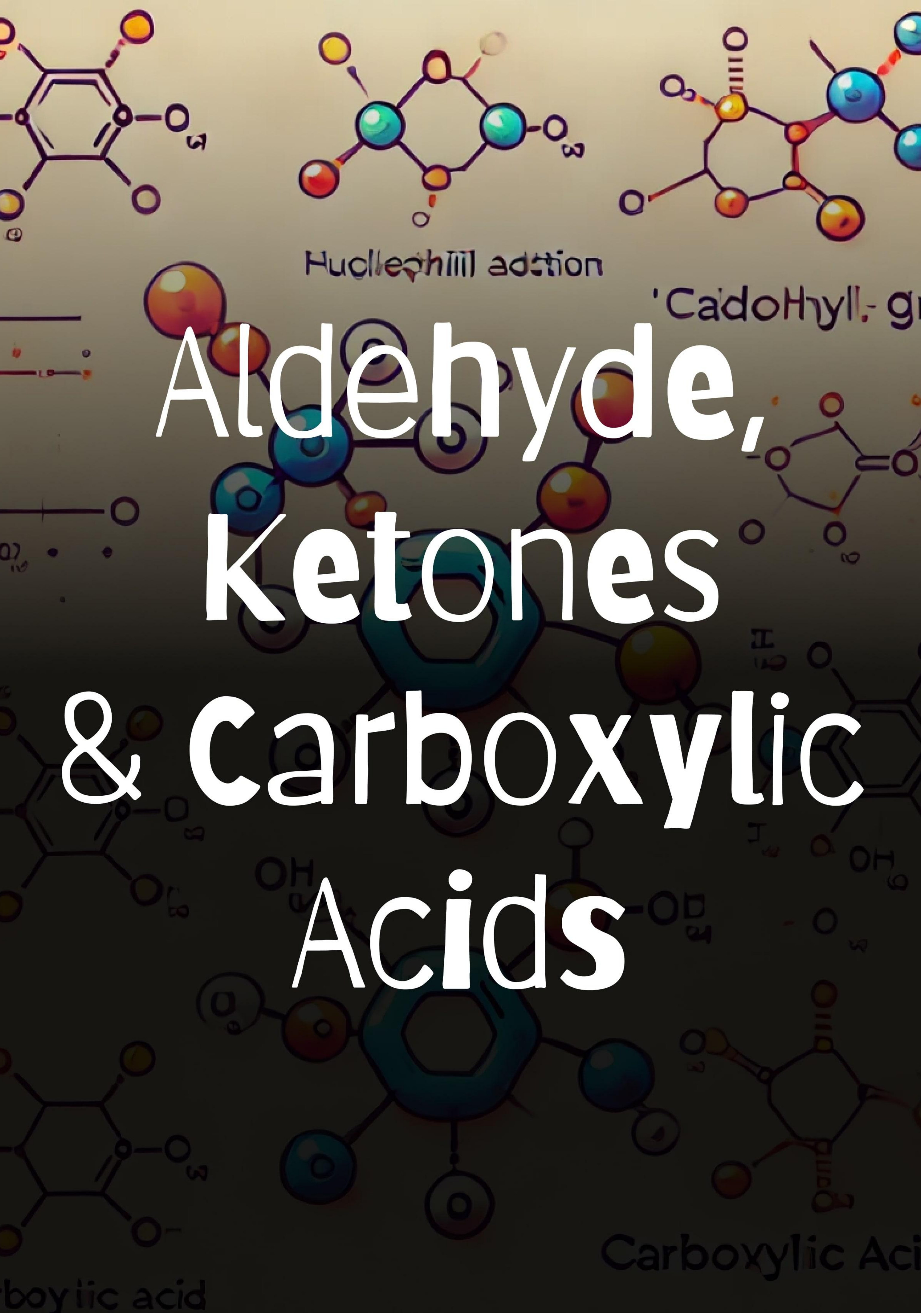
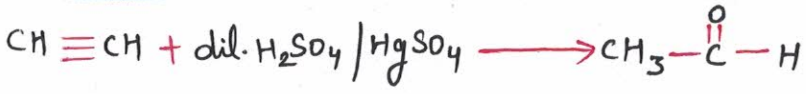


Aldehyde, Ketones & Carboxylic Acids

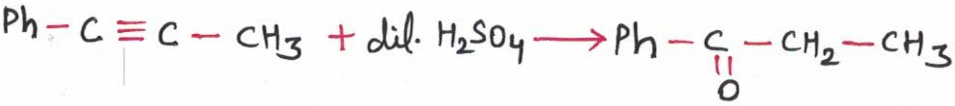
ALDEHYDE & KETONES

PREPARATION

1. By hydration of alkynes

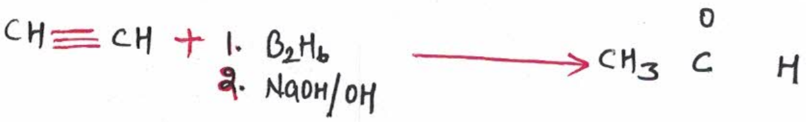


$CH \equiv CH + dil.\ H_2SO_4 / HgSO_4 \longrightarrow CH_3 - \overset{O}{\overset{\|}{C}} - H$

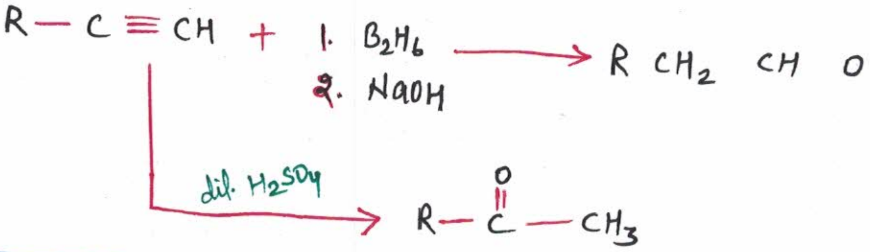


$Ph - C \equiv C - CH_3 + dil.\ H_2SO_4 \longrightarrow Ph - \underset{O}{\underset{\|}{C}} - CH_2 - CH_3$

2. Hydroboration & Oxidation of alkynes



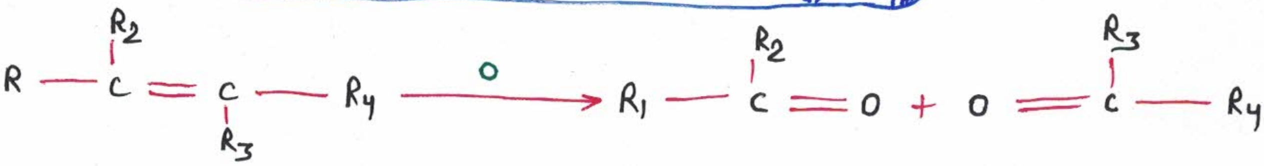
$CH \equiv CH + \begin{matrix} 1.\ B_2H_6 \\ 2.\ NaOH/OH \end{matrix} \longrightarrow CH_3\ \overset{O}{C}\ \ H$



$R - C \equiv CH + \begin{matrix} 1.\ B_2H_6 \\ 2.\ NaOH \end{matrix} \longrightarrow R\ CH_2\ \ CH\ \ O$

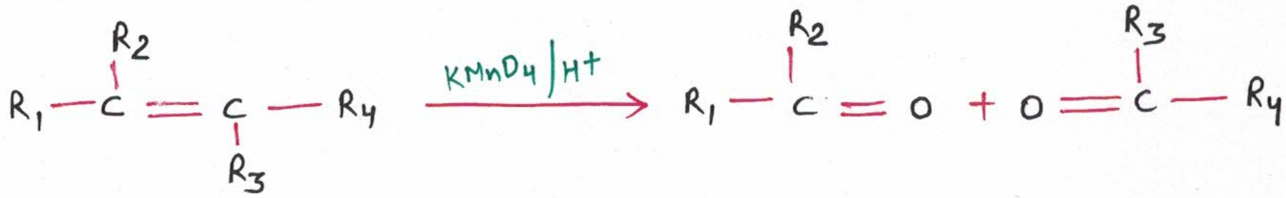
$\xrightarrow{dil.\ H_2SO_4} R - \overset{O}{\overset{\|}{C}} - CH_3$

3. Ozonolysis of alkenes



$R - \overset{R_2}{\overset{|}{C}} = \underset{R_3}{\underset{|}{C}} - R_4 \xrightarrow{O} R_1 - \overset{R_2}{\overset{|}{C}} = O + O = \overset{R_3}{\overset{|}{C}} - R_4$

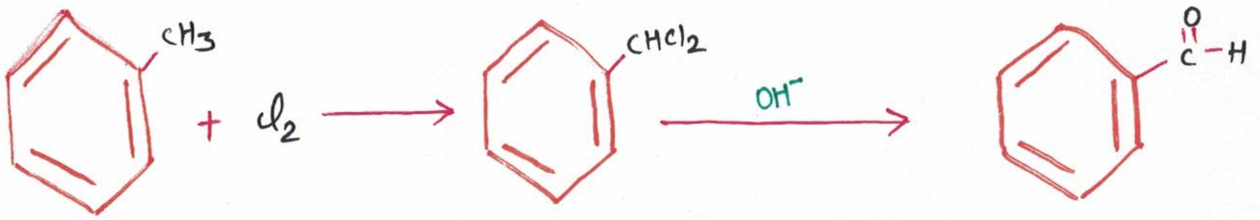
4. Oxidation cleavage of alkenes

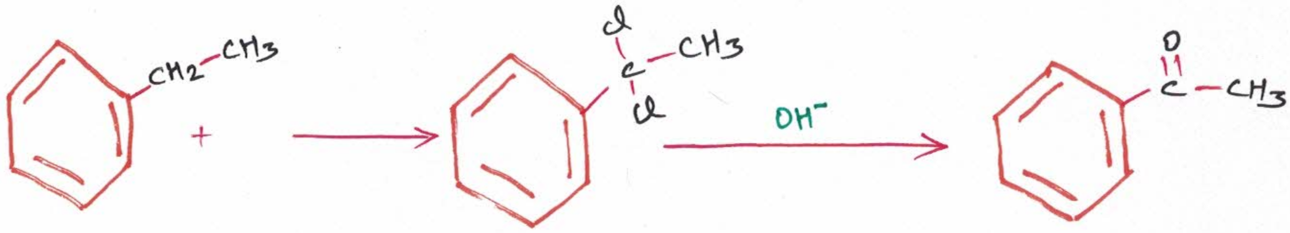


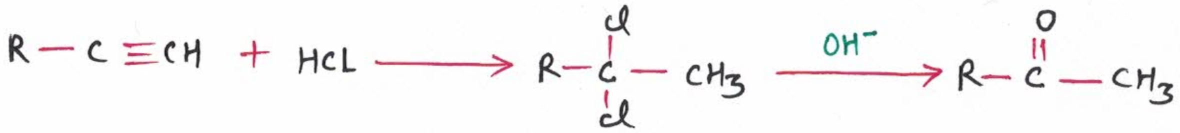
$$R_1-\overset{R_2}{\overset{|}{C}}=\underset{\underset{R_3}{|}}{C}-R_4 \xrightarrow{KMnO_4|H^+} R_1-\overset{R_2}{\overset{|}{C}}=O+O=\overset{R_3}{\overset{|}{C}}-R_4$$

5. By hydralysis of gemdihalides

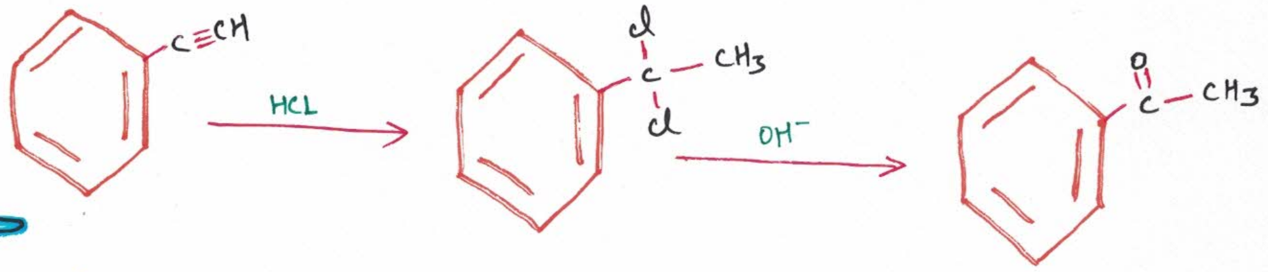
$$R\,[HCL_2+OH^- \longrightarrow R-\overset{O}{\overset{||}{C}}-H$$

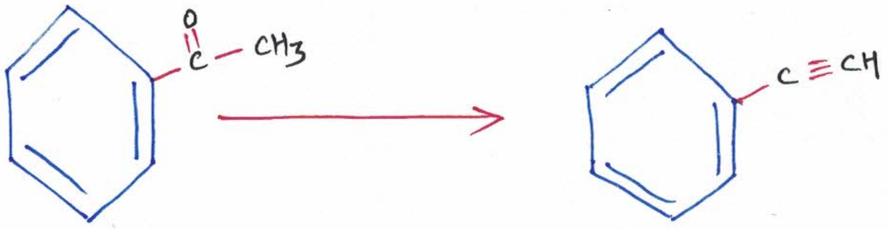


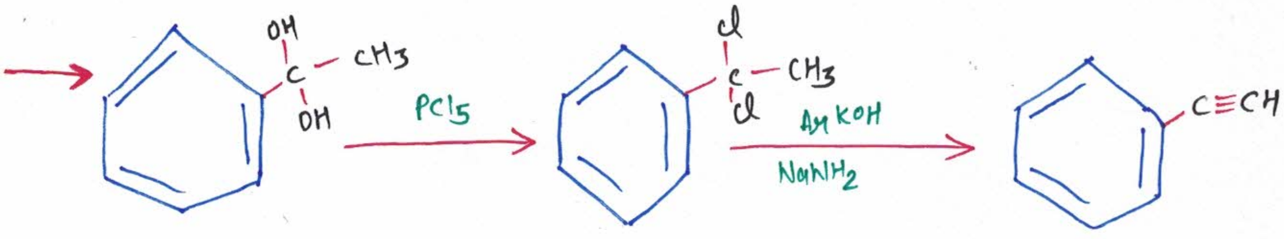




$$R-C\equiv CH+HCL \longrightarrow R-\underset{\underset{cl}{|}}{\overset{\overset{cl}{|}}{C}}-CH_3 \xrightarrow{OH^-} R-\overset{O}{\overset{||}{C}}-CH_3$$

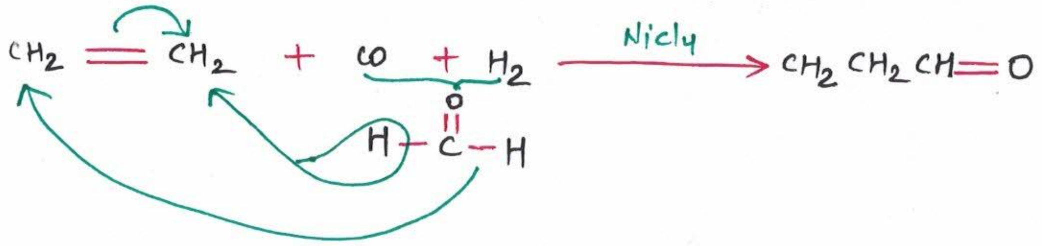






Terminal gemhalide → Aldehyde
Non Terminal gemhalide → ketone

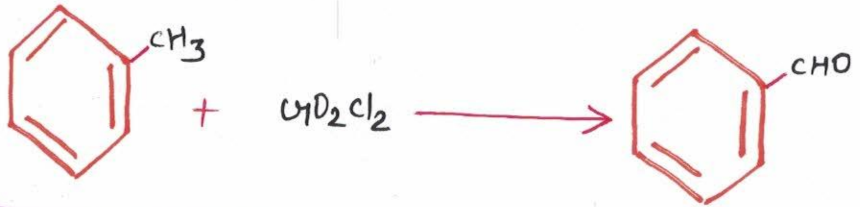
6. OXO reaction / Hydroformylation.



