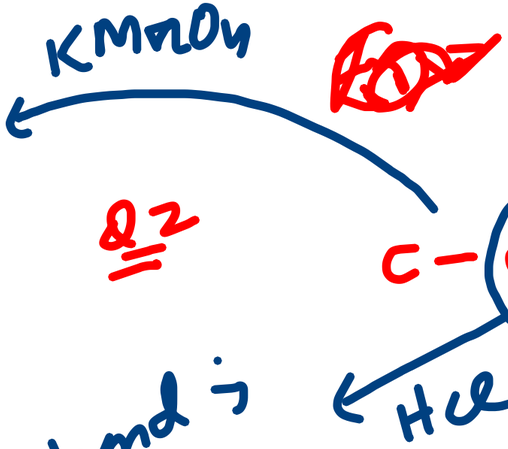
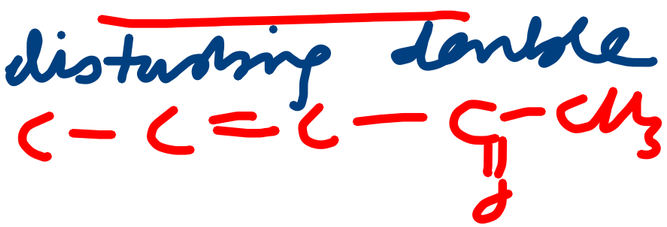
Exercise : JEE Mains Advance



double bond ⇒ reacting with HCl.

n2 ⇒ distubing double bond.

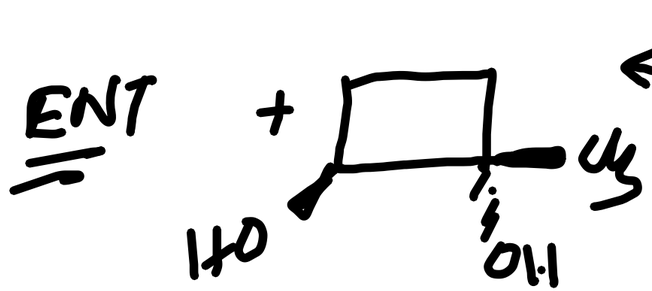


PCC ?
why n2.

CrO_3. HCl

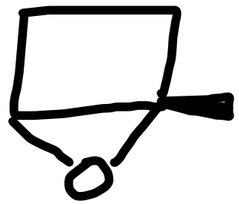
CrO_3 in glacial acetic acid. ⇒ better option.

Q1- Q.5 dis



mCPBA
+H2O.

mCPBA
not H2O present

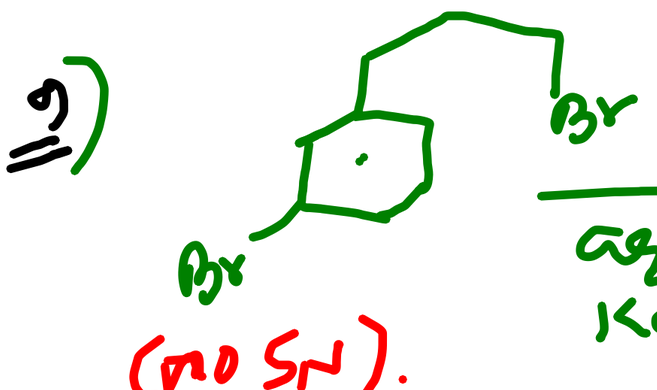


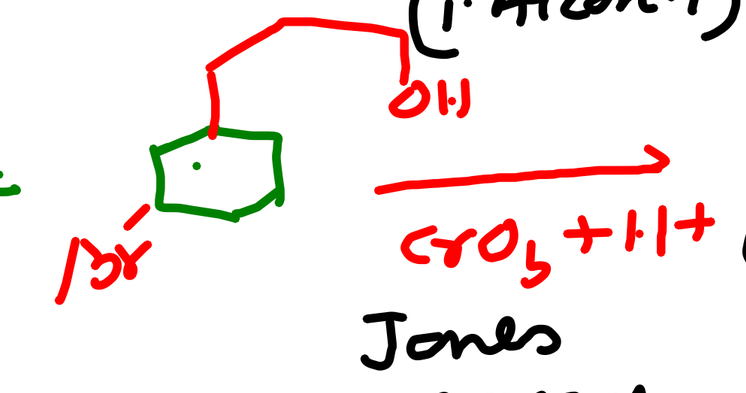
epoxide is the final product.

