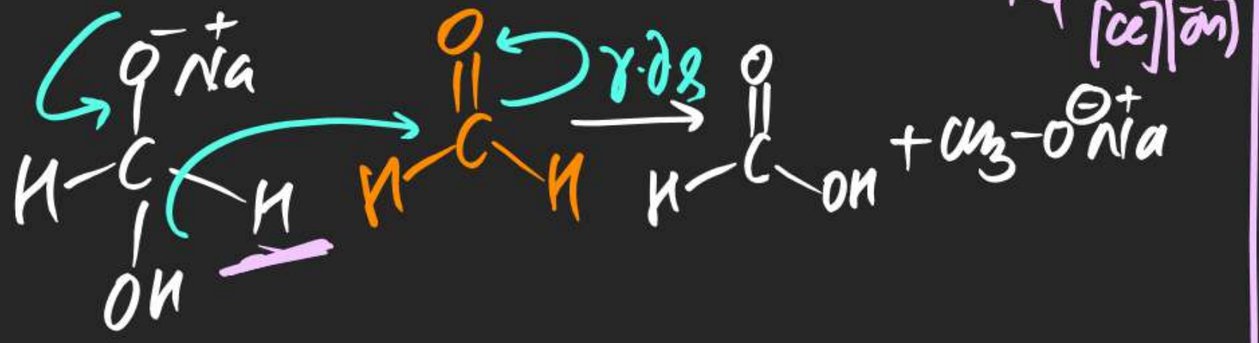
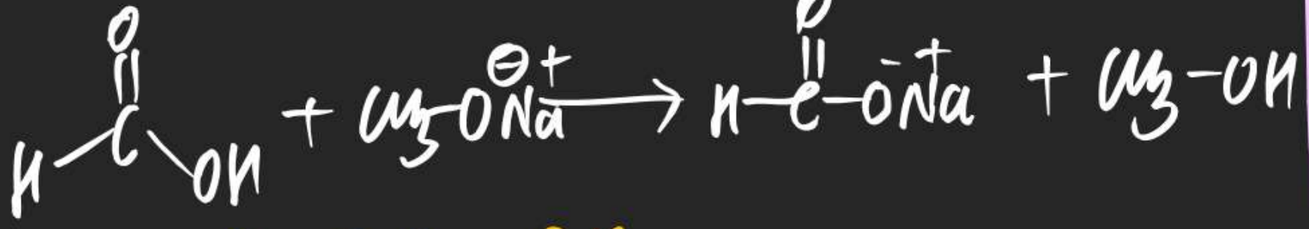
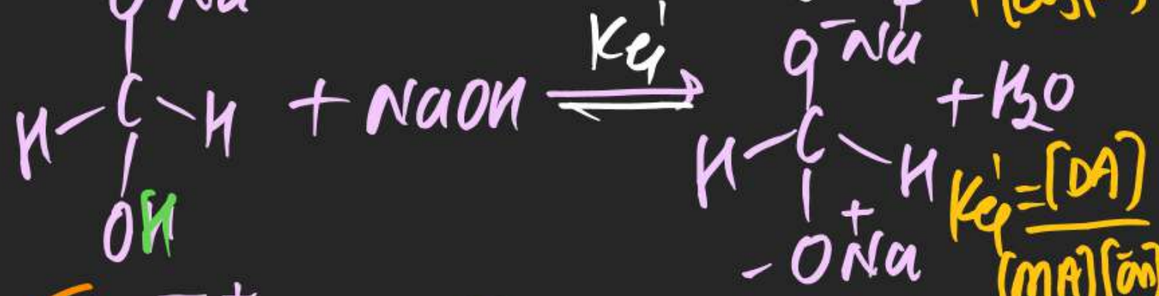
Mech^{n}