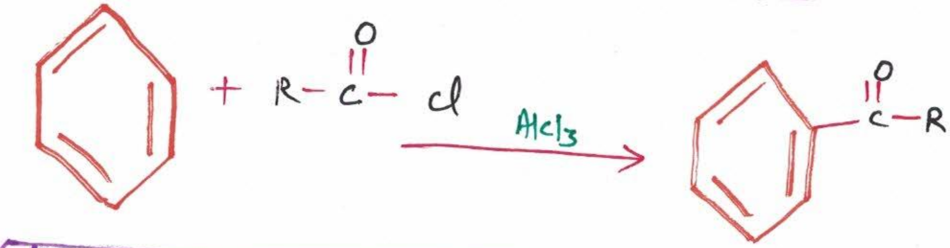
$$CH_2 = CH_2 + CO + H_2 \xrightarrow{NiCl_4} CH_2CH_2CH=O$$

$$CH \equiv CH + CO \quad H_2 \longrightarrow CH_2 = CH - CH = O$$

7. Etards Reaction

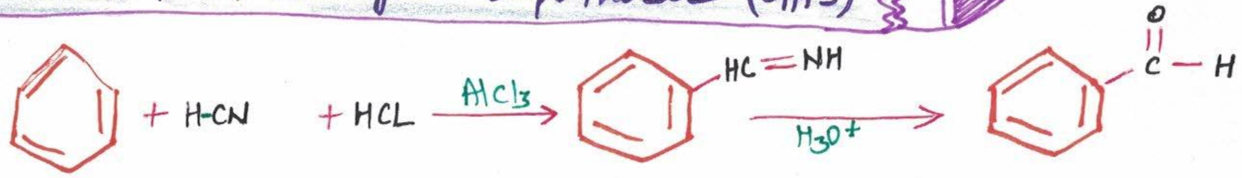


8. Friedal Crafts Acylation

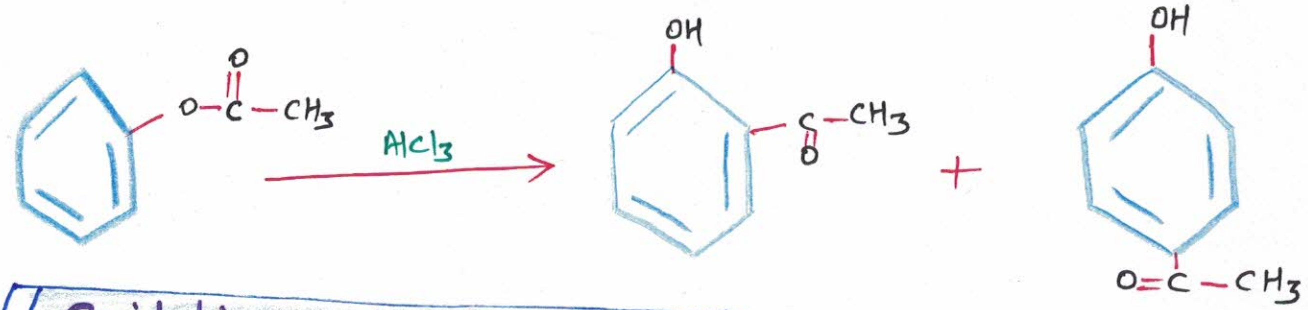


9. Gattermann Koch Aldehyde synthesis

10. Gattermann Aldehyde systhesis (GAS)



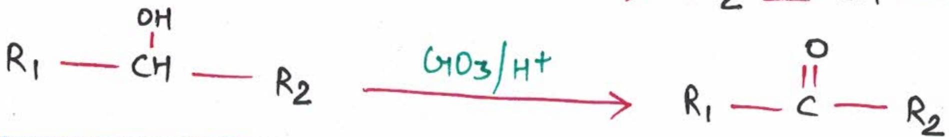
12. Reimer Teimann Reaction



13. Oxidation of alcohols

$R-CH_2-OH \xrightarrow{P.C.C} R-CH=O$

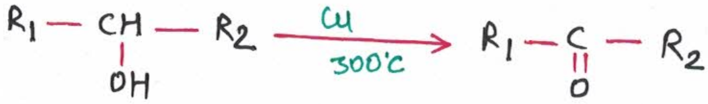
$CH_2=CH-CH_2-OH \xrightarrow{MnO_4} CH_2=CH-CH=O$



$R_1-\overset{OH}{\overset{|}{CH}}-R_2 \xrightarrow{CrO_3/H^+} R_1-\overset{O}{\overset{\|}{C}}-R_2$

14. Dehydrogenation of alcohols

$R-CH_2-OH \xrightarrow[300^\circ C]{Cu} R-CH=O$



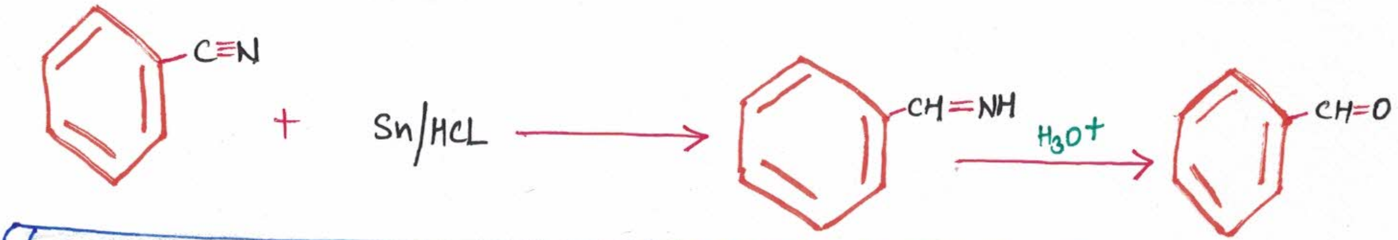
$R_1-\underset{OH}{\underset{|}{CH}}-R_2 \xrightarrow[300^\circ C]{Cu} R_1-\underset{O}{\underset{\|}{C}}-R_2$

1. Pinacol - Pinacolone rearrangement
2. HIO_4 cleavage

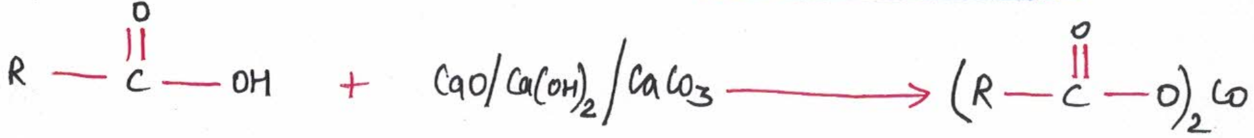
NEW REACTIONS

15. Stephen's reduction

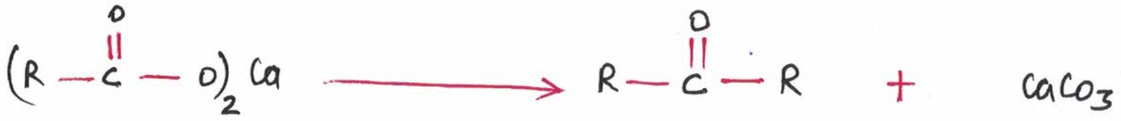
$R-C\equiv N + Sn/HCL \longrightarrow R-CH=NH \xrightarrow{H_3O^+} R-CH=O$



16. Dry distillation of calcium carboxylates

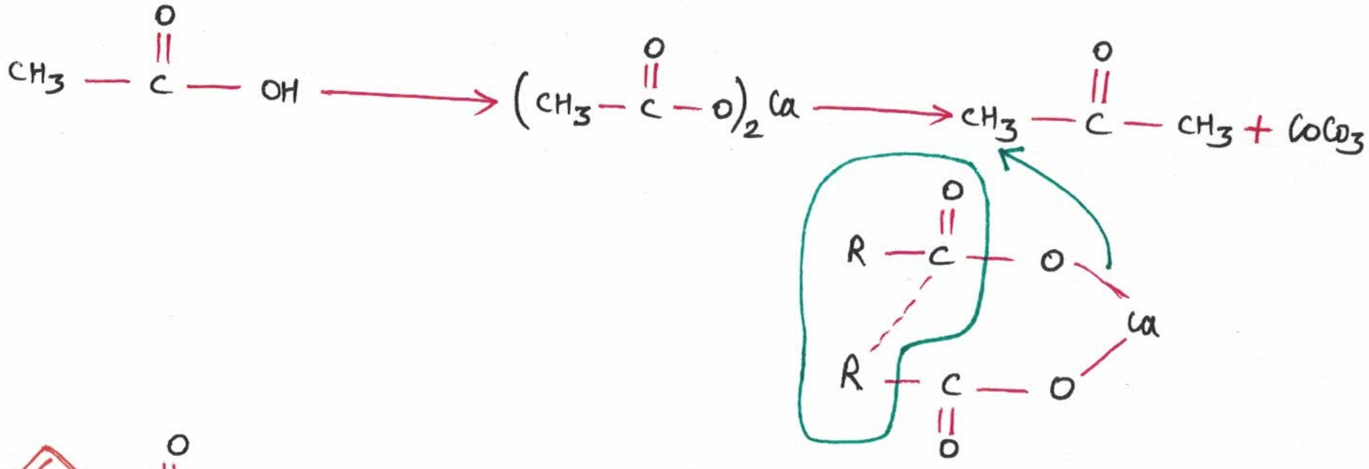


$R-\overset{O}{\overset{\|}{C}}-OH + CaO/Ca(OH)_2/CaCO_3 \longrightarrow (R-\overset{O}{\overset{\|}{C}}-O)_2Ca$

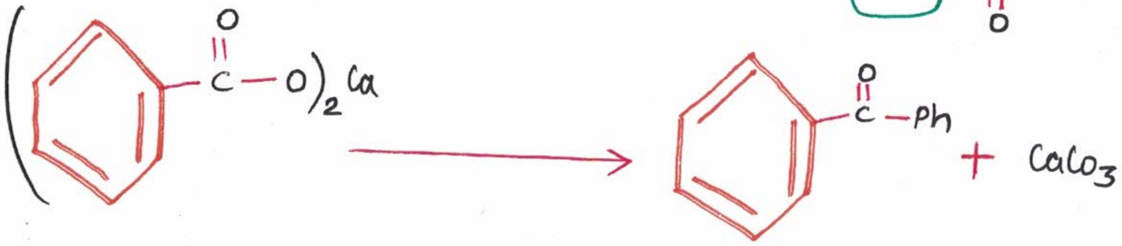


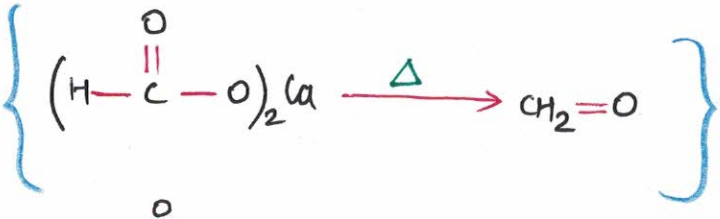
$$(R-\overset{O}{\overset{\|}{C}}-O)_2Ca \longrightarrow R-\overset{O}{\overset{\|}{C}}-R + CaCO_3$$

It is called dry distillation as no liquid reactant is involved in reaction.



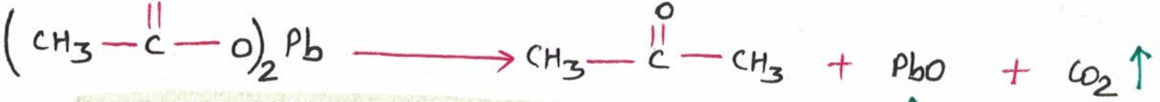
$$CH_3-\overset{O}{\overset{\|}{C}}-OH \longrightarrow (CH_3-\overset{O}{\overset{\|}{C}}-O)_2Ca \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CaCO_3$$





$$(H-\overset{O}{\overset{\|}{C}}-O)_2Ca \xrightarrow{\Delta} CH_2=O$$

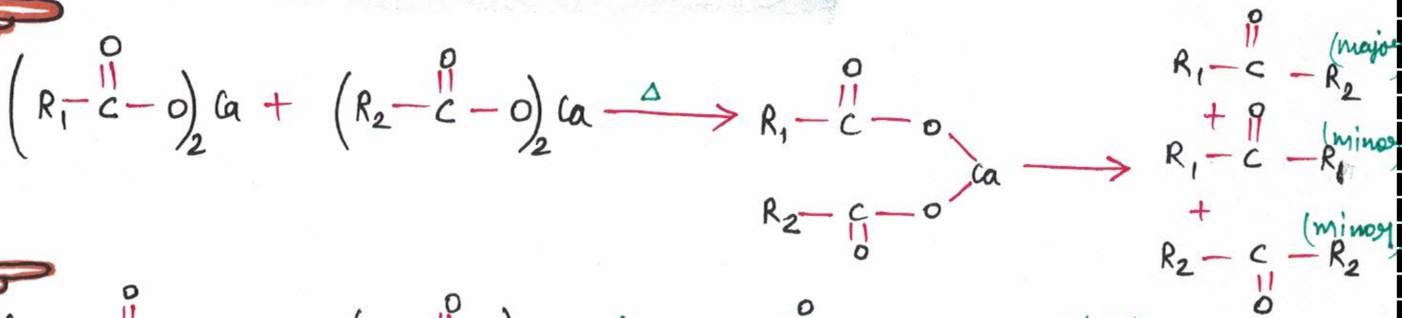
Method to prepare formalhyde



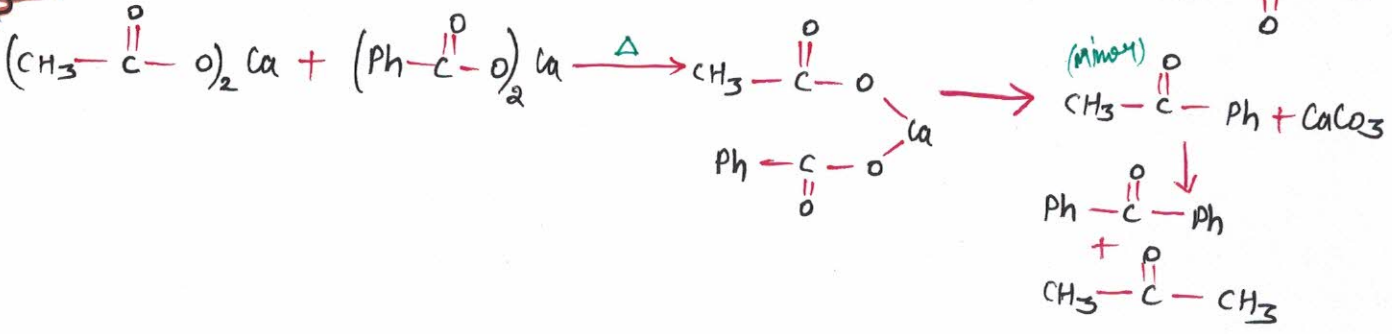
$$(CH_3-\overset{O}{\overset{\|}{C}}-O)_2Pb \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + \overset{\uparrow}{PbO} + CO_2\uparrow$$

PbO_3 is not formed because $PbCO_3$ is unstable at high temp. Hence it decomposes into PbO whereas $CaCO_3$ does not.

$$H_2O + D_2O \rightleftharpoons HOD$$



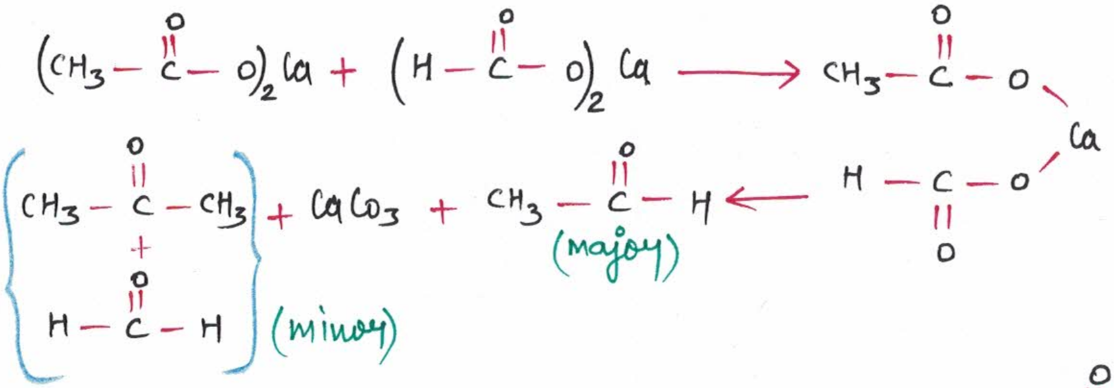
$$(R_1-\overset{O}{\overset{\|}{C}}-O)_2Ca + (R_2-\overset{O}{\overset{\|}{C}}-O)_2Ca \xrightarrow{\Delta} \begin{matrix} R_1-\overset{O}{\overset{\|}{C}}-O \\ R_2-\underset{O}{\underset{\|}{C}}-O \end{matrix} Ca \longrightarrow \begin{matrix} R_1-\overset{O}{\overset{\|}{C}}-R_2 \text{ (major)} \\ + \\ R_1-\overset{O}{\overset{\|}{C}}-R_1 \text{ (minor)} \\ + \\ R_2-\underset{O}{\underset{\|}{C}}-R_2 \text{ (minor)} \end{matrix}$$

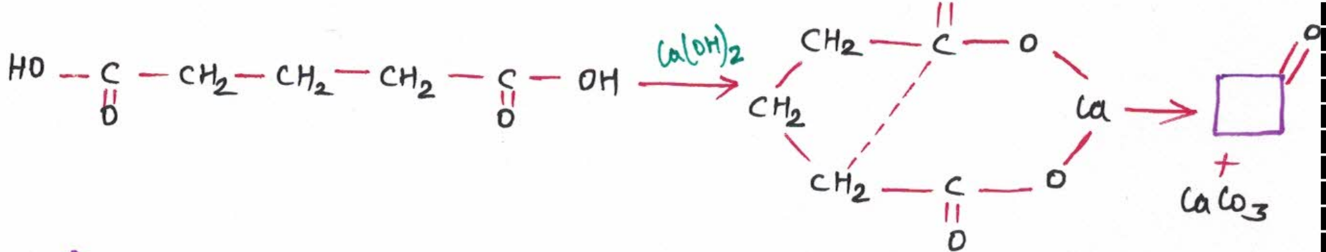


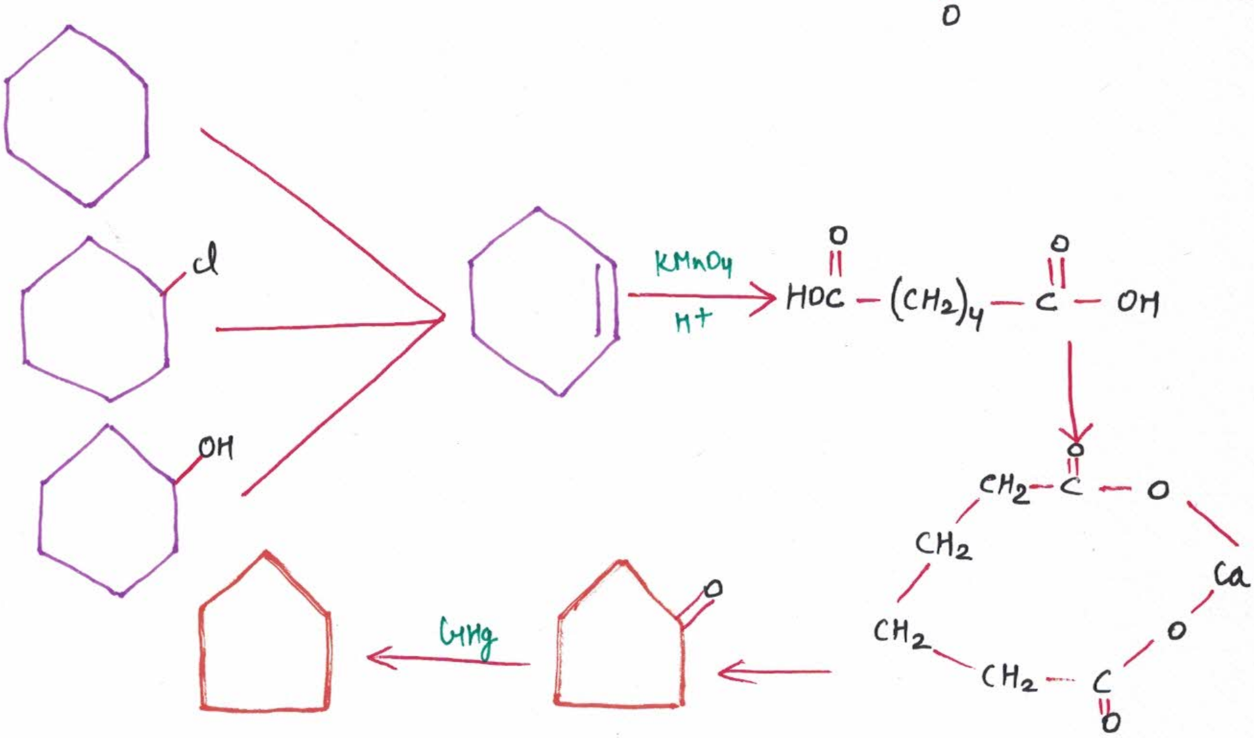
$$(CH_3-\overset{O}{\overset{\|}{C}}-O)_2Ca + (Ph-\overset{O}{\overset{\|}{C}}-O)_2Ca \xrightarrow{\Delta} \begin{matrix} CH_3-\overset{O}{\overset{\|}{C}}-O \\ Ph-\underset{O}{\underset{\|}{C}}-O \end{matrix} Ca \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Ph + CaCO_3$$