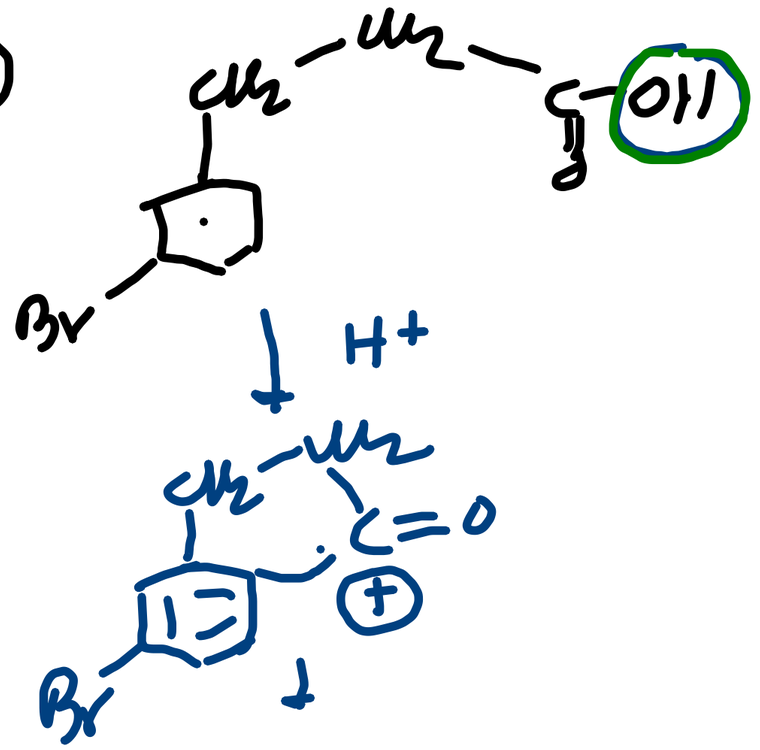
8) PCC can't oxidise 3° Alcohol.

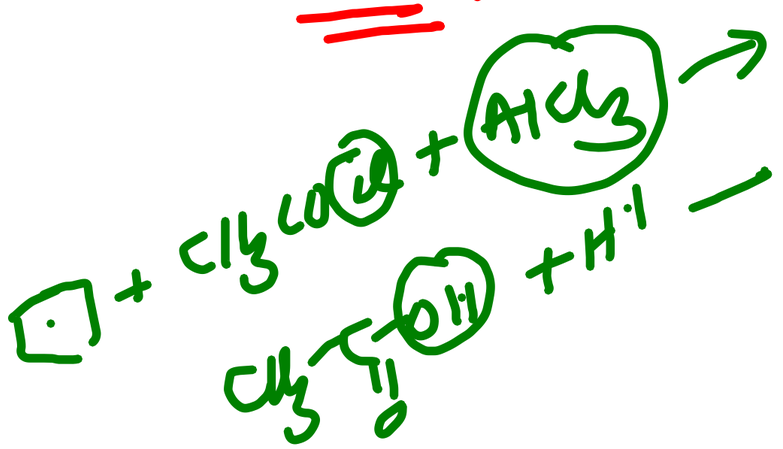
It only oxidises 1°/2° Alcohol.

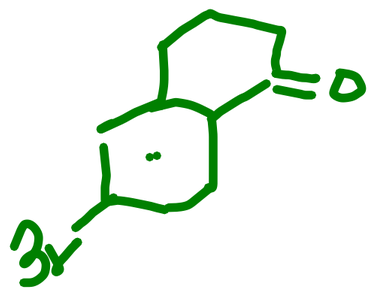
9)



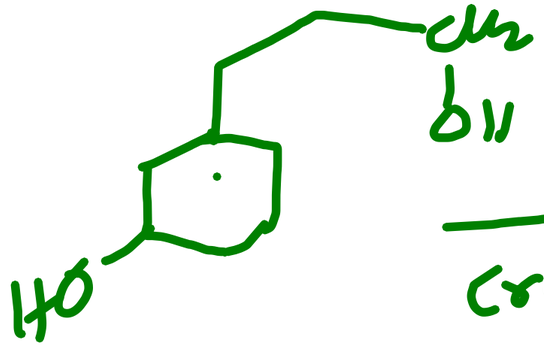




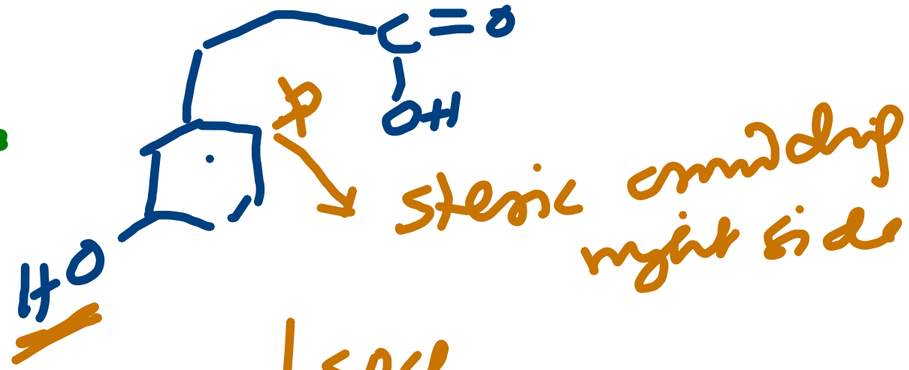




(10)