$K_{eq} = \frac{[MA]}{[C][OH]}$

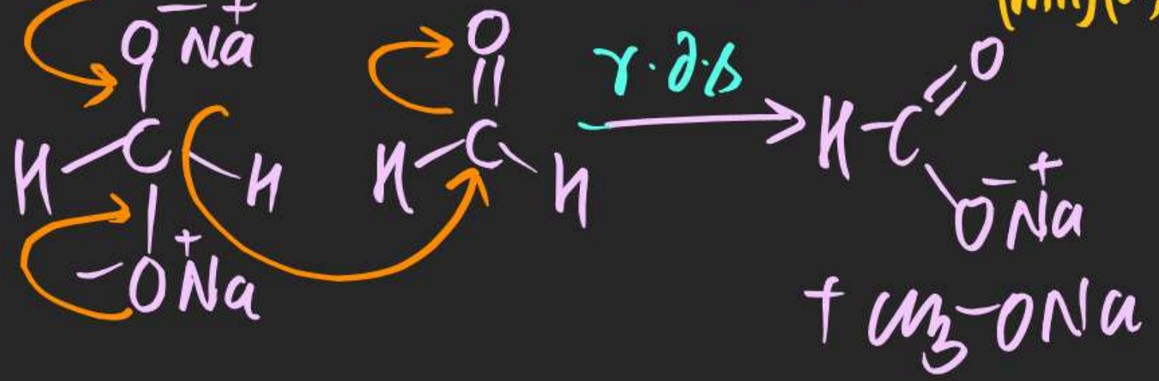




$K_{eq} = \frac{[MA]}{[C][OH]}$



$K_{eq}' = \frac{[DA]}{[MA][OH]}$



Note (i) Redox Rx^{n}

(ii) Self Cannizaro Rx^{n} is Disproportionation

(iii) Migration of Hydride ion is r.d.s

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(iv) rate exp

Excess Base Conc.

$r = K[CC][m\text{-}A]$

$= K'[CC][CC][\bar{O}n]$

$= K'[CC]^2[\bar{O}n]$

⇒ Bimolecular

⇒ III-order

$r = K[DA][CC]$

$= K'[mA][\bar{O}n][CC]$

$= K''[CC][\bar{O}n][\bar{O}n][CC]$

$= K''[CC]^2[\bar{O}n]^2$

⇒ Bimolecular

⇒ IV-order

⇒ Kinetic isotopic effect present

⇒ Cross Cannizzaro & intramolecular Cannizzaro Both are Redox But not disproportionation

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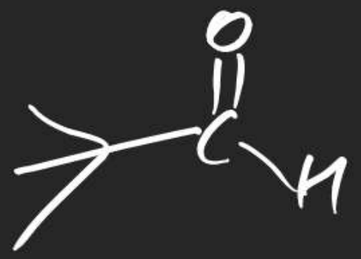
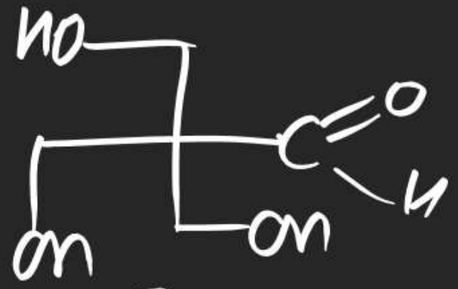
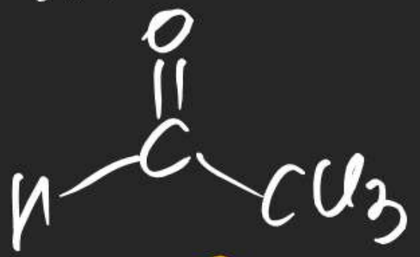
(2) $Ph-C(=O)-H \xrightarrow[KOH]{Conc.} Ph-COO^-\overset{+}{Na} + Ph-CH_2-OH$

(3)  $\xrightarrow{''}$

(4)  $\xrightarrow{''}$

(5)  $\xrightarrow{NaOH} CHCl_3 + H-COONa$

*** (6) $CH_3-C(=O)-H \xrightarrow[NaOH]{Conc.} CH_3-CH_2-OH + \text{"P"}$ $(CH_3-COONa)$

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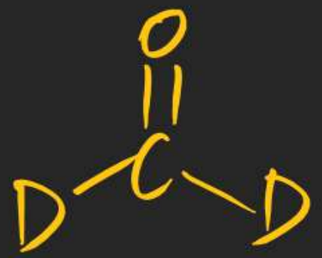
(7) $\xrightarrow[NaOH]{Conc.}$