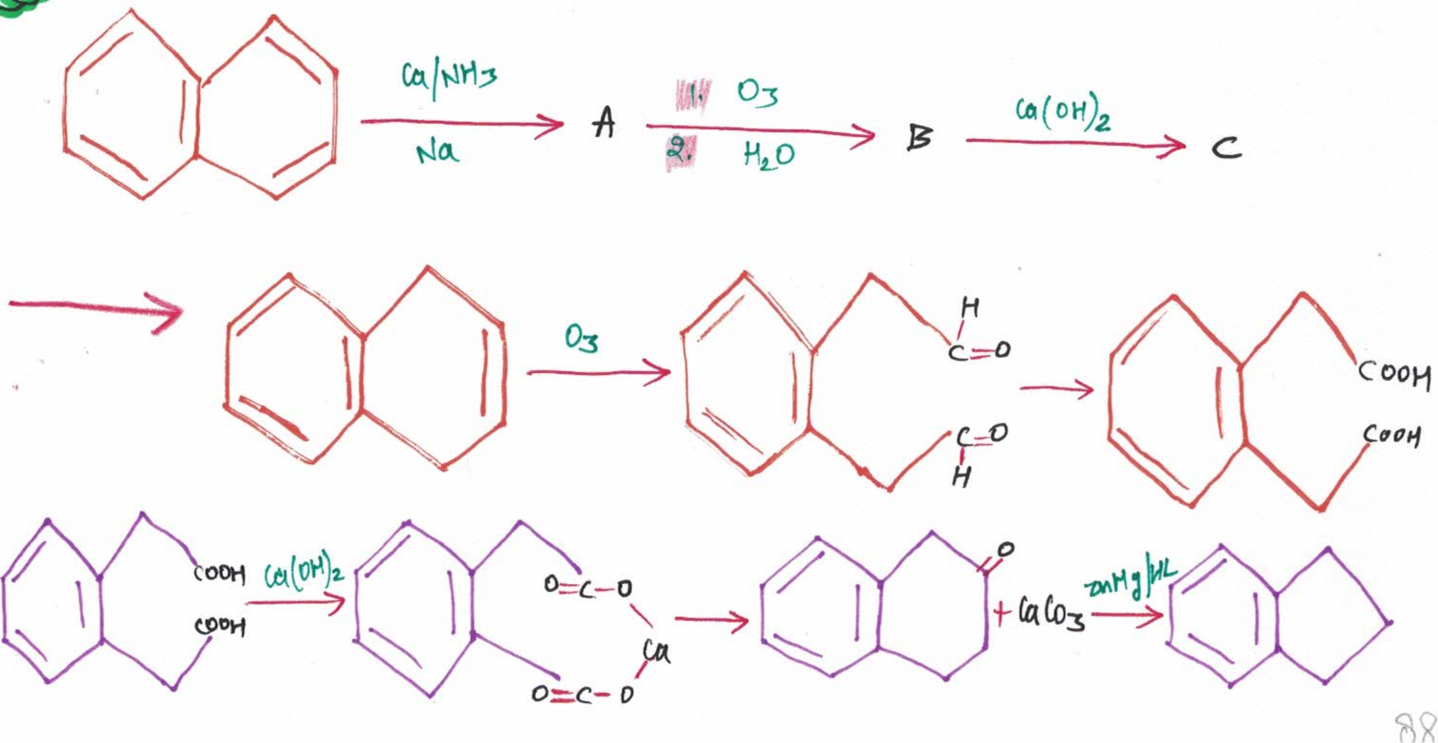
$$\downarrow$$

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

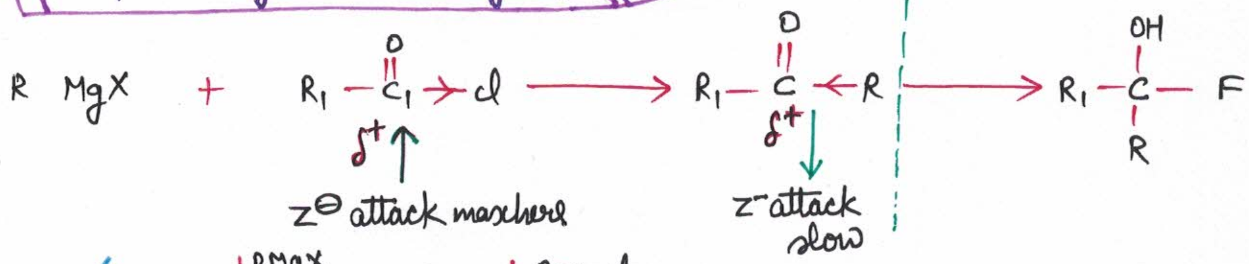

(CH3 – C(=O) – O)2 Ca + (H – C(=O) – O)2 Ca
CH3 – C(=O) – O – Ca – O – C(=O) – H
CH3 – C(=O) – CH3 + H – C(=O) – H
(minor)
+ CaCO3 + CH3 – C(=O) – H
(major)


HO – C(=O) – CH2 – CH2 – CH2 – C(=O) – OH
Ca(OH)2
CH2
CH2
CH2
Ca
+ CaCO3

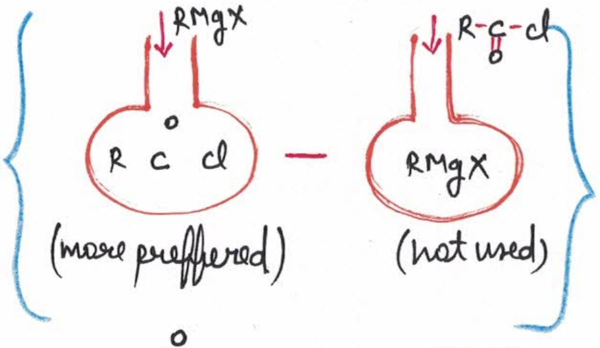

Cl
OH
KMnO4
H+
HOC – (CH2)4 – C – OH
CH2
CH2
CH2
CH2
Ca
ZnHg


Ca/NH3
Na
A
1. O3
2. H2O
B
Ca(OH)2
C
O3
H
C=O
COOH
COOH
Ca(OH)2
O=C–O
Ca
+ CaCO3
ZnHg/HCl

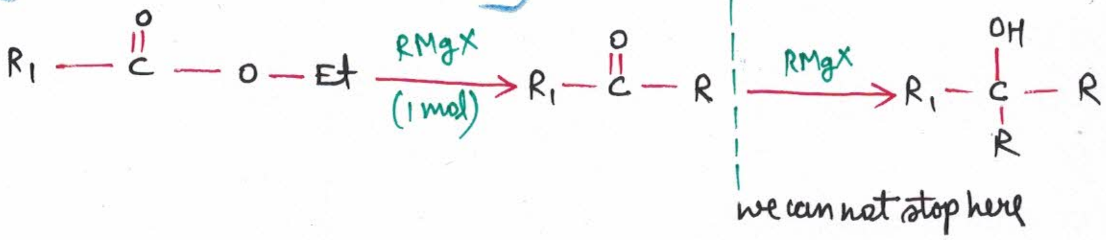
17. By Grignard Reagent



$R\,MgX + R_1-\overset{O}{\overset{\|}{C_1}}\rightarrow Cl \longrightarrow R_1-\overset{O}{\overset{\|}{C}}\leftarrow R \longrightarrow R_1-\underset{R}{\overset{OH}{C}}-F$

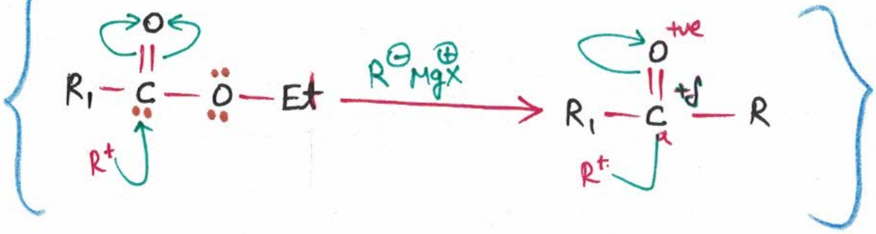


Dog Biscuit Concept.....



$R_1-\overset{O}{\overset{\|}{C}}-O-Et \xrightarrow[(1\,mol)]{RMgX} R_1-\overset{O}{\overset{\|}{C}}-R \xrightarrow{RMgX} R_1-\underset{R}{\overset{OH}{C}}-R$

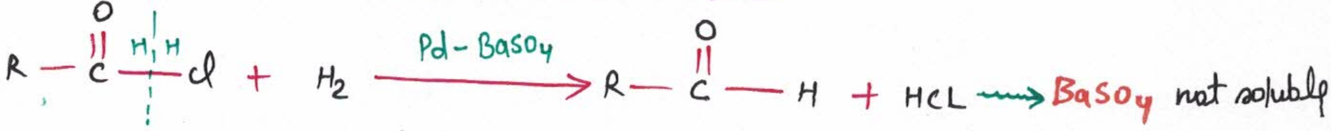
we can not stop here



$R_1-\overset{O}{\overset{\|}{C}}-\ddot{O}-Et \xrightarrow{R^\ominus\,\overset{\oplus}{MgX}} R_1-\overset{O^{+ve}}{\overset{\|}{C}}-R$

not possible

18. By Rosemmund Reduction

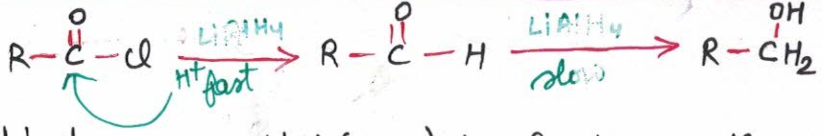


$R-\overset{O}{\overset{\|}{C}}\overset{H}{|}\overset{H}{-}Cl + H_2 \xrightarrow{Pd-BaSO_4} R-\overset{O}{\overset{\|}{C}}-H + HCL \rightsquigarrow BaSO_4$ not soluble

we can not use Lindlar catalyst because HCL released can react with $CaCO_3$ to form $CaCl_2 + CO_2$ and hence catalyst is destroyed. so, only Pd-$BaSO_4$ is used.

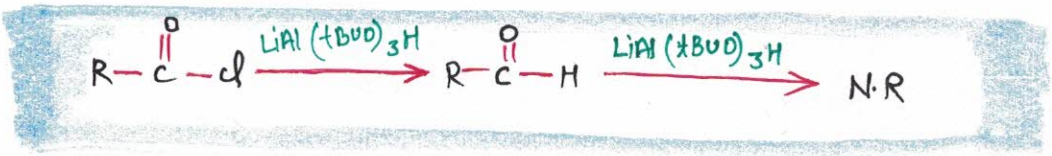
19. By Reduction of $R\overset{O}{C}Cl$ using $LiAl(tBuO)_3H$

we know,



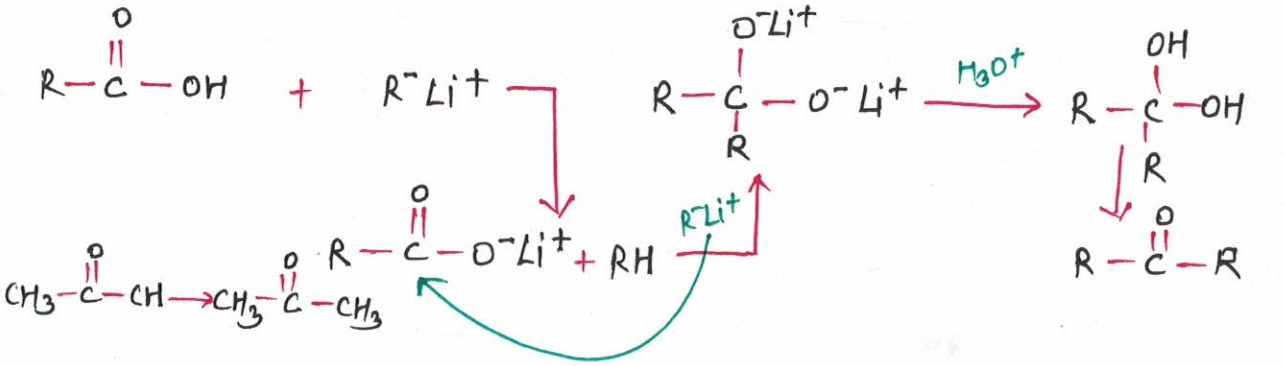
$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[H^+\ fast]{LiAlH_4} R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[slow]{LiAlH_4} R-\overset{OH}{CH_2}$

To get only aldehyde, we use $LiAl(tBuO)_3H$, Due to crowding, once we get aldehyde no further reaction takes place.

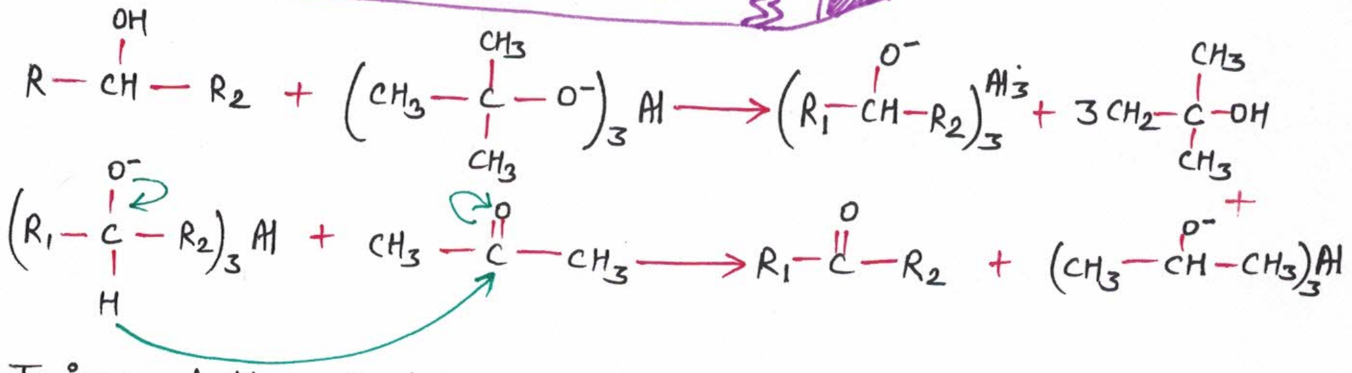


$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{LiAl(tBuO)_3H} R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{LiAl(tBuO)_3H} N.R$

20. By reaction of R-COOH R⁻Li⁺



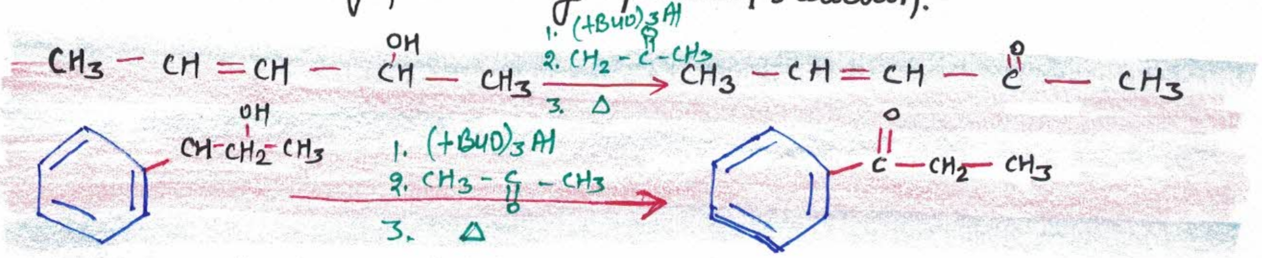
21. Oppeneaur oxidation



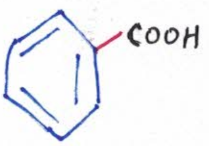
It is a selection method to oxidise secondary alcohols.

$$CH_3-CH=CH-\overset{OH}{CH}-CH_3 \longrightarrow CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

This reaction is only possible by openeaur reaction.

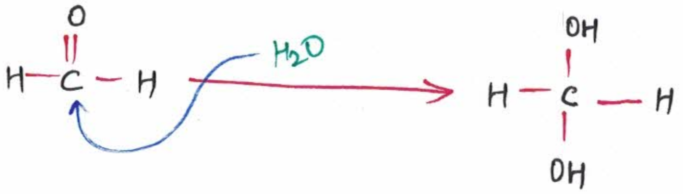


If we use $KMnO_4/H^+$, we will get $CH_3CH=O + O=CH-\underset{O}{\underset{\|}{C}}-CH_3$ &



PROPERTIES

$H-\overset{O}{\overset{\|}{C}}-H$ is a gas $R-\overset{O}{\overset{\|}{C}}-H$ is a liquid. If malecular wt. is very high, it exists as solid. Formaldehyde is highly soluble.