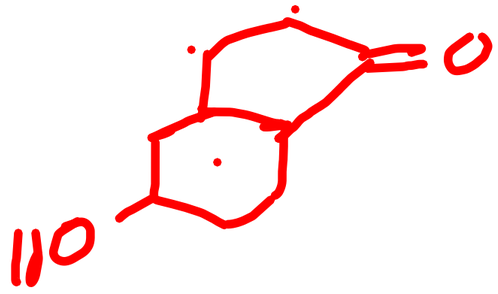


$CrO_3 + H^+$



$SOCl_2$

(Aliphatic + Aromatic)



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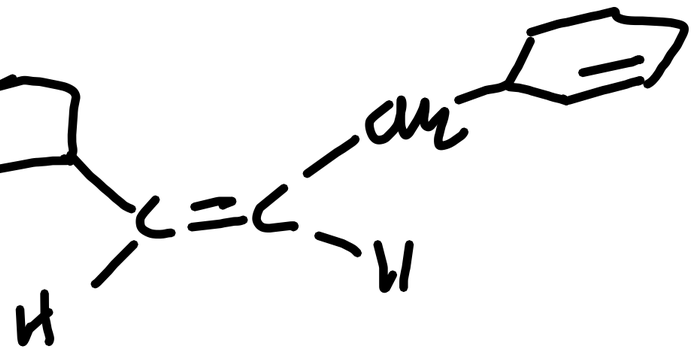
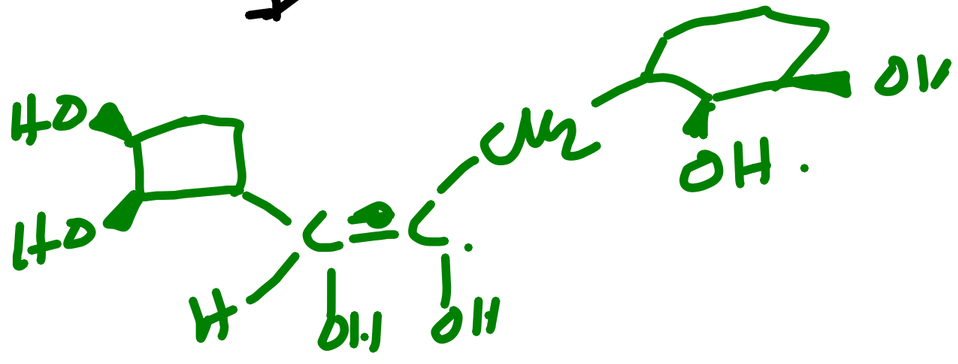
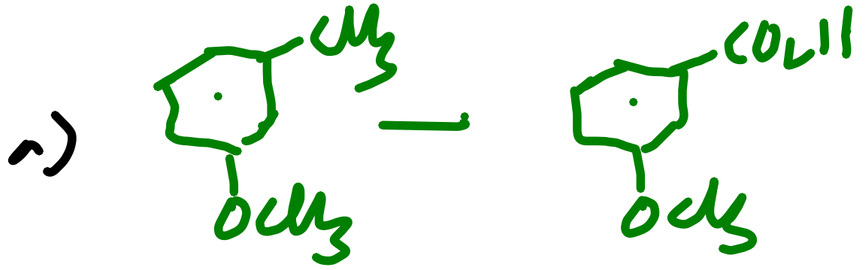


1. $KMnO_4$



a) 

a) $NaBH_4$

b) $LiAlH$

~~c)~~ $KMnO_4$

d) $HCl, Zn(Hg)$

In which reaction aldehyde is not formed.

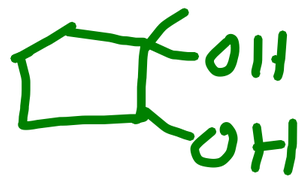
Q1

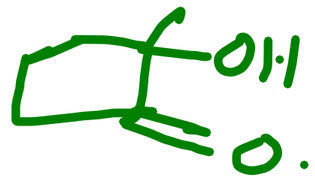
$CH_3CH_2OH \xrightarrow[\Delta]{Cu} CH_3CH=O$

$CH_2=CH_2 + O_2 \xrightarrow[H_2O]{Pd(II)} CH_3CH=O$

$CH_3CN \xrightarrow[DIBALH]{} CH_3CH=O$

$CH_3CH_2OH \xrightarrow[Jones\ reagent\ (SOA)]{CrO_3 + H_2SO_4} CH_3CO_2H$

(X) 