(8)  $\xrightarrow[NaOH]{Conc.}$

(9) $\xrightarrow[NaOD]{Conc.}$

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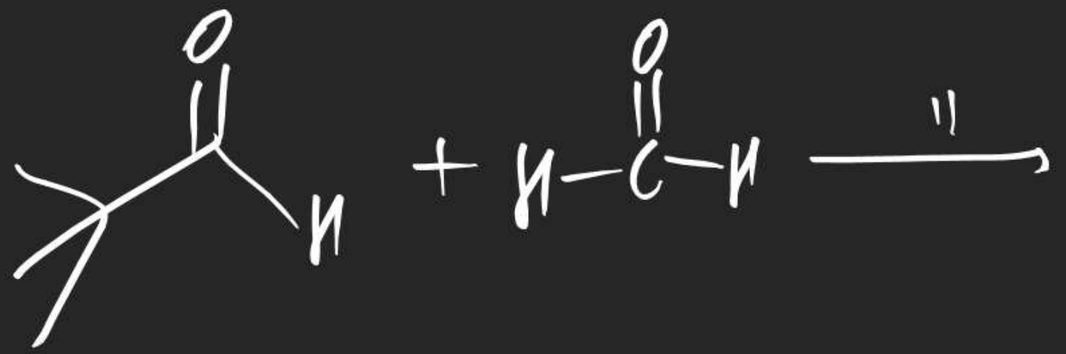
(#) Cross Cannizaro's Rxn :-

(10) $Ph-\underset{\underset{O}{\|}}{C}-H + H-\underset{\underset{O}{\|}}{C}-H \xrightarrow[K^+\bar{O}H]{Conc.} Ph-\underset{OH}{CH_2} + H-C(=O)-OK$

- most ⇒ Acid
  Electrophilic
- less ⇒ Alcohol
  electrophilic

(11)

(12) 

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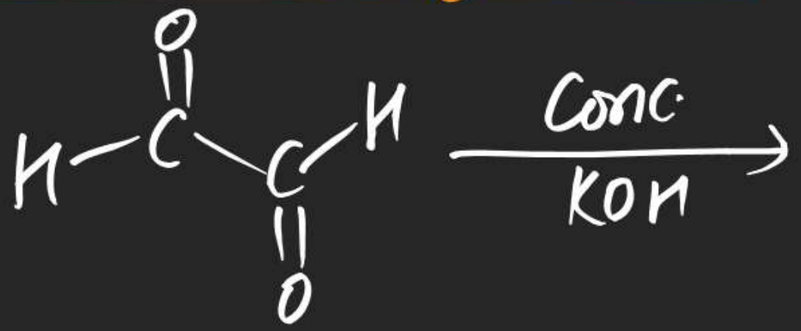
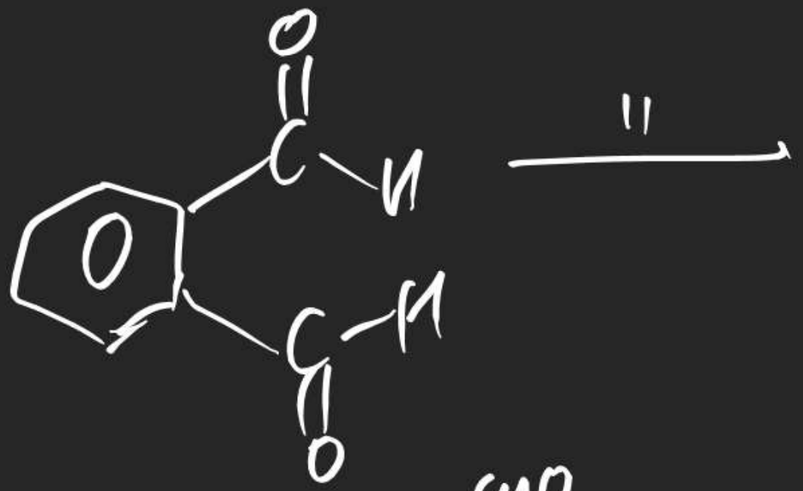
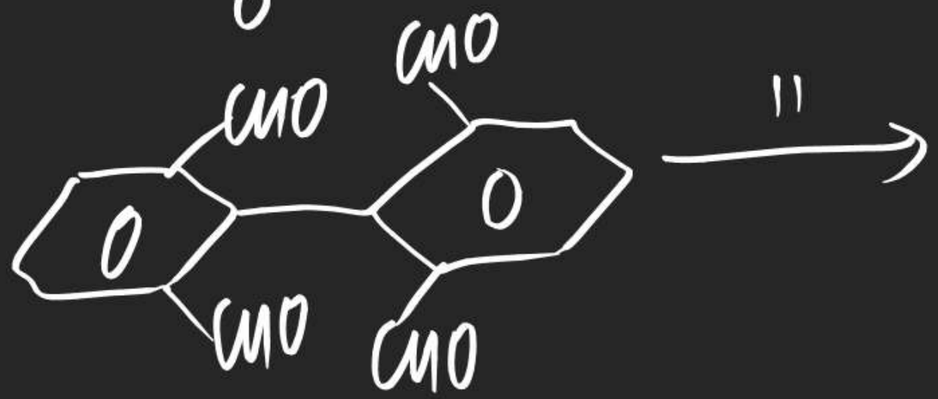
Intramolecular Cannizaro's Rxn.:

(13) 

(14) 

(15) 

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(16)

(#) Perkin Reaction:-

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HydroCarbon

⟹ Alkane C_nH_{2n+2}
Alkene C_nH_{2n}
Alkyne C_nH_{2n-2}

⟹ Alkane is least Reactive due to having absence of any Reactive functional group.

(#) Method of Preparation :

(1) By Hydrolysis of metallic Carbide :-

metallic Carbides on hydrolysis gives HydroCarbon as a Product.

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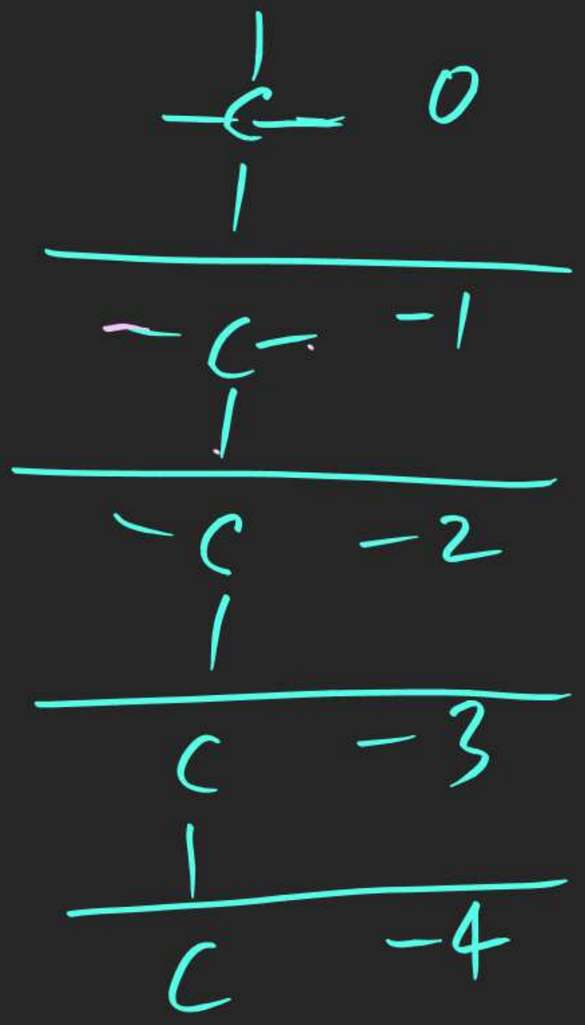
M.Imp (1) $Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3$

M.Imp (2) $CaC_2 + 2H_2O \longrightarrow H-C\equiv C-H + Ca(OH)_2$

M.Imp (3) $Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2$

M.Imp (4) $Mg_2C_3 + 4H_2O \longrightarrow H_3C-C\equiv CH + 2Mg(OH)_2$



(#) **Wittig Reaction:**

⇒ In this Reaction Carbonyl compound gives alkene as a Product or Reaction with phosphorus ylide.

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(1)

(phosphorus ylide)

(2)

mechⁿ!