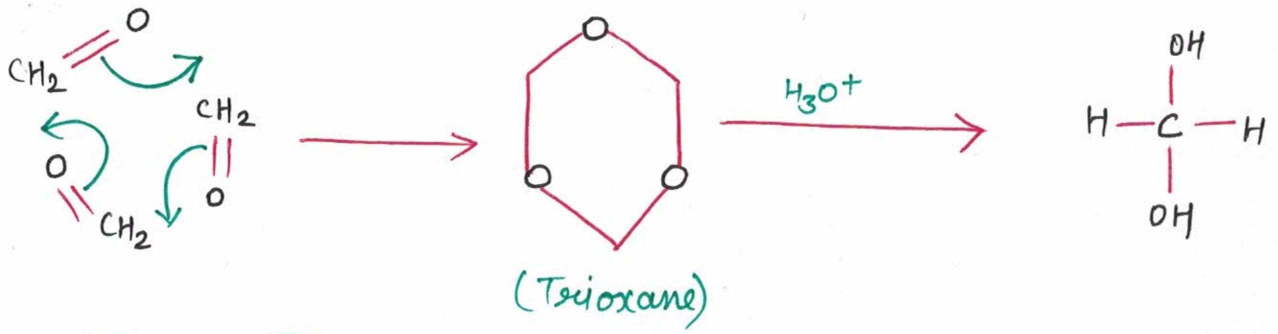


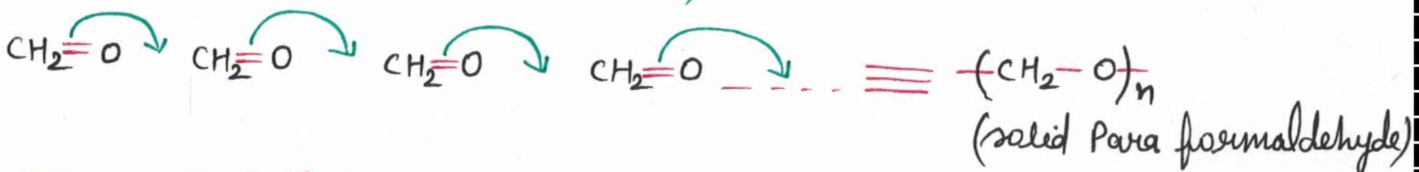
$$H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2O} H-\underset{OH}{\overset{OH}{C}}-H$$

(Hydrated formaldehyde)

Formalein

(40% solution)
of formaldehyde in water to



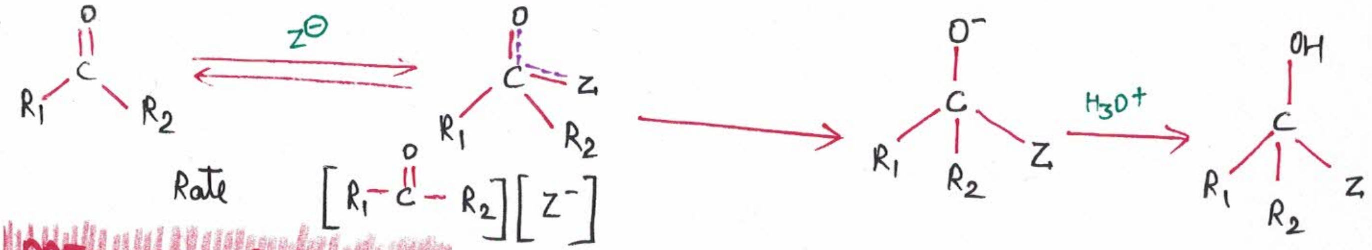


$CH_2=O\ \ CH_2=O\ \ CH_2=O\ \ CH_2=O \ldots \equiv -(CH_2-O)_n-$

(solid Para formaldehyde)

PROPERTIES OF CARBONYL COMPOUNDS

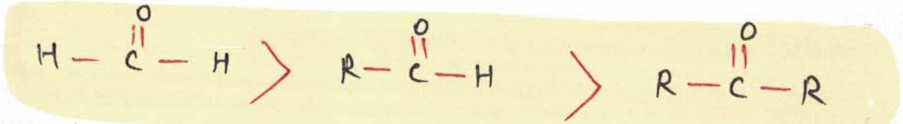
1. Nucleophilic addition



$R_1-\overset{\overset{O}{\|}}{C}-R_2 \underset{}{\overset{Z^{\ominus}}{\rightleftharpoons}} R_1-\overset{\overset{O}{\|}}{C}\cdots Z \longrightarrow R_1-\overset{\overset{O^-}{|}}{\underset{\underset{R_2}{|}}{C}}-Z \xrightarrow{H_3O^+} R_1-\overset{\overset{OH}{|}}{\underset{\underset{R_2}{|}}{C}}-Z$

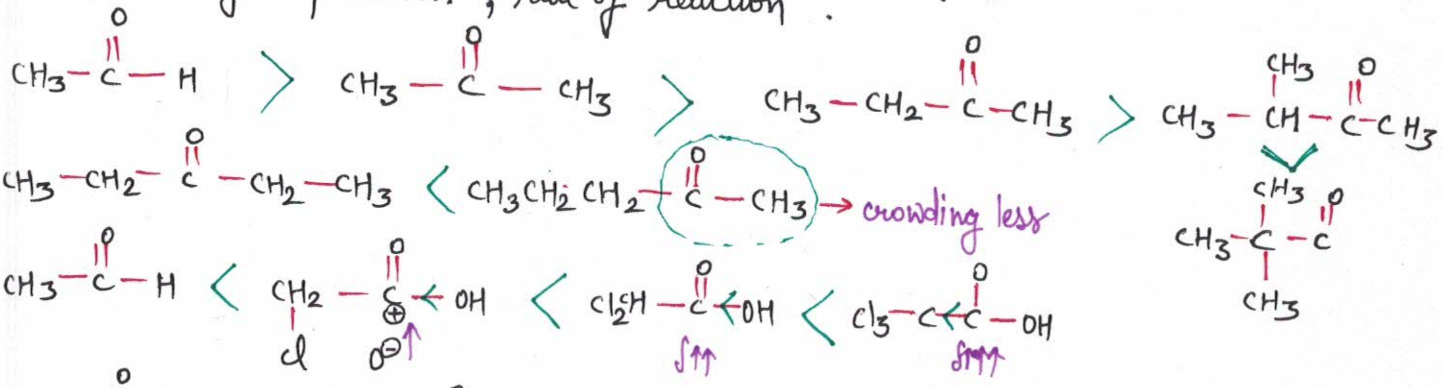
Rate $[R_1-\overset{\overset{O}{\|}}{C}-R_2][Z^-]$

RATE OF REACTION



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

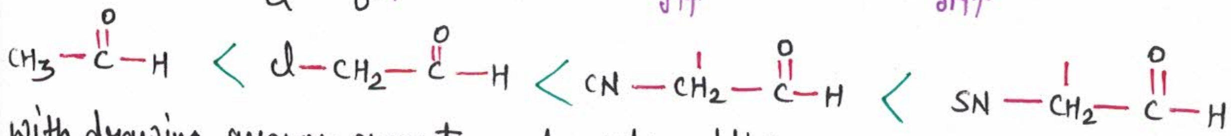
Rate is least in ketones because of crowding in T.S of ketone formed.
As branching at β carbon , rate of reaction .



$CH_3-\overset{\overset{O}{\|}}{C}-H > CH_3-\overset{\overset{O}{\|}}{C}-CH_3 > CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 > CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-CH_3 > CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}$

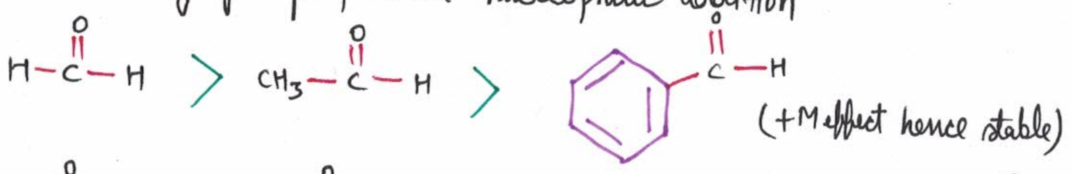
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 < CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow$ crowding less

$CH_3-\overset{\overset{O}{\|}}{C}-H < \underset{\underset{Cl}{|}}{CH_2}-\overset{\overset{O}{\|}}{\underset{\underset{\delta^{\ominus}}{\oplus}}{C}}\leftarrow OH < Cl_2CH-\overset{\overset{O}{\|}}{\underset{\delta\uparrow\uparrow}{C}}\leftarrow OH < Cl_3-C\leftarrow\overset{\overset{O}{\|}}{\underset{\delta\uparrow\uparrow\uparrow}{C}}-OH$

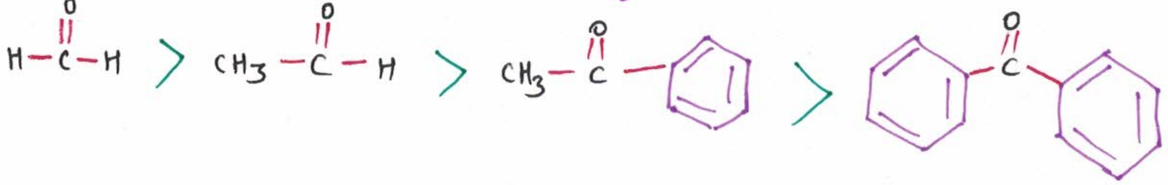


$CH_3-\overset{\overset{O}{\|}}{C}-H < Cl-CH_2-\overset{\overset{O}{\|}}{C}-H < CN-CH_2-\overset{\overset{O}{\|}}{C}-H < SN-CH_2-\overset{\overset{O}{\|}}{C}-H$

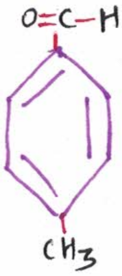
with drawing groups promote nucleophilic addition

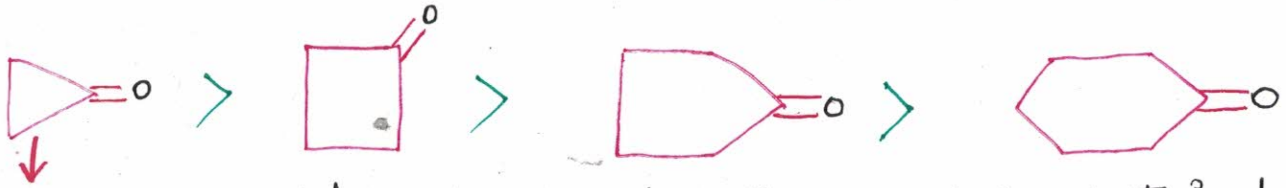


$H-\overset{\overset{O}{\|}}{C}-H > CH_3-\overset{\overset{O}{\|}}{C}-H > C_6H_5-\overset{\overset{O}{\|}}{C}-H$ (+M effect hence stable)



$H-\overset{\overset{O}{\|}}{C}-H > CH_3-\overset{\overset{O}{\|}}{C}-H > CH_3-\overset{\overset{O}{\|}}{C}-C_6H_5 > C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5$

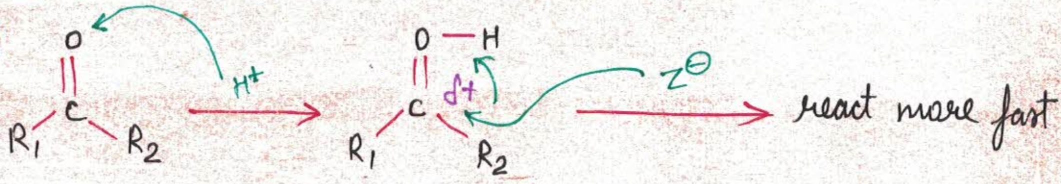




It is more because before addition it was sp² (60°) most strained. The moment nucleophile is added it changes to sp³ & hence gets most relief.

Nucleophilic addition of carbonyls is catalysed by an acid.

REASON



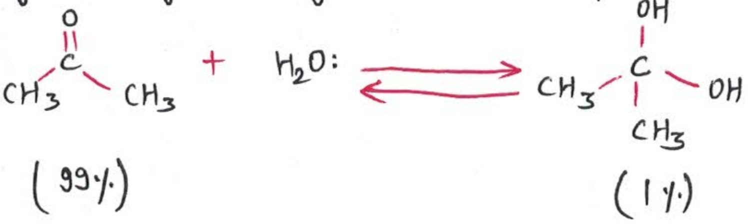
Every aldehyde (except HCHO) upon N.A. will give a resolvable mixture (D/L)

All unsymmetrical ketons upon N.A will give resolvable mixture (D/L)

HYDRATION OF CARBONYLS

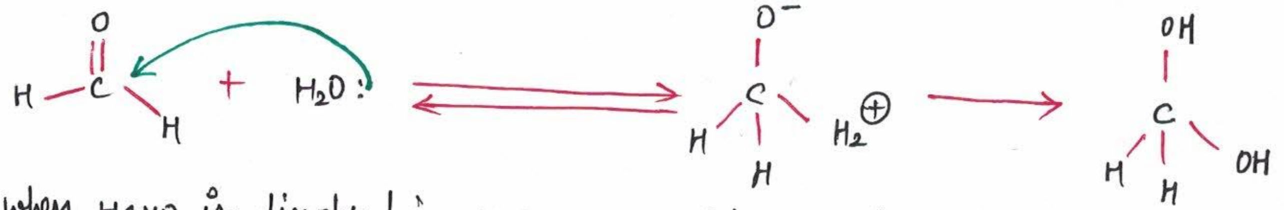
(formation)

Hydration of carbonyls is a nucleophilic addition

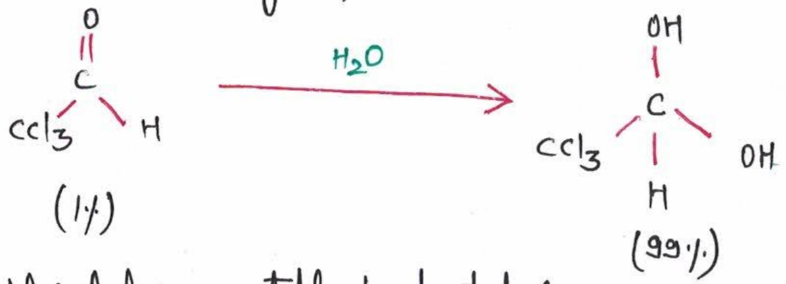


So, higher the rate of nucleophilic addition, higher is the ability to stay in the hydrated form.

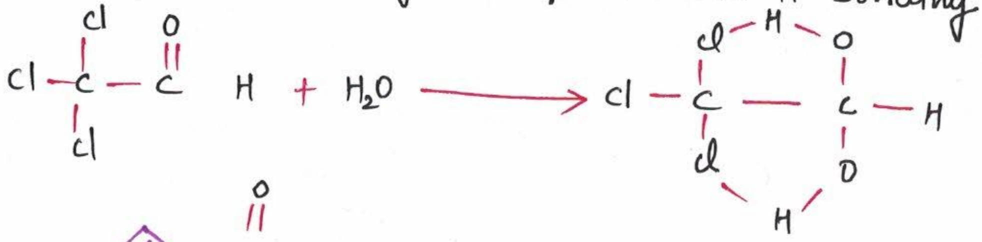
Hydrated forms exist in aqueous mix only.

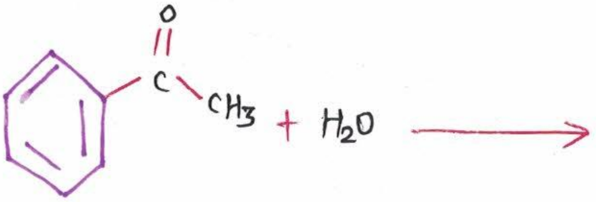


when HCHO is dissolved in H_2O, 99% exist in the form of formaliin whereas CH_3CHO exist only 5%..

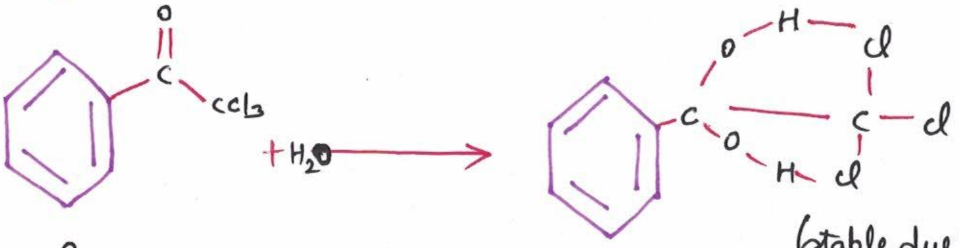


chloral forms stable hydrated form due to H-bonding.

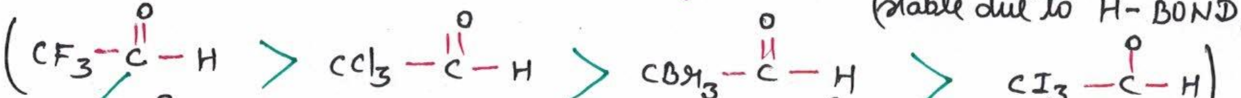




does not dissolve

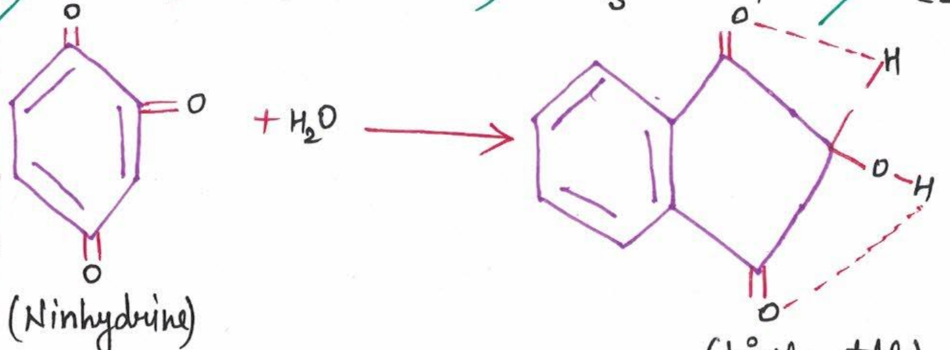


(stable due to H-BOND, NH)



$$\left(CF_3-\overset{O}{\overset{\|}{C}}-H > CCl_3-\overset{O}{\overset{\|}{C}}-H > CBr_3-\overset{O}{\overset{\|}{C}}-H > CI_3-\overset{O}{\overset{\|}{C}}-H\right)$$

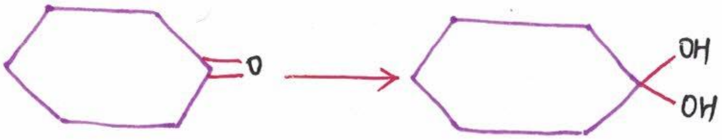
It will form most stable hydrate.



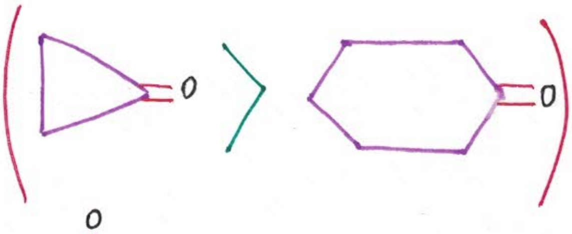
(Ninhydrine)

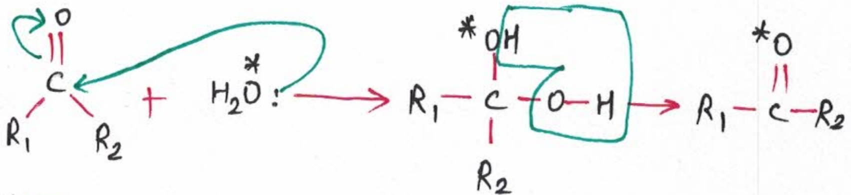
(highly stable)

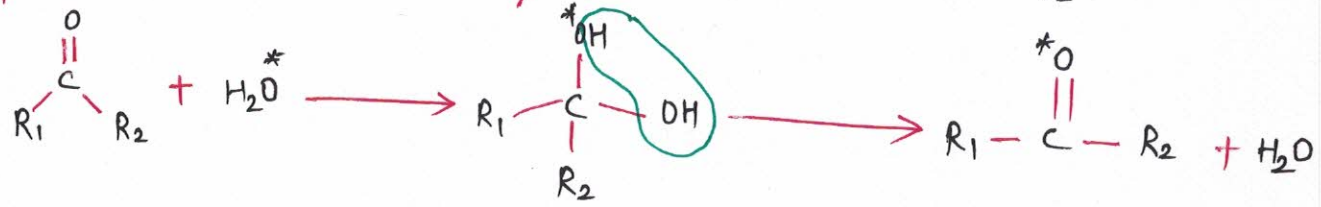
similarly,



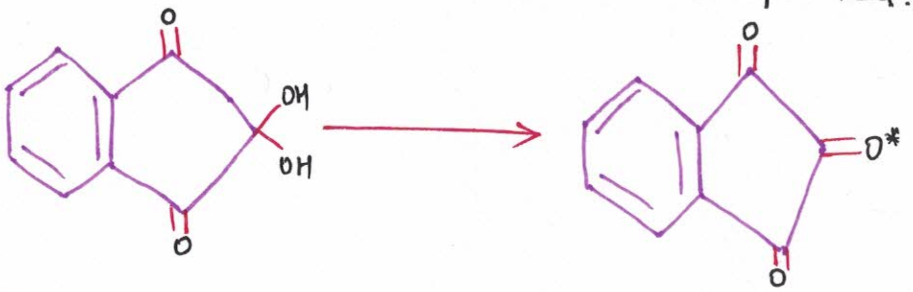
(does not form reaction moves backward.)