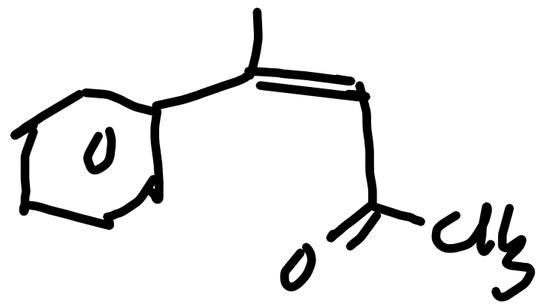
Y ⇒ 

$CH_3CH_2CH_3$ ⟶ $CH_3CH_2CH=O$

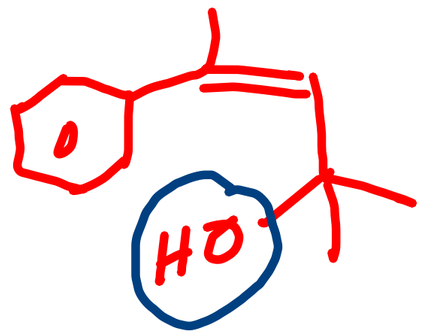
Molybdenum oxide ✓

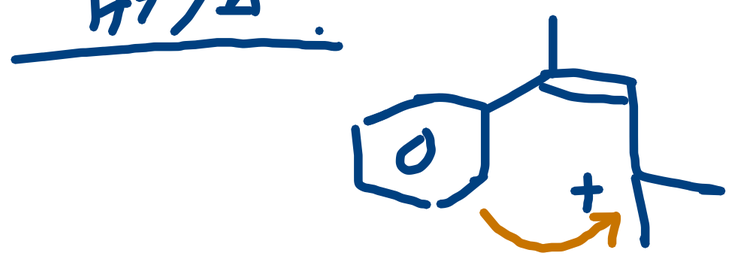
CH_4 ⟶ $HCH=O$.

CH_3CH_3 ⟶ $CH_3CH=O$.

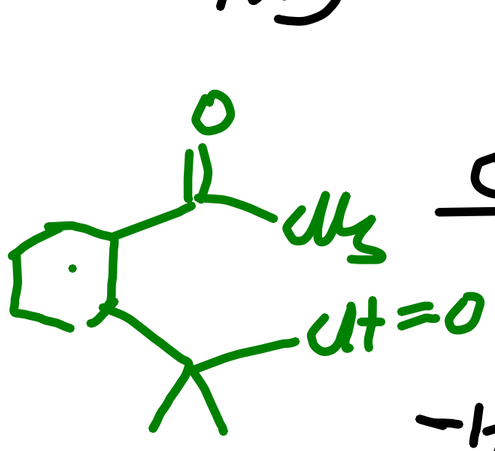


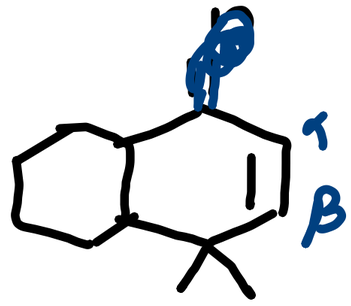
(+ve iodoform test)

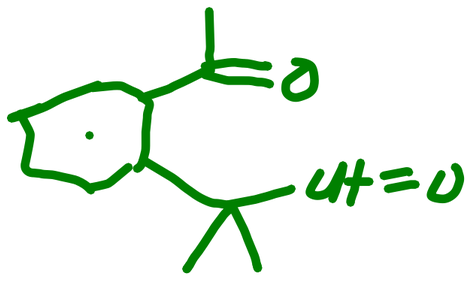


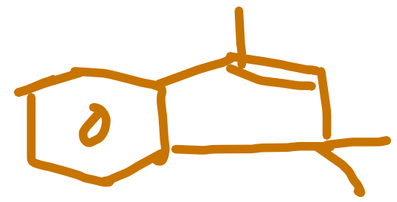


intramolecular reaction









$-H_2O$

intra Aldol condensation.

Aldol condensation:

Self Aldol

i) $CH_3CH=O + CH_3CH=O \xrightarrow[\bar{O}H/\text{low temp}]{} CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH=O$ Aldol formation.

ii) $CH_3CH=O + CH_3CH=O \xrightarrow[\bar{O}H/\Delta]{} CH_3CH=CH-\underset{O}{\underset{||}{C}}-H$. Ald^l condensation.

Self ketol

i) $CH_3-\underset{O}{\underset{||}{C}}-\overset{\alpha}{CH_3}$ (−H) $+ CH_3\underset{O}{\underset{||}{C}}-CH_3$ (+H) $\xrightarrow[\text{low temp}]{\bar{O}H}$ $CH_3-\underset{O}{\underset{||}{C}}-CH_2-\underset{OH}{\underset{|}{C}}(CH_3)_2$ ketol formation.

ii) $CH_3-\underset{CH_3}{\underset{|}{C}}=O + CH_3-\underset{O}{\underset{||}{C}}-CH_3 \xrightarrow[\Delta]{\bar{O}H} CH_3-\underset{CH_3}{\underset{|}{C}}=CH-\underset{O}{\underset{||}{C}}-CH_3$ Mesityl oxide. Ketol condensation.