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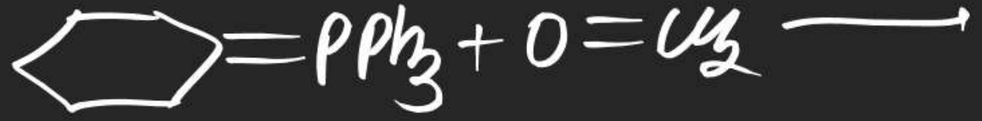
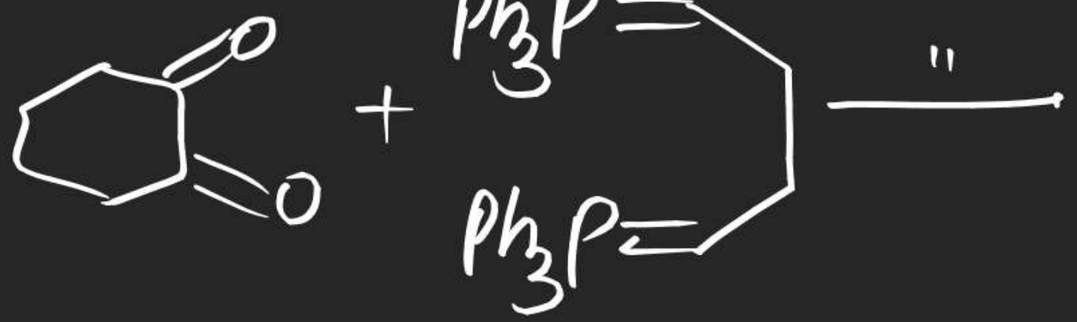
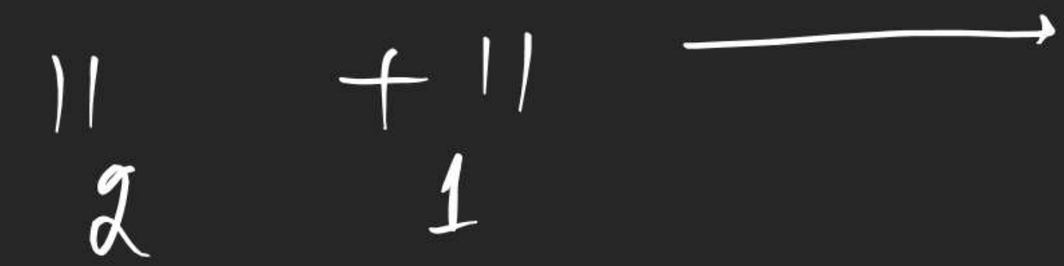
(3) $+ Ph_3P=CH_2 \longrightarrow$

(4)  $+ O=CH_2 \longrightarrow$

(5)  $\xrightarrow{\text{''}}$

(6) $Ph_3P=CH-CH_3 + CO_2 \longrightarrow$

(7) 

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(8) $Ph_3P = CH - CH_3 + O_2 \longrightarrow$

(9) $\quad '' \quad + \quad '' \longrightarrow$

$\quad 2 \quad : \quad 1$

(10) $Ph_3P = CH - CH_3 + H_2O \longrightarrow$

(11) $+ Ph_3P \longrightarrow$

(12) $+ Ph_3P \longrightarrow$

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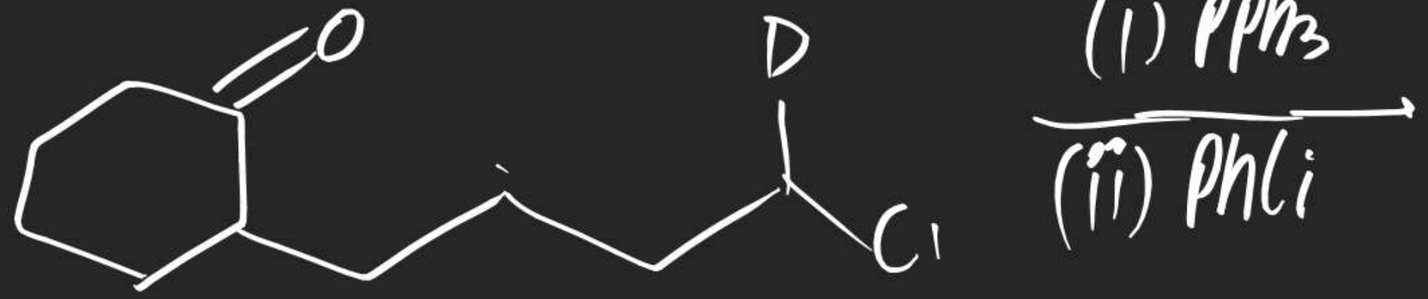
(13)

(14)