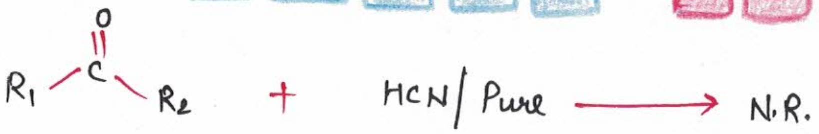


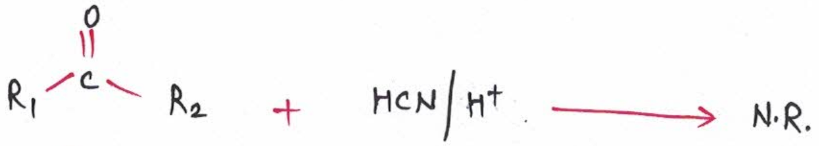


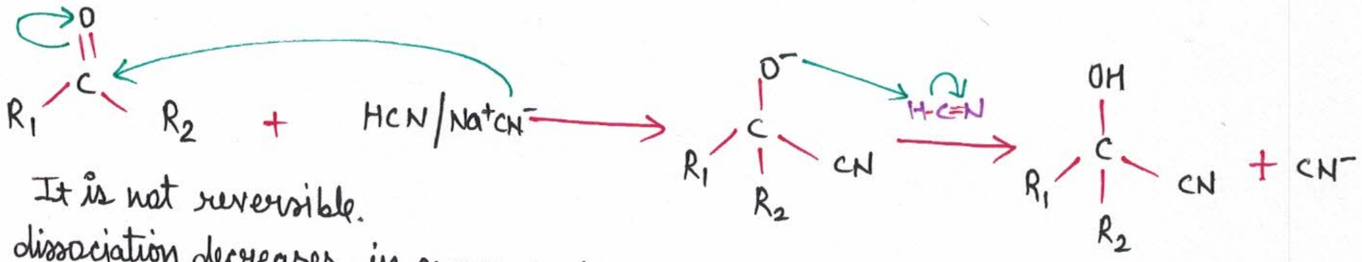
Backword & forward reactions both are possible.



REACTION WITH HCN

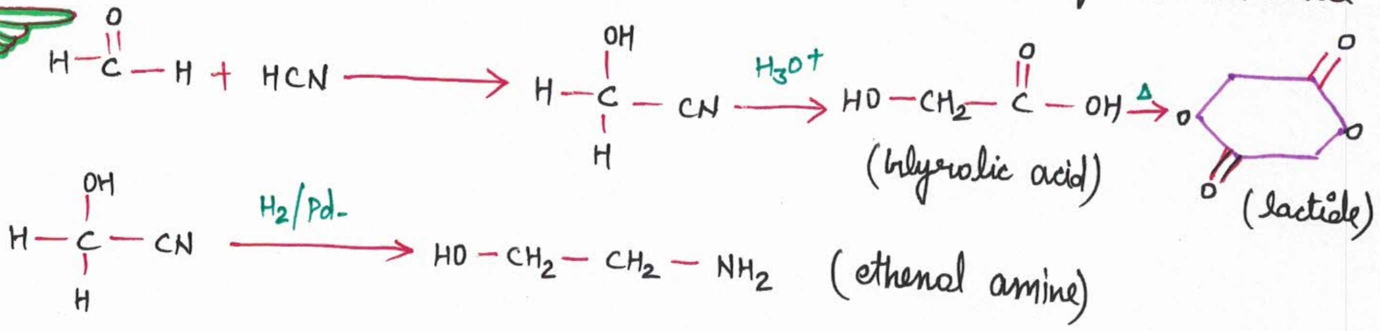


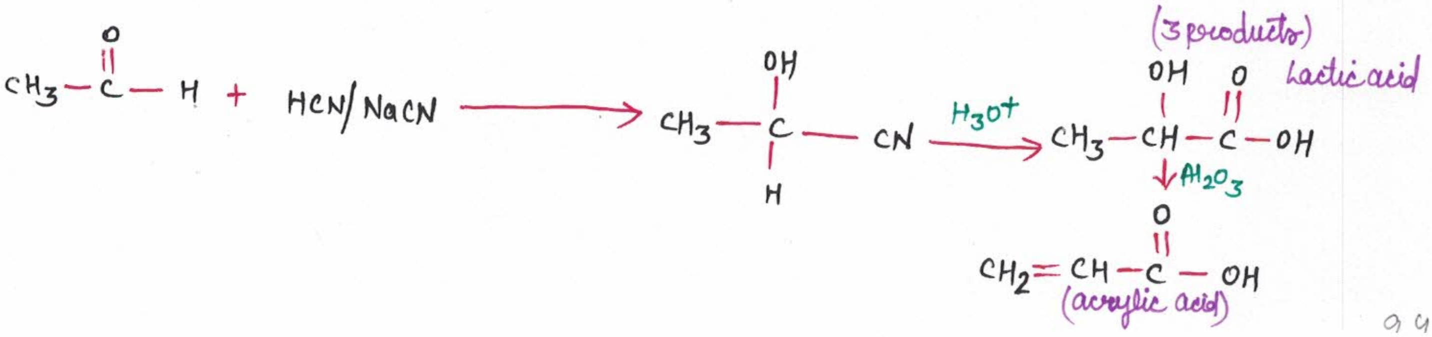


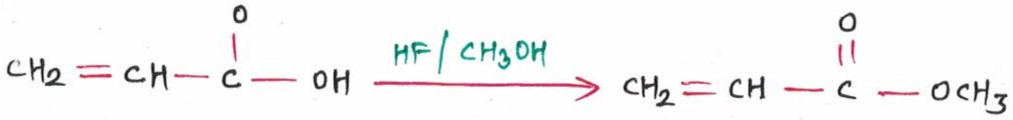


It is not reversible.

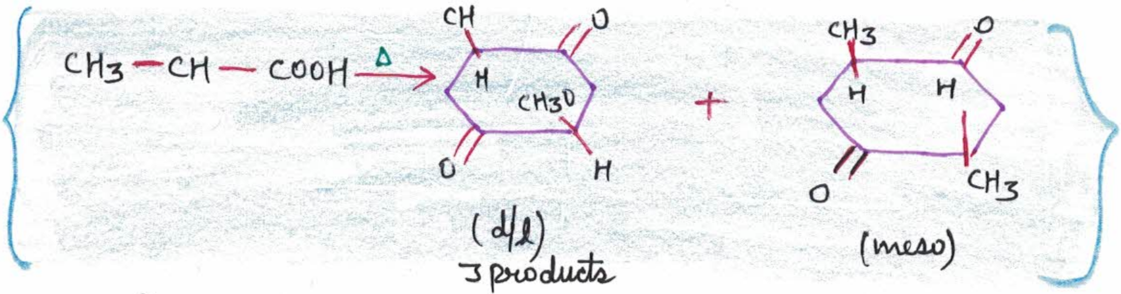
HCN dissociation decreases in presence of H+ Hence CN− does not form and hence no reaction.

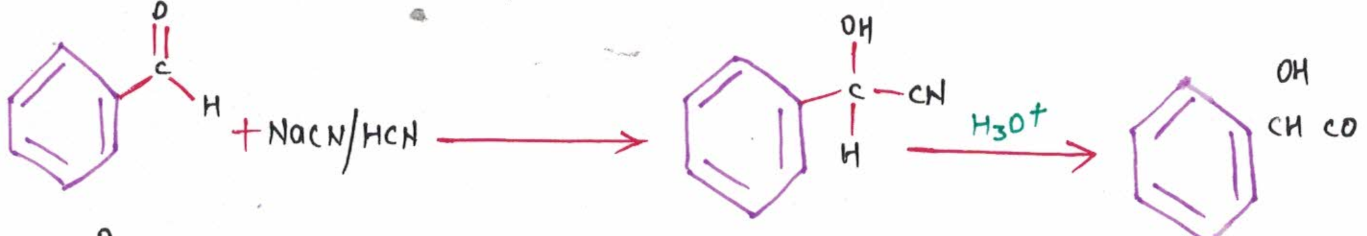




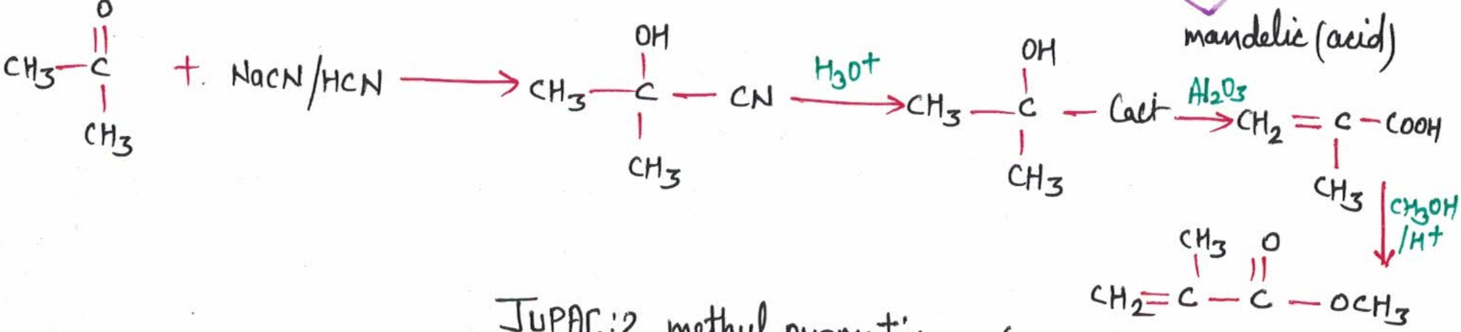


$$CH_2=CH-\overset{O}{\overset{|}{C}}-OH \xrightarrow{HF/CH_3OH} CH_2=CH-\overset{O}{\overset{||}{C}}-OCH_3$$





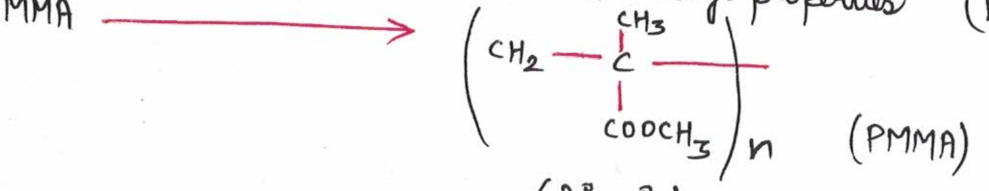
mandelic (acid)



$$CH_3-\overset{O}{\overset{||}{C}}-CH_3 + NaCN/HCN \longrightarrow CH_3-\underset{CH_3}{\overset{OH}{C}}-CN \xrightarrow{H_3O^+} CH_3-\underset{CH_3}{\overset{OH}{C}}-COOH \xrightarrow{Al_2O_3} CH_2=\underset{CH_3}{C}-COOH \xrightarrow{CH_3OH/H^+} CH_2=\overset{CH_3}{C}-\overset{O}{\overset{||}{C}}-OCH_3$$

IUPAC: 2 methyl propenties

(MMA) (Methyl methaacrylate)

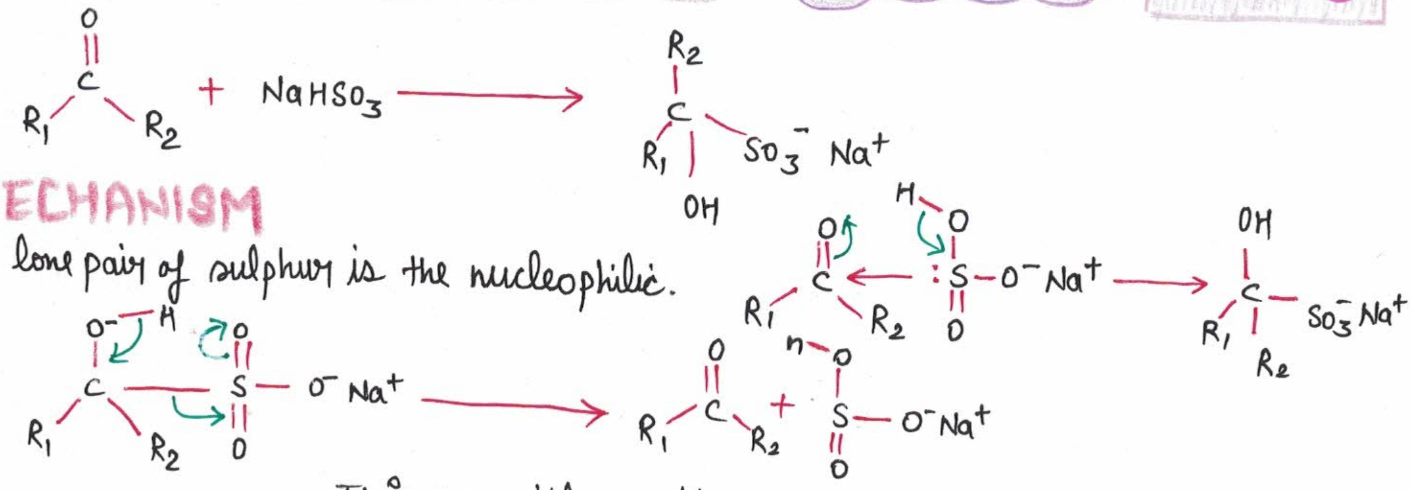


$$MMA \longrightarrow \left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}} \right)_n$$

(PMMA)

(Piropix)

REACTION WITH $NaHSO_3$



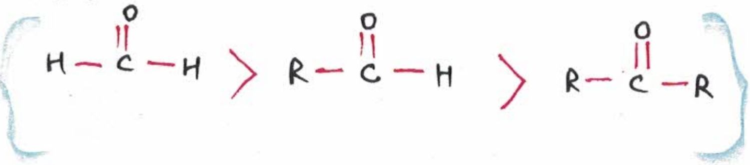
$$\underset{R_1\ \ \ R_2}{\overset{O}{\overset{||}{C}}} + NaHSO_3 \longrightarrow R_1-\underset{OH}{\overset{R_2}{C}}-SO_3^-\,Na^+$$

MECHANISM

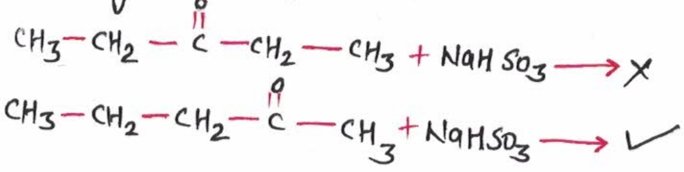
The lone pair of sulphur is the nucleophilic.

It is reversible reaction

only methyl ketons undergo nucleophilic addition by $NaHSO_3$, other ketones do not.



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



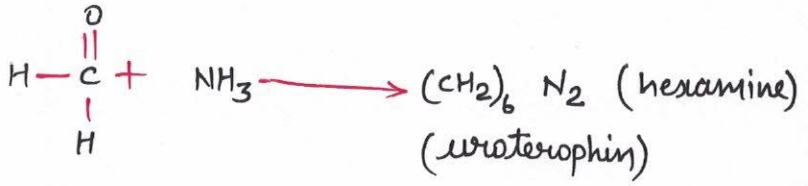
$$CH_3-CH_2-\overset{O}{\overset{||}{C}}-CH_2-CH_3 + NaHSO_3 \longrightarrow \times$$

$$CH_3-CH_2-CH_2-\overset{O}{\overset{||}{C}}-CH_3 + NaHSO_3 \longrightarrow \checkmark$$

Reaction of HCN is faster than $NaHSO_3$ because C^- is better nucleophilic than sulphur.