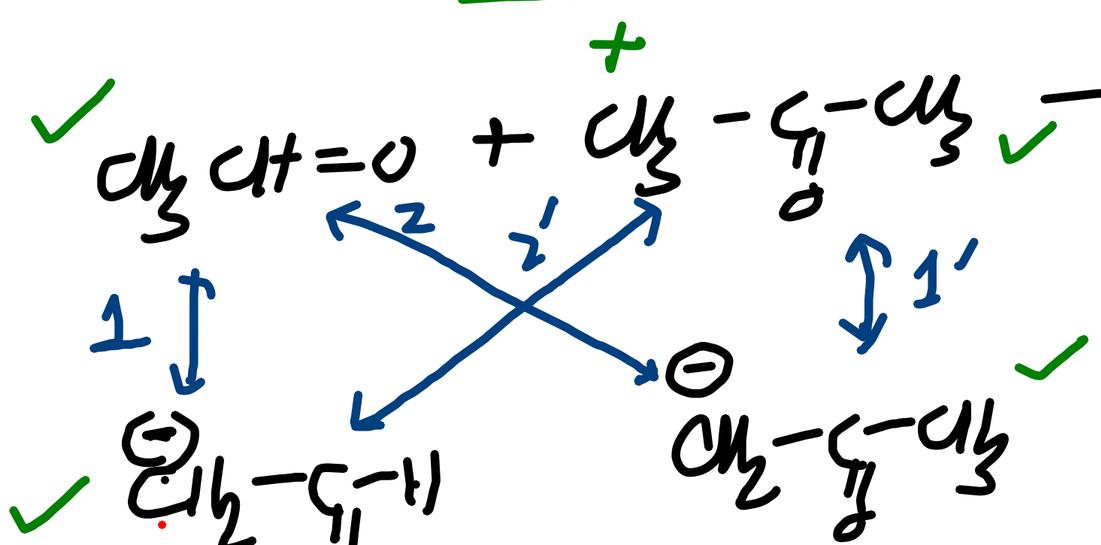
Crossed - Aldol

$PhCH=O$ (×) $+ CH_3CH=O$

Aromatic Aldehyde ↓ Aliphatic aldehyde

$\downarrow PhCH=CH-CH=O$ [Cinnamaldehyde]

Crossn Aldol. + self Aldn.



1+1' : self Aldn.

2+2' : Crossn Aldl.

2 : $H_3C-\overset{O}{\overset{\|}{C}}-CH=CH-CH_3$ (2pdts)

1 : $CH_3CH=CH-\overset{O}{\overset{\|}{C}}-H$ (2pdt).

1' $CH_2-C(CH_3)=\overset{O}{\overset{\|}{C}}-CH_3$. (1pdt)

$H_3C-C(CH_3)=CH-\overset{O}{\overset{\|}{C}}-H$ (1pdt)

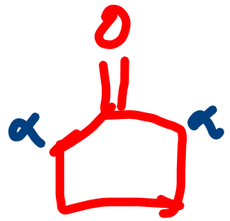
(Total = 6pdts)

2 different carbonyl system.

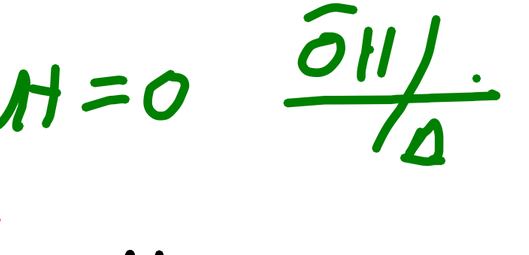
one having αH and another does not have.

a) $PhCH=O + CH_3CH=O \xrightarrow[\Delta]{\bar{O}H}$ $PhCH=CH-CH=O$ (cinnamaldehyde)

b) $HCH=O + CH_3-CH=O \xrightarrow[\Delta]{\bar{O}H}$ $H_2C=C(CH_3)-CH=O$ (methacrolein)

c)  $+ HCHO \xrightarrow{\bar{O}H}$ 

(1 : 4)



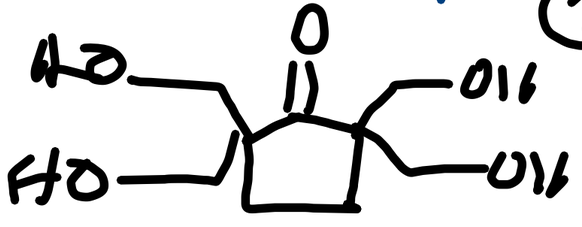
$+ HCHO \rightarrow$

(1 : 5)

$+ HCO_2^- \xleftarrow[\bar{O}H]{HCHO}$

crossed cannizzaro

$H_2C=O/\bar{O}H$ (3 eqv)



4 times Aldol.