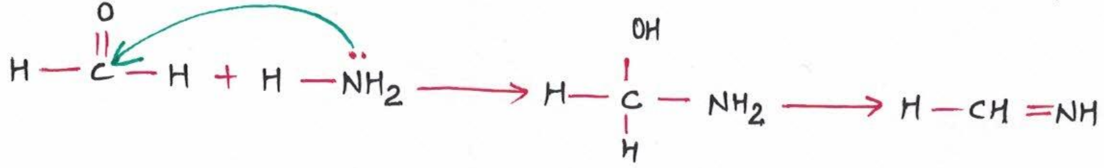
REACTION WITH NH_3 AND ITS DERIVATION

1. With NH_3

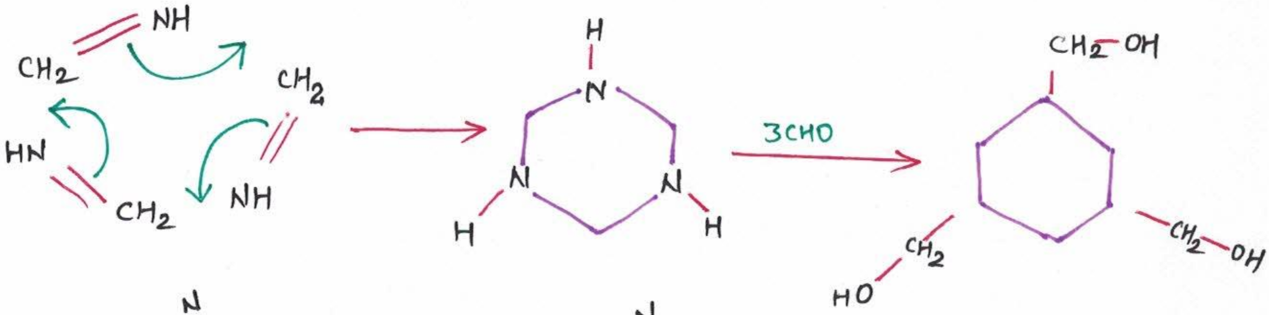


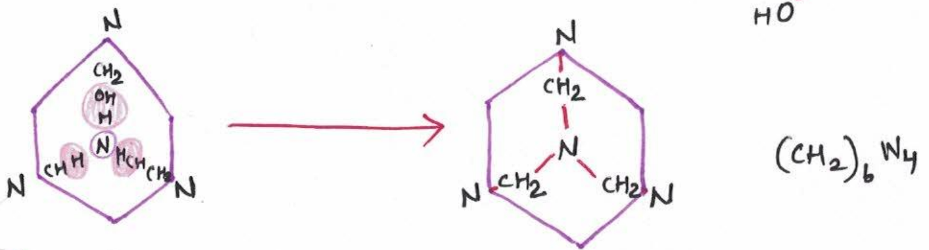
$$H-\overset{\overset{O}{\|}}{C}-H + NH_3 \longrightarrow (CH_2)_6N_2 \text{ (hexamine)}$$

(urotropin)

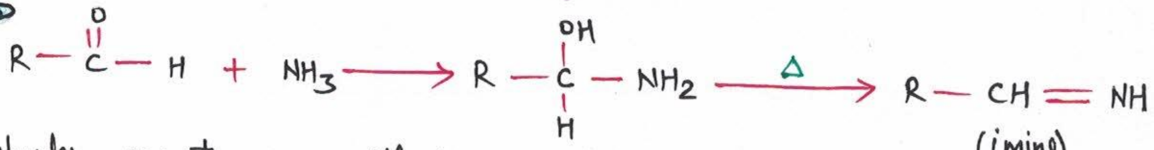


$$H-\overset{\overset{O}{\|}}{C}-H + H-\ddot{N}H_2 \longrightarrow H-\underset{H}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-NH_2 \longrightarrow H-CH=NH$$





$(CH_2)_6N_4$

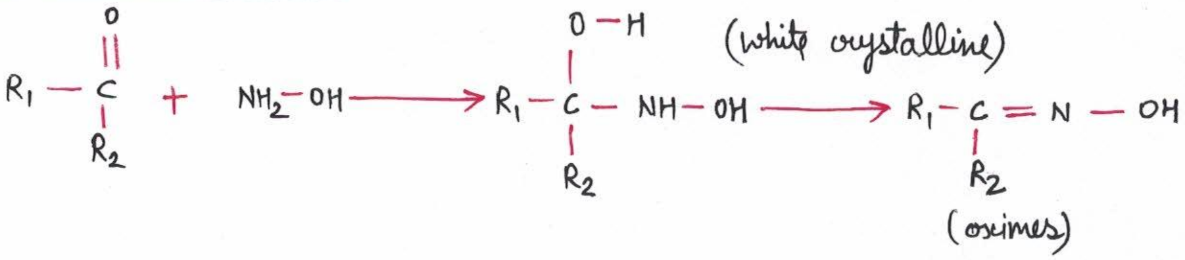


$$R-\overset{\overset{O}{\|}}{C}-H + NH_3 \longrightarrow R-\underset{H}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-NH_2 \xrightarrow{\Delta} R-CH=NH$$

(imine)

All aldehydes except HCHO will form imine on reaction with NH_3.

2. With NH_2-OH

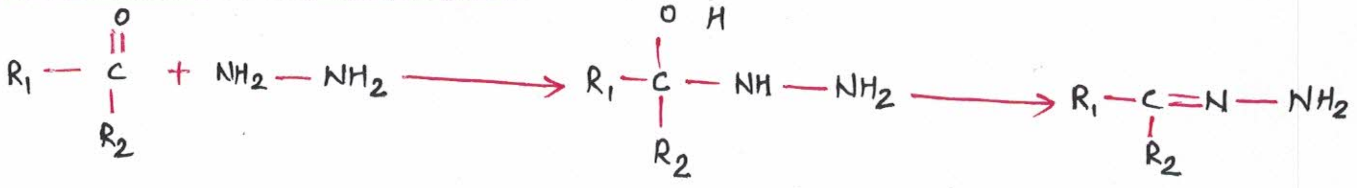


$$R_1-\underset{R_2}{\underset{|}{\overset{\overset{O}{\|}}{C}}} + NH_2-OH \longrightarrow R_1-\underset{R_2}{\underset{|}{\overset{O-H}{\overset{|}{C}}}}-NH-OH \longrightarrow R_1-\underset{R_2}{\underset{|}{C}}=N-OH$$

(white crystalline)

(oximes)

3. With NH_2-NH_2 (hydrozone)

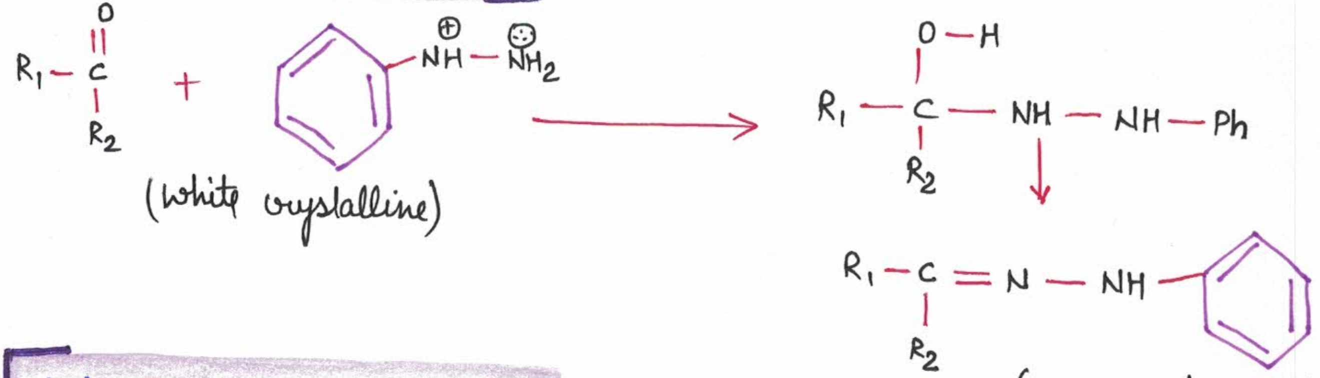


$$R_1-\overset{O}{\overset{\|}{C}}-R_2 + NH_2-NH_2 \longrightarrow R_1-\overset{OH}{\underset{R_2}{C}}-NH-NH_2 \longrightarrow R_1-\underset{R_2}{C}=N-NH_2$$

(white crystalline)

(hydrozones)

4. With Phenyl hydrozone

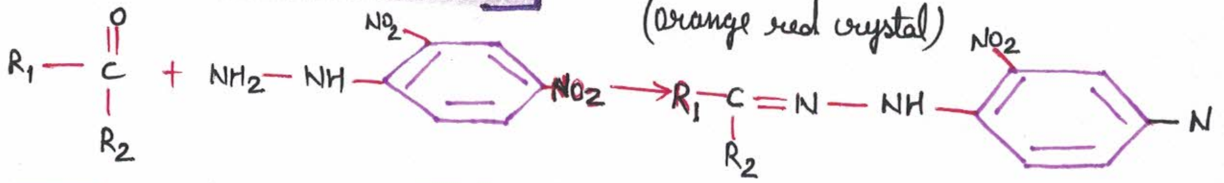


(white crystalline)

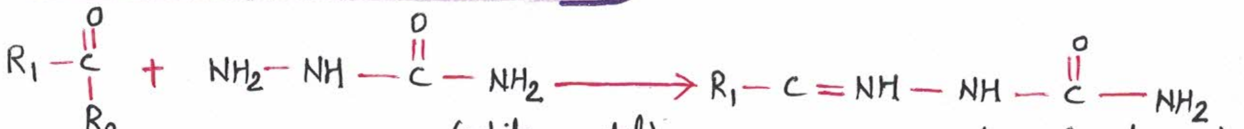
(Phenyl Rudrazine)

5. With 2,4 - DNP

(orange red crystal)



6. With Semi carbozide



$$R_1-\overset{O}{\overset{\|}{C}}-R_2 + NH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow R_1-\underset{R_2}{C}=NH-NH-\overset{O}{\overset{\|}{C}}-NH_2$$

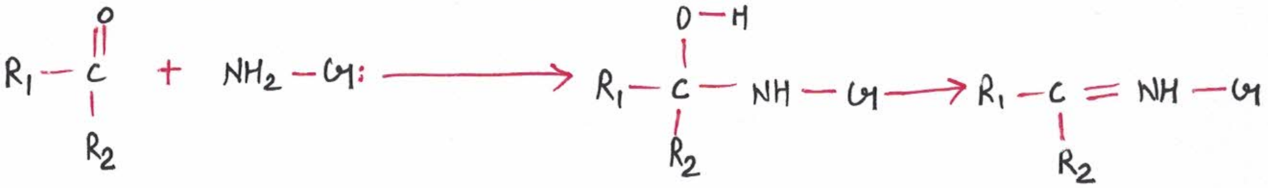
(white crystal)

(semicarbozone)

All of these reactions are test for carbonyl compounds.

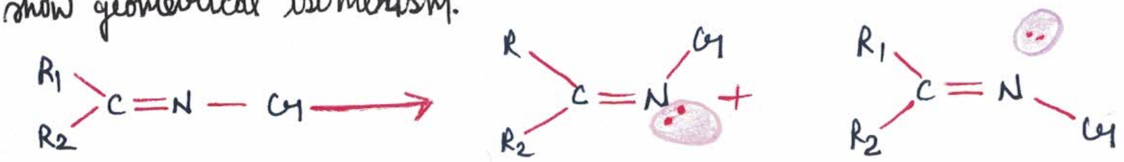
x gives oximes, hydrozones & gives a ⊕, test with 2,4 - DNP means x is a carbonyl compound.

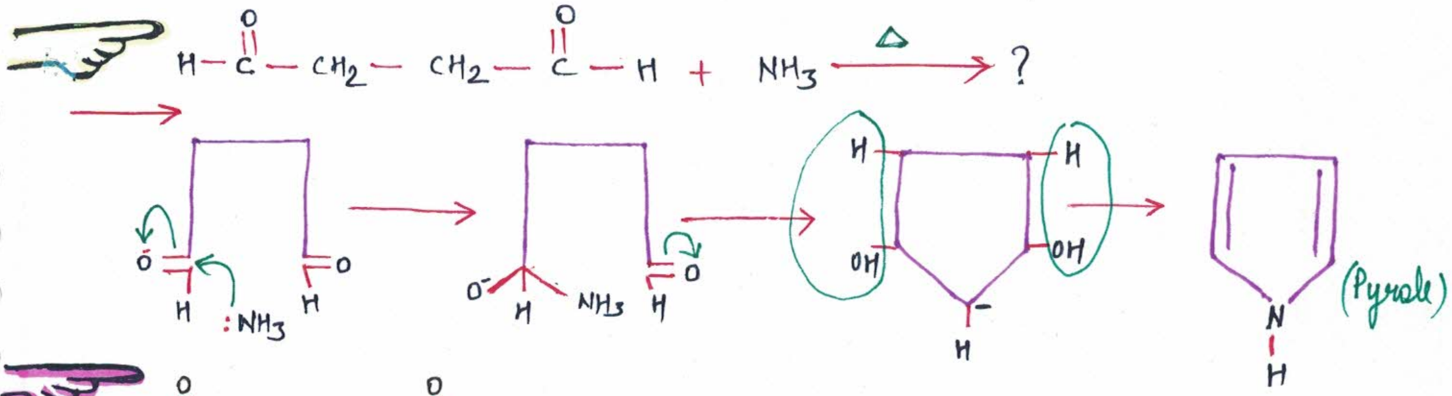
GENERAL MECHANISM

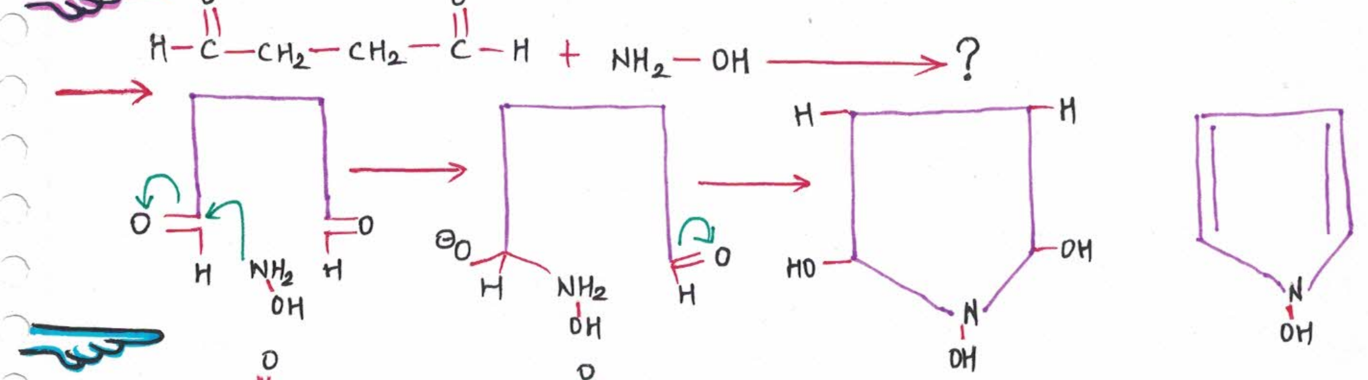


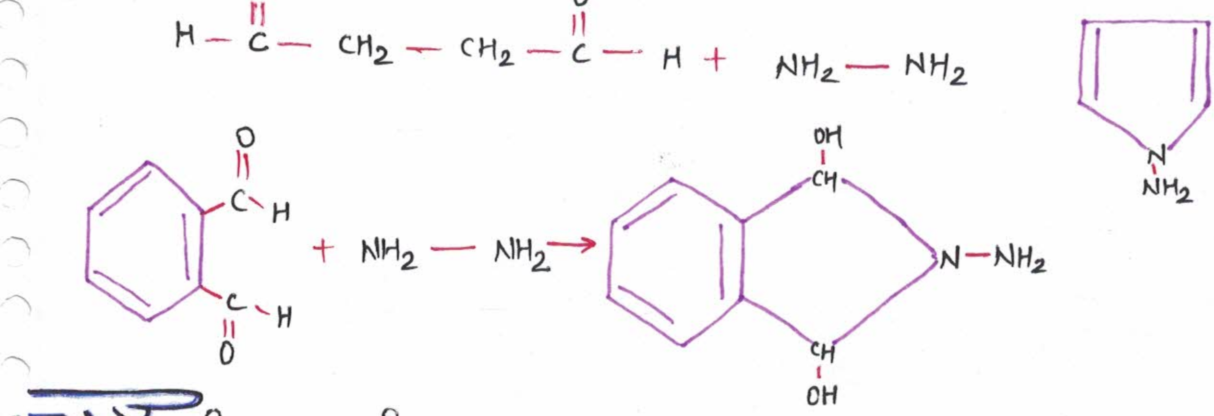
$$R_1-\overset{O}{\overset{\|}{C}}-R_2 + NH_2-G: \longrightarrow R_1-\overset{O-H}{\underset{R_2}{C}}-NH-G \longrightarrow R_1-\underset{R_2}{C}=NH-G$$

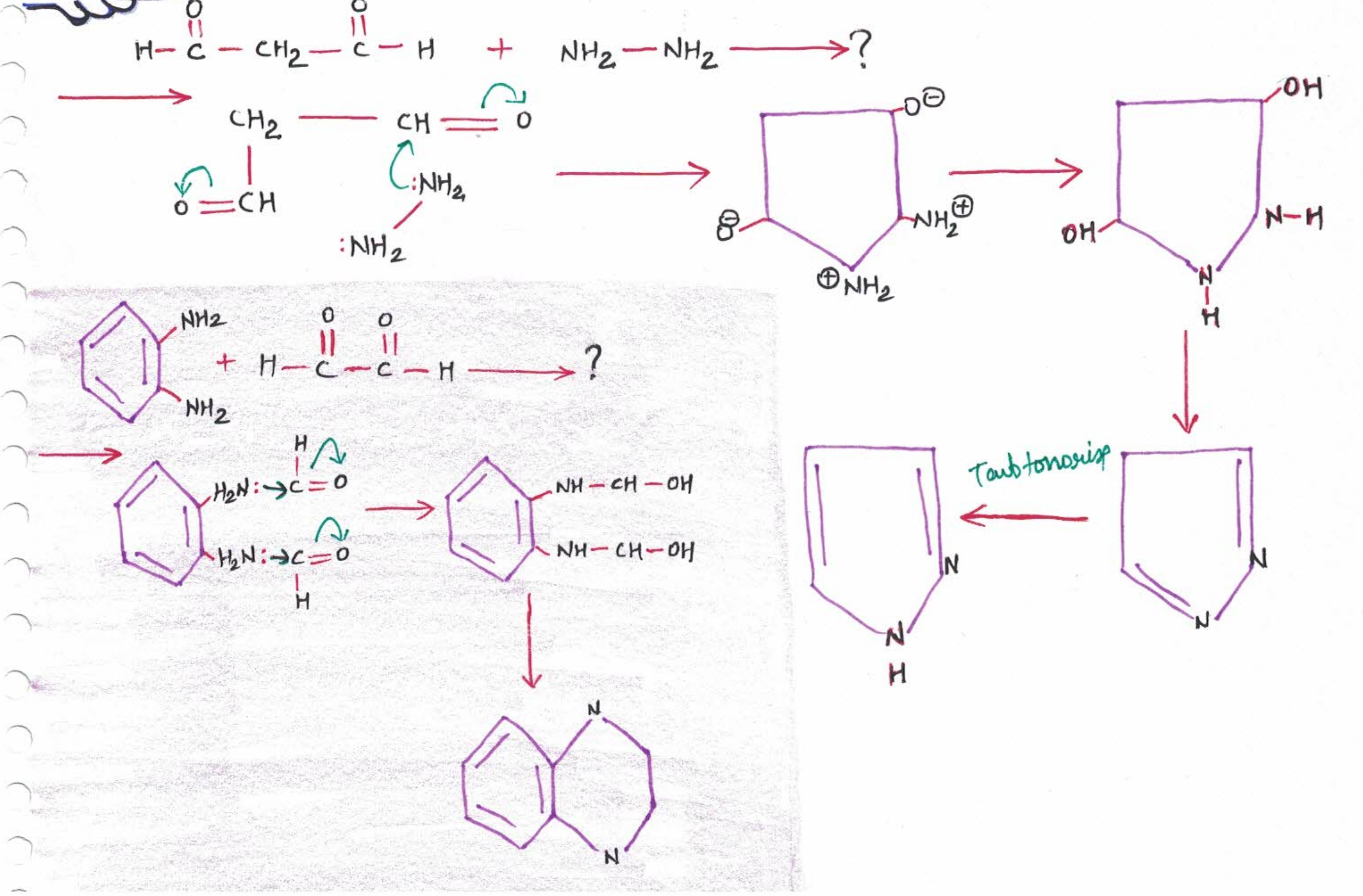
All ammonia derivations of unsymmetrical ketones and aldehydes except HCHO will show geometrical isomerism.