$Me_2\overset{\alpha}{C}H-CH=O$ — $HCH=O$, OH^- → X — $HCHO$, $/OH$ → $Y + HCO_2^-$

1 Ald + 1 Cann →

X: $Me_2C(CH_2OH)-CH=O$

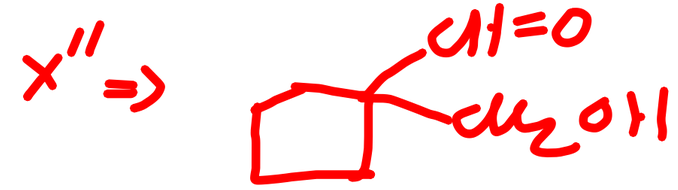
$Me_2CH-\overset{\alpha}{C}H_2CH=O$ — $HCH=O$, OH^- → X′ — $HCHO$, $/OH$ → $Y' + HCO_2^-$

2 Ald. + 1 Cann.

Y: $Me_2C(CH_2OH)-CH_2OH$

+ $HCHO/OH$ → X″ — $HCHO$, $/OH$ → $Y'' + HCO_2^-$

X′: $Me_2CH-C(CH_2OH)_2-CH=O$



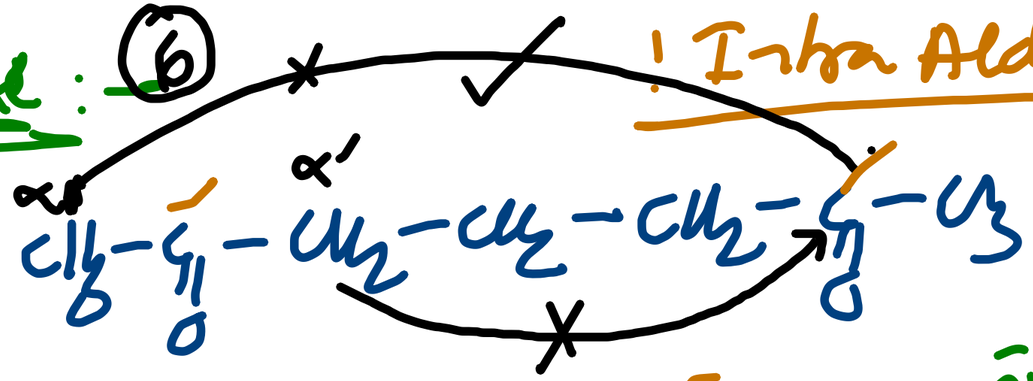
1 Ald +
1 Cannil.

Y′: $Me_2CH-C(CH_2OH)_2-CH_2OH$

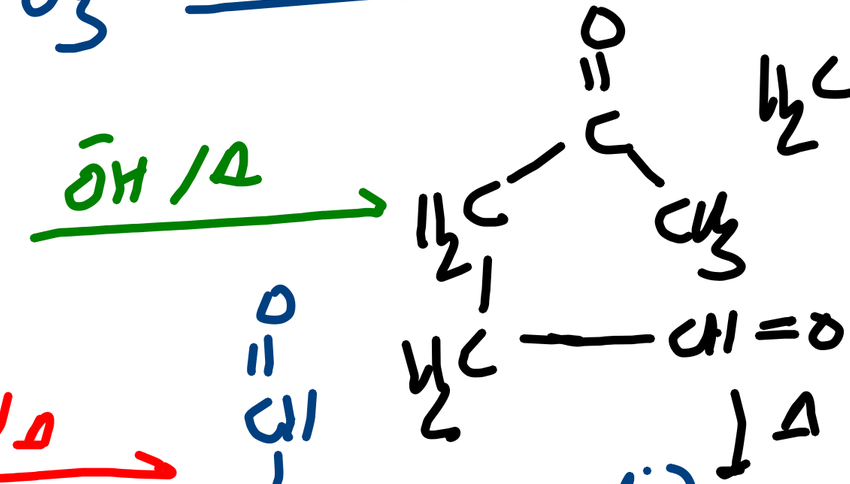
Criteria : 6

Di carbonyl 5/6 membered ring should be formed.

! Intra Ald ↑ :