H–C(=O)–CH2–CH2–C(=O)–H + NH3 → ?
Δ
:NH3
(Pyrole)


H–C(=O)–CH2–CH2–C(=O)–H + NH2–OH → ?


H–C(=O)–CH2–CH2–C(=O)–H + NH2–NH2
+ NH2–NH2 →
N–NH2

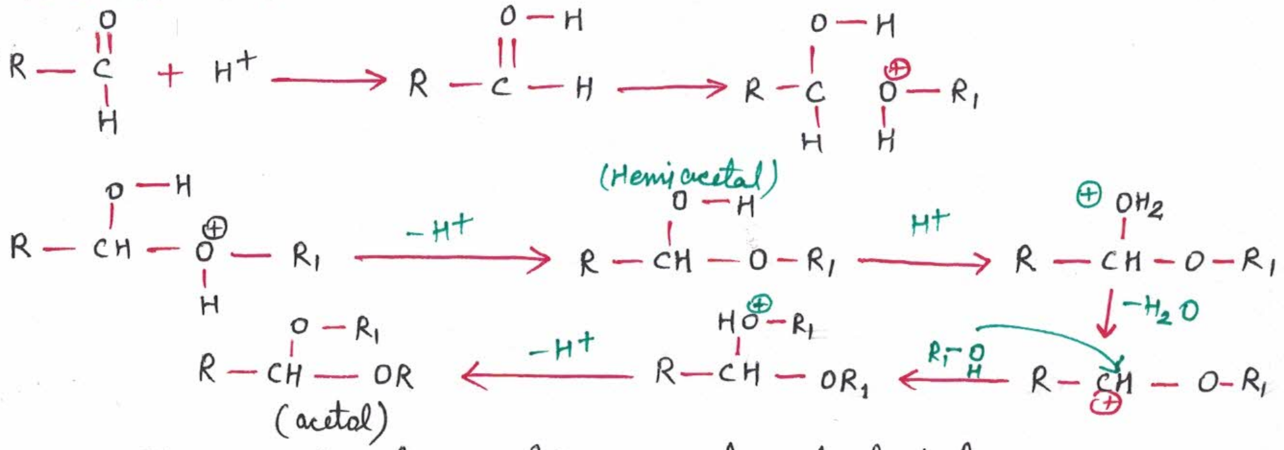

H–C(=O)–CH2–C(=O)–H + NH2–NH2 → ?
+ H–C(=O)–C(=O)–H → ?
NH–CH–OH
Tautomerism

REACTION WITH ALCOHOLS

$$R-\overset{\overset{O}{\|}}{\underset{H}{C}} + R_1-OH \rightleftharpoons R-\overset{O-R_1}{\underset{H}{C}}-O-R_1 + H_2O$$

(acetals)

MECHANISM



$$R-\overset{\overset{O}{\|}}{\underset{H}{C}} + H^+ \longrightarrow R-\overset{\overset{O-H}{\|}}{C}-H \longrightarrow R-\overset{O-H}{\underset{H}{C}}\;\; \overset{\oplus}{\underset{H}{O}}-R_1$$

$$R-\overset{O-H}{CH}-\underset{H}{\overset{\oplus}{O}}-R_1 \xrightarrow{-H^+} R-\overset{O-H}{CH}-O-R_1 \xrightarrow{H^+} R-\overset{\oplus\, OH_2}{CH}-O-R_1$$

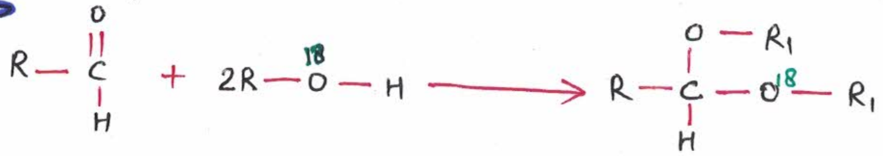
(Hemiacetal)

$$\downarrow -H_2O$$

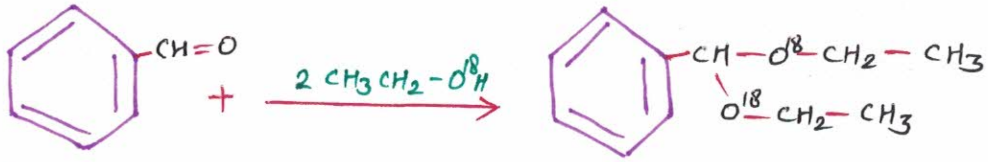
$$R-\overset{O-R_1}{CH}-OR \xleftarrow{-H^+} R-\overset{H\overset{\oplus}{O}-R_1}{CH}-OR_1 \xleftarrow{R_1-\underset{H}{O}} R-\underset{\oplus}{CH}-O-R_1$$

(acetal)

Every carbonyl requires 2 moles of alcohol.



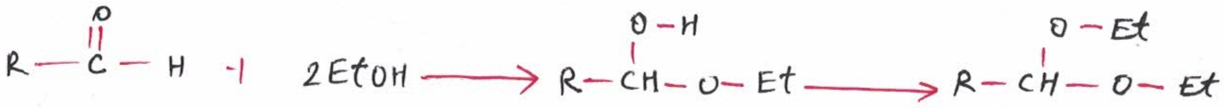
$$R-\overset{\overset{O}{\|}}{\underset{H}{C}} + 2R-\overset{18}{O}-H \longrightarrow R-\overset{O-R_1}{\underset{H}{C}}-O^{18}-R_1$$



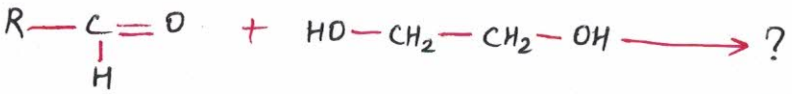
Crowding decreases rate of reaction b/w alcohal & aldehyde.

Most reactive mixture is $CH_3OH + HCHO$

$$H-\overset{\overset{O}{\|}}{C}-H > R-\overset{\overset{O}{\|}}{C}-H \gg R-\overset{\overset{O}{\|}}{C}-R$$



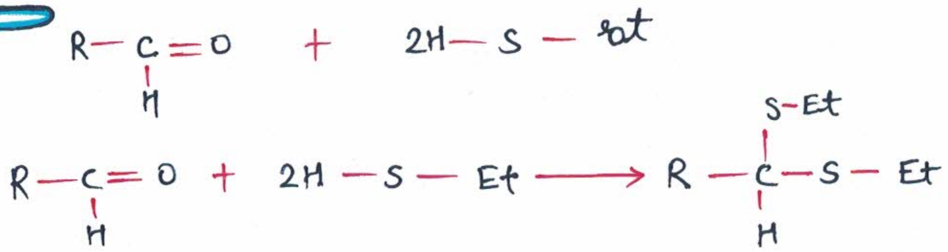
$$R-\overset{\overset{O}{\|}}{C}-H + 2EtOH \longrightarrow R-\overset{O-H}{CH}-O-Et \longrightarrow R-\overset{O-Et}{CH}-O-Et$$



$$R-\underset{H}{C}=O + HO-CH_2-CH_2-OH \longrightarrow ?$$

First reaction → intermolecular
2^{nd} reaction → intramolecular
Intra > Inter (rate)

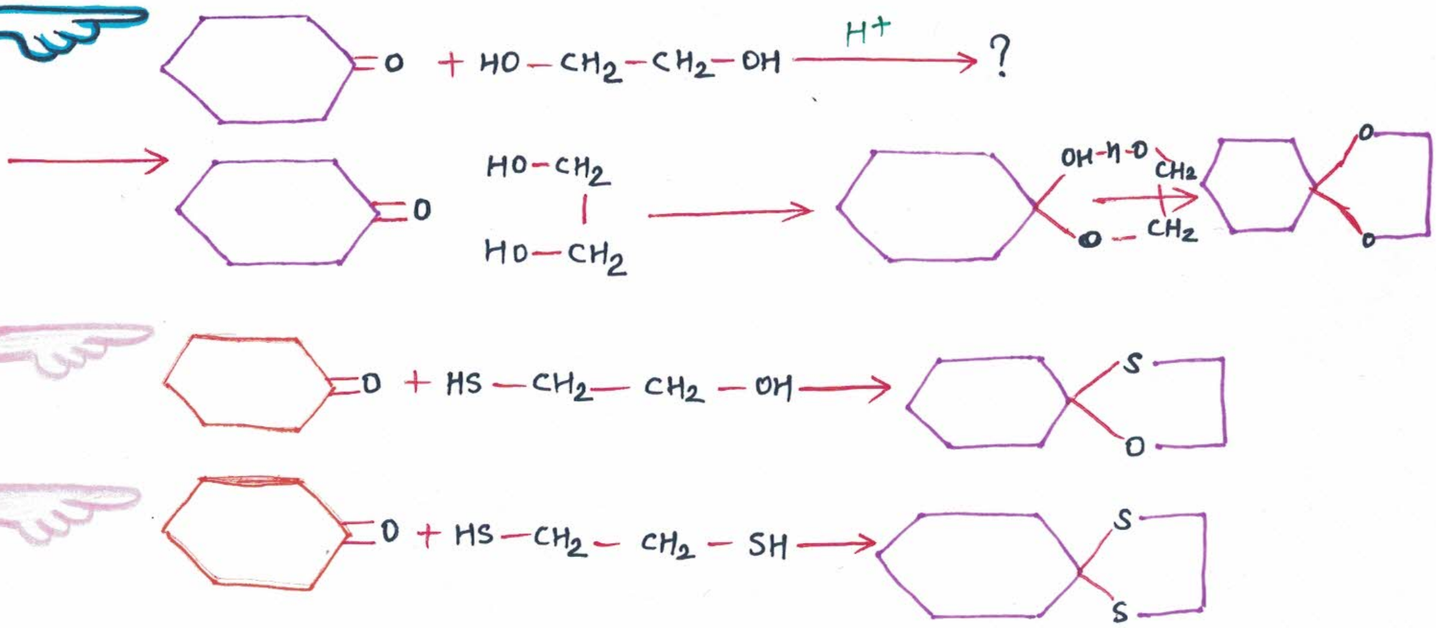
This reaction is faster than previous ones.



$R-\underset{H}{C}=O + 2H-S-Et$

$R-\underset{H}{C}=O + 2H-S-Et \longrightarrow R-\underset{H}{\overset{S-Et}{C}}-S-Et$

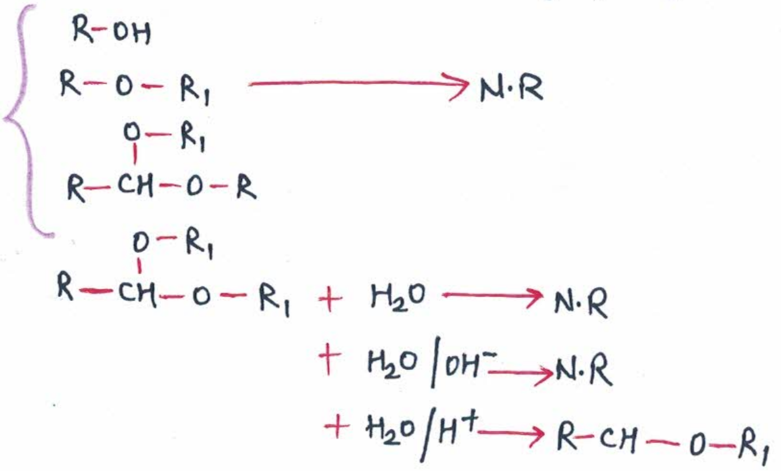
Thiols are better nucleophiles than alcohols this reaction is faster than alcohols.



From aldehydes ⟶ acetals
From ketons ⟶ ketons

All of these reactions are reversible.

Like alcohols & ethers, acetals also do not undergo hydrolysis in basic & neutral medium as the laving groups (-8-R) is unstable.



$R-OH$

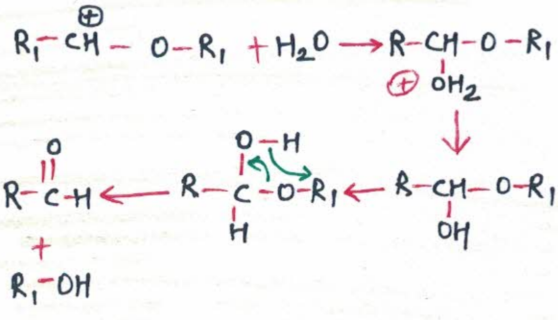
$R-O-R_1 \longrightarrow N.R$

$R-\overset{O-R_1}{CH}-O-R$

$R-\overset{O-R_1}{CH}-O-R_1 + H_2O \longrightarrow N.R$

$+ H_2O/OH^- \longrightarrow N.R$

$+ H_2O/H^+ \longrightarrow R-CH-O-R_1$



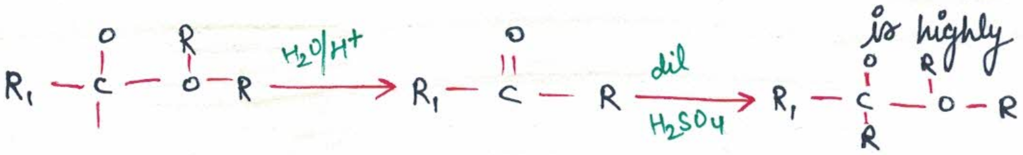
$R_1-\overset{\oplus}{CH}-O-R_1 + H_2O \longrightarrow R-\underset{\oplus\,OH_2}{CH}-O-R_1$

$\downarrow$

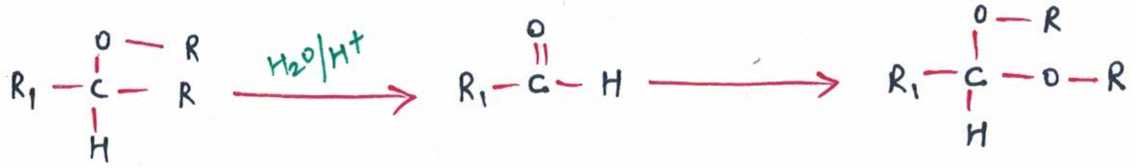
$R-\overset{O}{\overset{\|}{C}}-H \longleftarrow R-\underset{H}{\overset{O-H}{C}}-O-R_1 \longleftarrow R-\underset{OH}{CH}-O-R_1$

$+ R_1-OH$

Acetals are not stable in acidic medium. they undergo hydrolysis Δ carbocation $R-\overset{\oplus}{CH}-\ddot{O}-R$ is highly stable.

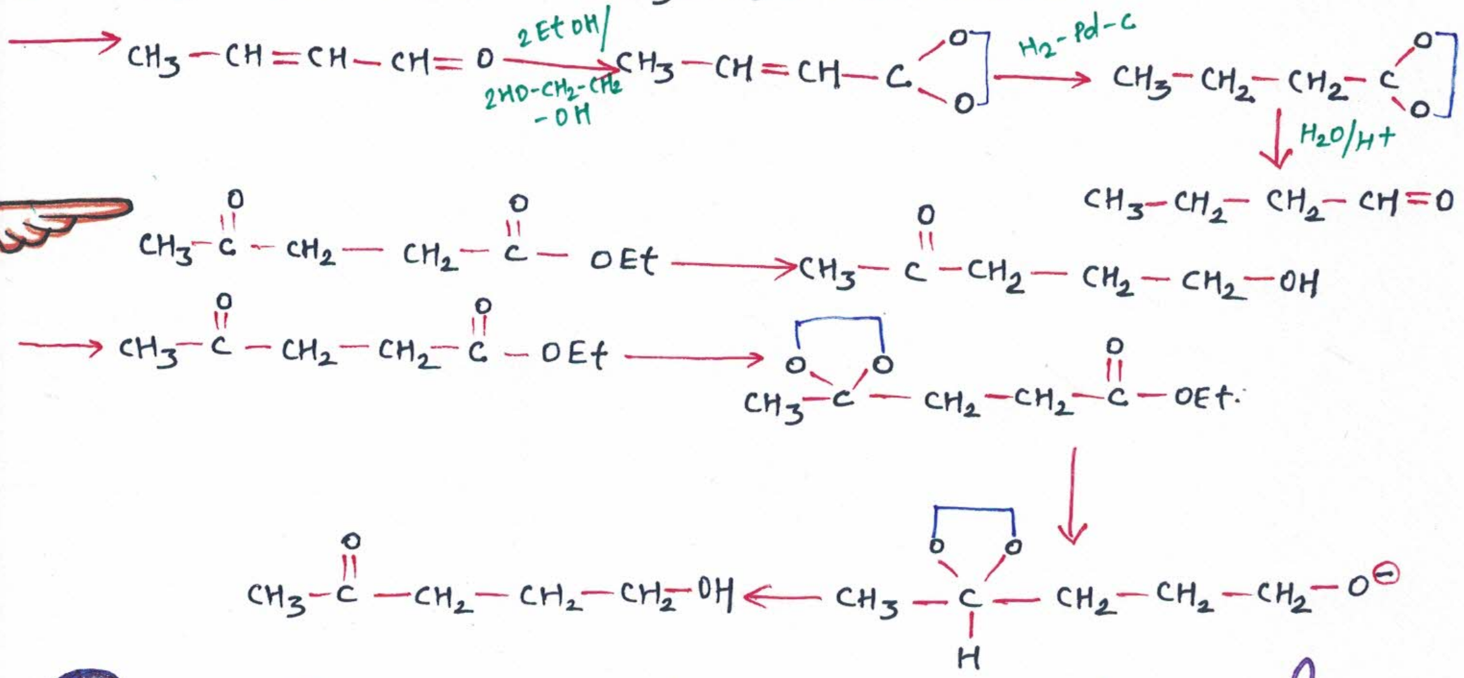


$R_1-\overset{O}{\underset{|}{\overset{|}{C}}}-\overset{R}{\overset{|}{O}}-R \xrightarrow{H_2O/H^+} R_1-\overset{O}{\overset{\|}{C}}-R \xrightarrow[H_2SO_4]{dil} R_1-\underset{R}{\overset{O}{C}}-\overset{R}{O}-R$



$$R_1-\overset{O-R}{\underset{H}{C}}-R \xrightarrow{H_2O/H^+} R_1-\overset{O}{\overset{\|}{C}}-H \longrightarrow R_1-\overset{O-R}{\underset{H}{C}}-O-R$$