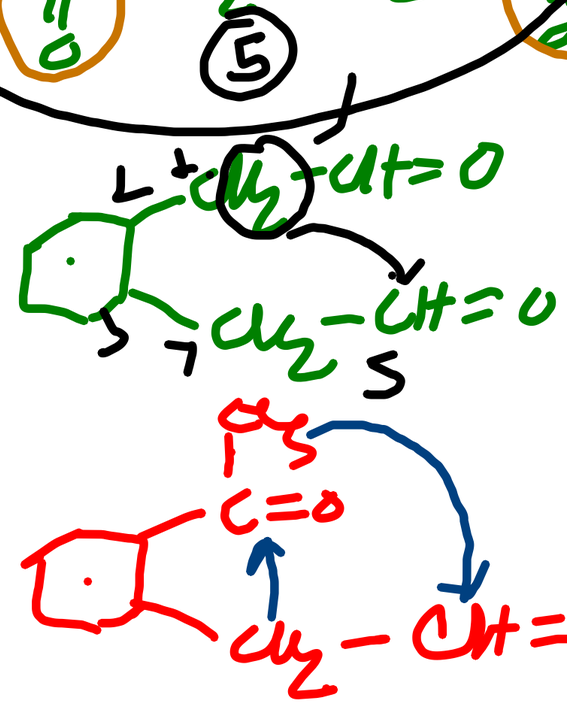


$\bar{O}H/\Delta$



$\bar{O}H/\Delta$

$\bar{O}H/\Delta$

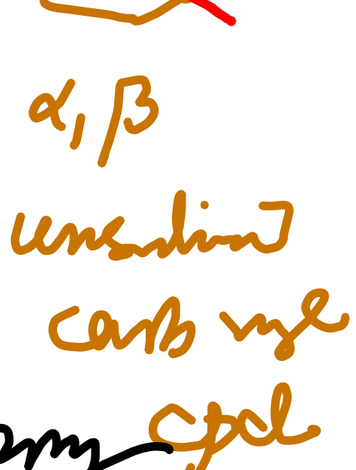


$\bar{O}H/\Delta$

$\bar{O}H/\Delta$

α,β unsaturated carbonyl cpd

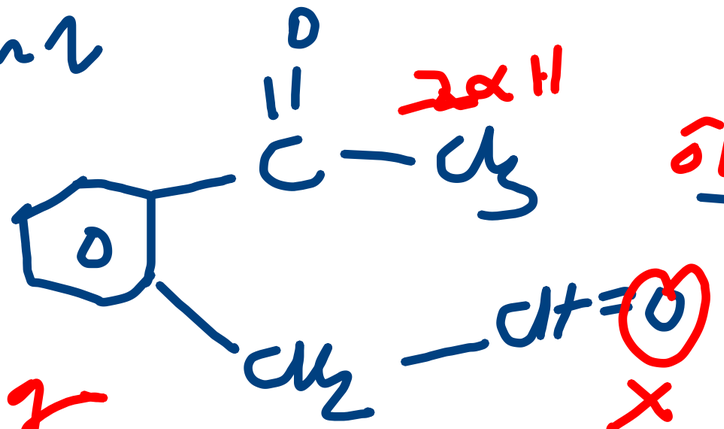
α,β unsaturated carbonyl cpd



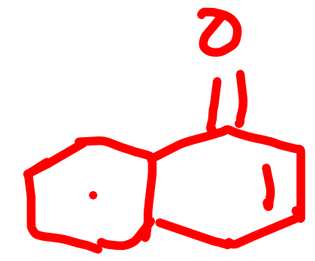
Aldehyde > Ketone,

carbanion is formed in such a way that it reacts with aldehyde group.

Acid catalyzed Aldol: [enol form reacting]



$\xrightarrow{\text{OH}/\Delta}$



α, β unsaturated carbonyl product

$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ (2 eq)

H+ to another pronated form of carbonyl cpd.

$CH_3-C(=O)-CH_3 + CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[-H_2O]{} CH_3-C(CH_3)=CH-\underset{\underset{O}{\|}}{C}-CH_3$

(Aldol condensation product)

$CH_3-C(=O)-CH_3 + H^+ \rightleftharpoons CH_3-C(CH_3)=\overset{+}{O}H$ (Protonated carbonyl cpd)

(Electrophile)

$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_2=C(OH)-CH_3$ (enol) + $CH_3-C(CH_3)=\overset{+}{O}H$

$\rightarrow H_3C-C(OH)(CH_3)-CH_2-C(=\overset{+}{O}H)-CH_3$

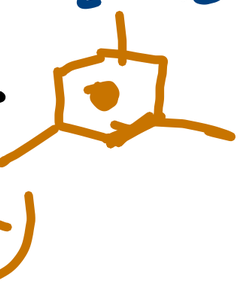
$\rightarrow H_3C-C(OH)(CH_3)-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

$CH_3-C(CH_3)=CH-\underset{\underset{O}{\|}}{C}-CH_3$ $\xrightarrow{-H_2O}$

(3eq)

∴ $CH_3-C(=O)-CH_3$ + conc. HCl $\xrightarrow[\text{trimerisation}]{\text{open chain}}$ Phorone. (Pdt) [3eq CH_3COCH_3 → 3eq. H_2O].

(3eq.) $CH_3-C(=O)-CH_3$ + conc. H_2SO_4 $\xrightarrow[\text{trimerisation.}]{\text{cyclic}}$ Mesitylene (Pdt)

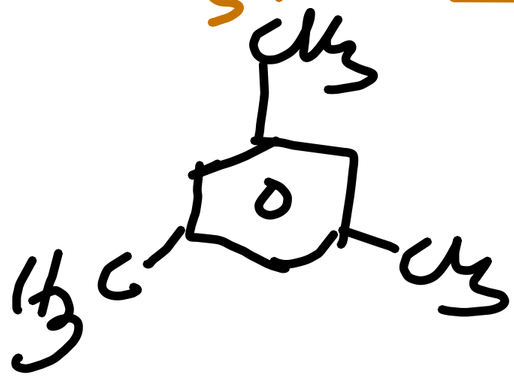


$H_3C-C(=O)-CH_3$ + $CH_3-C(=O)-CH_3$ + $O=C(CH_3)-CH_3$

↓

$CH_3-C(CH_3)=CH-C(=O)-CH=C(CH_3)-CH_3$ (Phorone)

$CH_3-C(=O)-CH_3$ + conc H_2SO_4 → (3eq) − 3eq. H_2O.

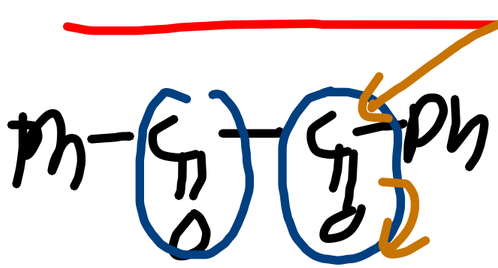


1,3,5 tri-ethyl benzene (Mesitylene)

$3 \times C_3H_6O - 3 \times H_2O \longrightarrow C_9H_{18}O_3 - H_6O_3 \rightarrow C_9H_2$

Benzil–Benzilic Acid rearrangement

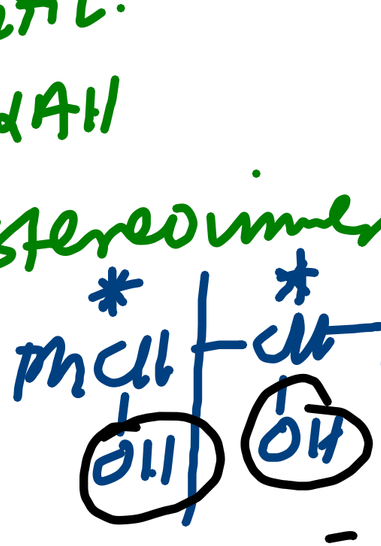
Name reaction { Cannizzaro + Aldol / Quest.



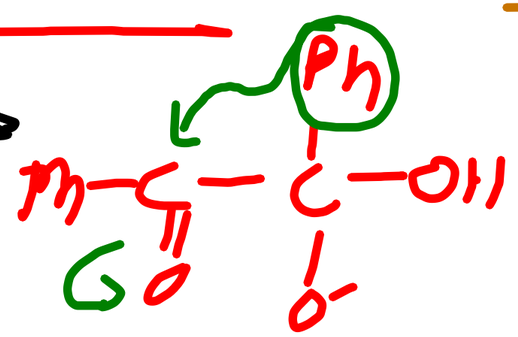
Benzil.

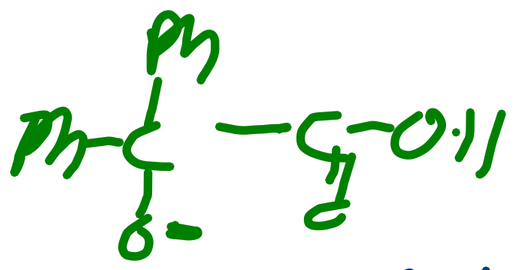
↓ dil

No. of stereoisomers.



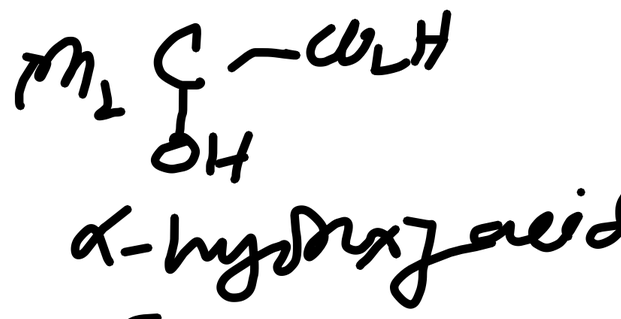
(Pinacol)





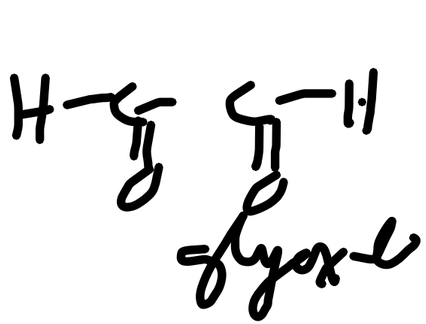
Salt of benzilic Acid

↓ H+



α-hydroxy acid

(Benzilic Acid)



glyoxal

Intra cannizzaro reaction.