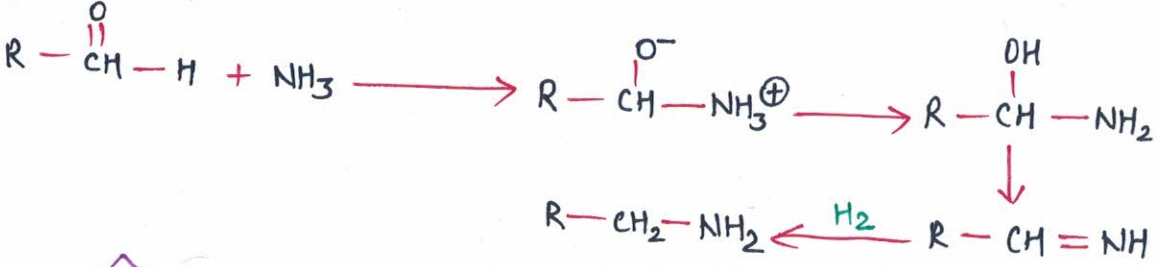
$$CH_3-CH=CH-CH=O \longrightarrow CH_3-CH_2-CH_2-CH=O$$



REDUCTIVE Amination of carbonyls

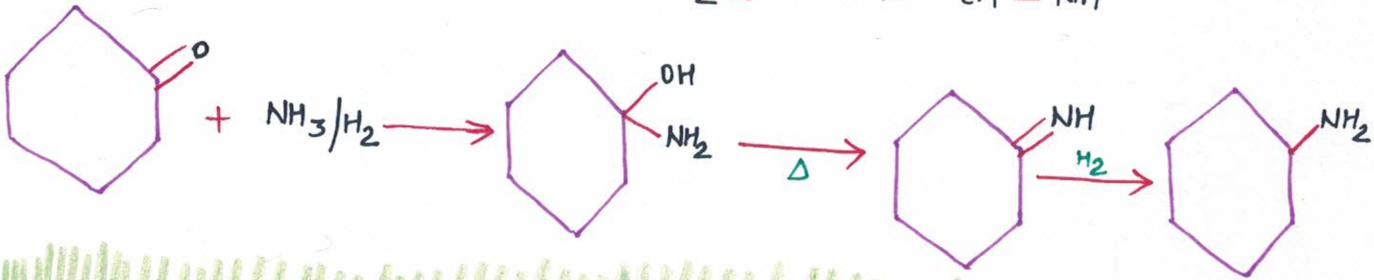
$$R-CH=O + NH_3/H_2 \xrightarrow[\Delta]{Ni-C} R-CH_2-NH_2$$

MECHANISM



$$R-\overset{O}{\overset{\|}{CH}}-H + NH_3 \longrightarrow R-\overset{O^-}{CH}-NH_3^{\oplus} \longrightarrow R-\overset{OH}{CH}-NH_2$$

$$R-CH_2-NH_2 \xleftarrow{H_2} R-CH=NH$$



REDUCTION OF CARBONYLS

① By Catalytic hydrogenation

$R-CH=O \xrightarrow{H_2-NiC} R-CH_2-OH$ (Primary)

$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{H_2-NiC} R-\overset{OH}{CH}-R$ (secondary)

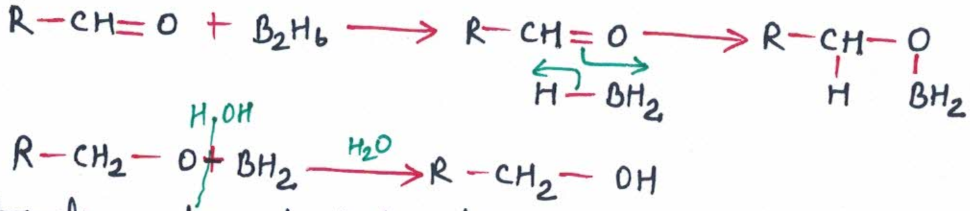
{By clemenson, Wolf Rishner, P+HI Refer to alkane chapter}

② Reduction by $NaBH_4/LiBH_4$

③ Reduction by $LiAlH_4$

④ By Borevault Blanc reaction (refer alcohols)

⑤ By hydroboration of carbonyls

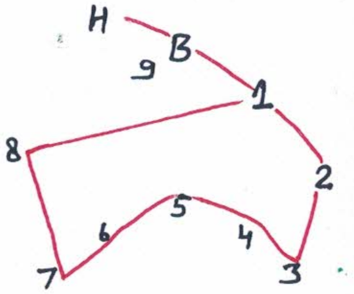


$$R-CH=O + B_2H_6 \longrightarrow R-\underset{H-BH_2}{CH=O} \longrightarrow R-\underset{H}{CH}-\underset{BH_2}{O}$$

$$R-CH_2-\overset{H,OH}{O+BH_2} \xrightarrow{H_2O} R-CH_2-OH$$

carbonyls undergo hydroboration faster than alkens because 'O' is better than base and cyclic mechanism takes place.

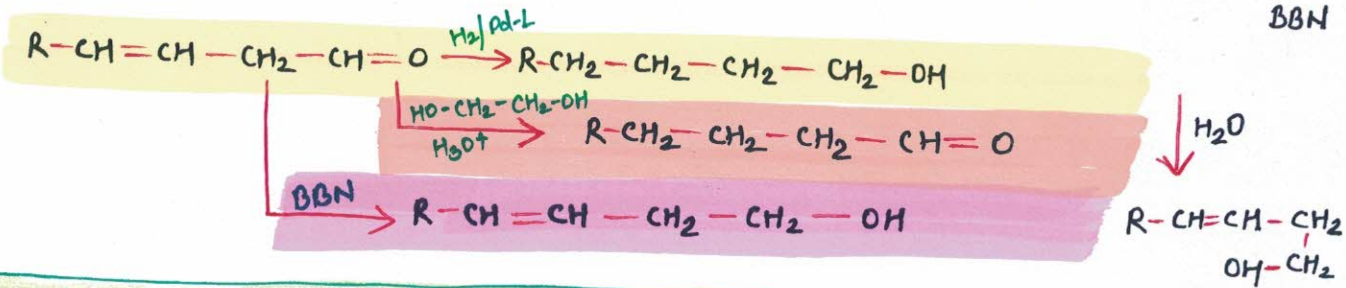
⑥ Reduction of 9BBN



9 boro bicyclo nonane (9BBN)

9 BBN reacts only with reactive carbonyl not with alkene.

$$R-CH=CH-CH_2-CH=O + 9BBN \longrightarrow R-CH=CH-CH_2-CH_2-OH + OH\text{ BBN}$$



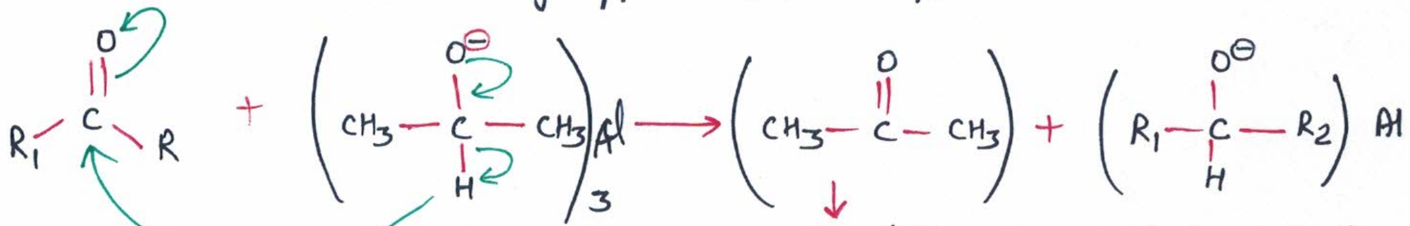
$$R-CH=CH-CH_2-CH=O \xrightarrow{H_2/Pd-L} R-CH_2-CH_2-CH_2-CH_2-OH$$

$$\xrightarrow[H_3O^+]{HO-CH_2-CH_2-OH} R-CH_2-CH_2-CH_2-CH=O \xrightarrow{H_2O} R-CH=CH-\underset{OH-CH_2}{CH_2}$$

$$\xrightarrow{BBN} R-CH=CH-CH_2-CH_2-OH$$

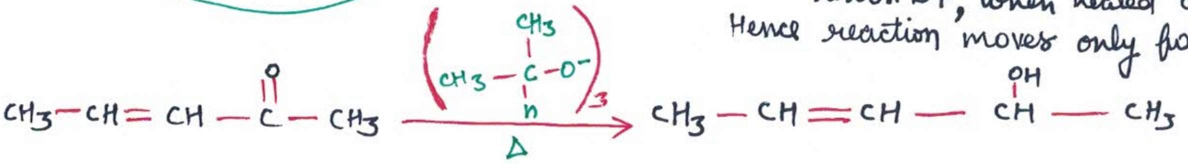
⑦ Mirwin Pondorff Verely reduction (MPV red.)

It is a reversible reaction of oppeneaur reaction.



$$R_1-\overset{O}{\overset{\|}{C}}-R + \left(CH_3-\underset{H}{\overset{O^{\ominus}}{C}}-CH_3\right)_3Al \longrightarrow \left(CH_3-\overset{O}{\overset{\|}{C}}-CH_3\right) + \left(R_1-\underset{H}{\overset{O^{\ominus}}{C}}-R_2\right)Al$$

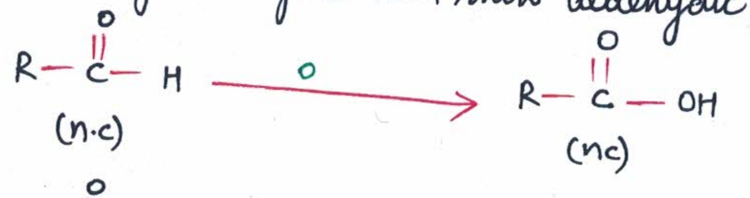
Lowest B.P, when heated distilled out.
Hence reaction moves only forward.



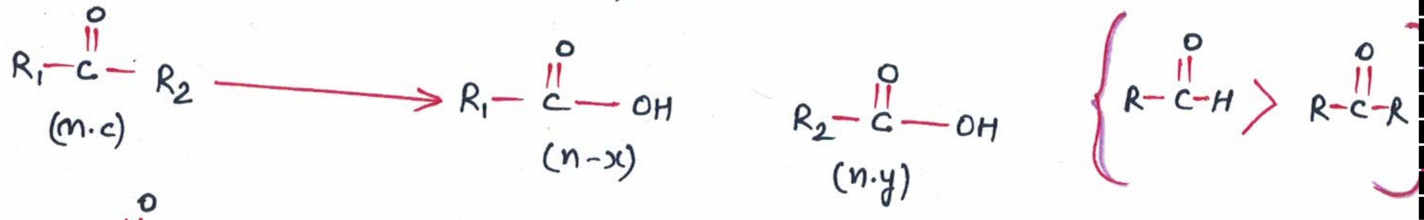
$$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{\left(CH_3-\underset{H}{\overset{CH_3}{C}}-O^-\right)_3} CH_3-CH=CH-\overset{OH}{CH}-CH_3$$

OXIDATION OF CARBONYLS

Oxidation of aldehydes will show aldehydic hydrogen isotopic effects.

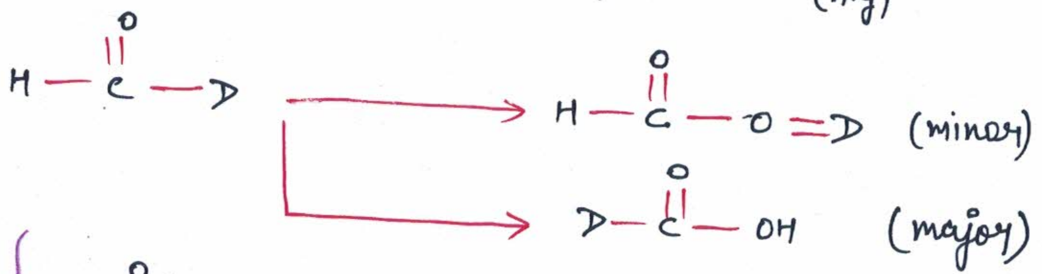


$R-\overset{O}{\overset{||}{C}}-H \xrightarrow{O} R-\overset{O}{\overset{||}{C}}-OH$ (n.c) (nc)



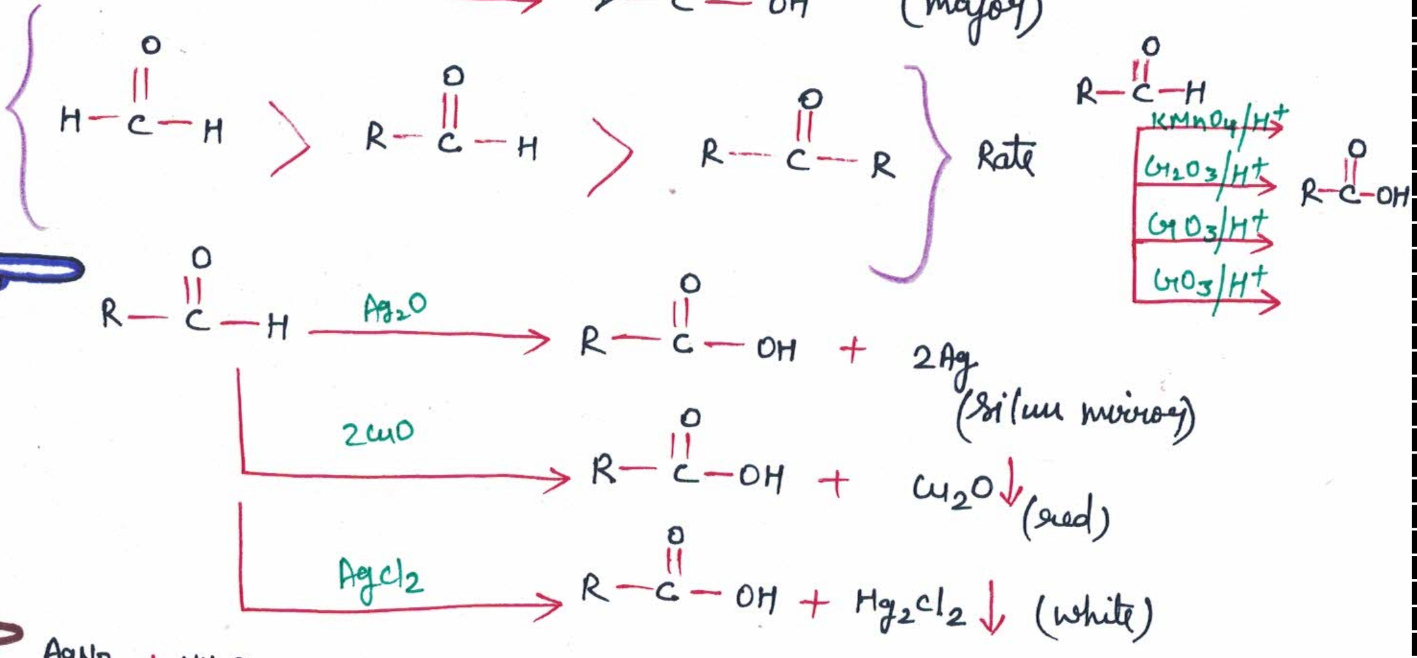
$R_1-\overset{O}{\overset{||}{C}}-R_2 \longrightarrow R_1-\overset{O}{\overset{||}{C}}-OH$ (n-x) $\quad R_2-\overset{O}{\overset{||}{C}}-OH$ (n.y) (m.c)

$\left\{R-\overset{O}{\overset{||}{C}}-H > R-\overset{O}{\overset{||}{C}}-R\right\}$



$H-\overset{O}{\overset{||}{C}}-D \longrightarrow H-\overset{O}{\overset{||}{C}}-O-D$ (minor)

$\longrightarrow D-\overset{O}{\overset{||}{C}}-OH$ (major)



$\left\{H-\overset{O}{\overset{||}{C}}-H > R-\overset{O}{\overset{||}{C}}-H > R-\overset{O}{\overset{||}{C}}-R\right\}$ Rate

$R-\overset{O}{\overset{||}{C}}-H \xrightarrow{KMnO_4/H^+,\ Cr_2O_3/H^+,\ CrO_3/H^+,\ CrO_3/H^+} R-\overset{O}{\overset{||}{C}}-OH$

$R-\overset{O}{\overset{||}{C}}-H \xrightarrow{Ag_2O} R-\overset{O}{\overset{||}{C}}-OH + 2Ag$ (silver mirror)

$\xrightarrow{2CuO} R-\overset{O}{\overset{||}{C}}-OH + Cu_2O\downarrow$ (red)

$\xrightarrow{HgCl_2} R-\overset{O}{\overset{||}{C}}-OH + Hg_2Cl_2\downarrow$ (white)

$AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3$

$AgOH + 2NH_4OH \rightleftharpoons [Ag(NH_3)_2]OH$ (tollen's reagent)

$2AgOH \longrightarrow Ag_2O + H_2O$

$R-\overset{O}{\overset{||}{C}}-H + Ag_2O \longrightarrow R-\overset{O}{\overset{||}{C}}-OH + 2Ag\downarrow$

Tollen's reagent is soluble in NH_4OH so AgOH is converted into it and at the time of reaction AgOH is generated back.

only aldehydes give this test.

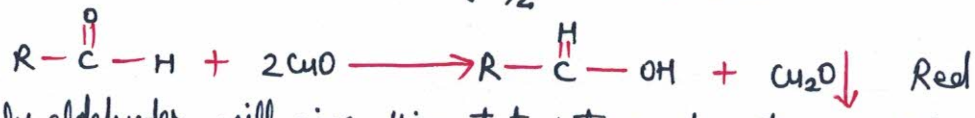
Ketones do not undergo this reaction.

For Every carbonyl, two moles of $AgNO_3$ is required.

FAHLING'S REAGENT

$CuSO_4$ is fahling's A.
Sodium potassium Tartarate is fahling's B.

$$F.A + F.B \longrightarrow Cu(OH)_2 \xrightarrow{\Delta} CuO$$

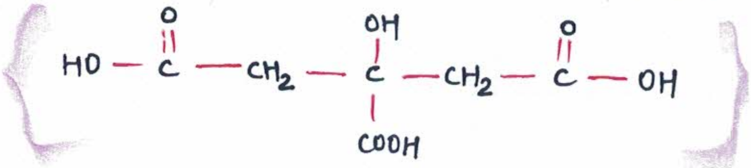


$$R-\overset{O}{\overset{\|}{C}}-H + 2CuO \longrightarrow R-\overset{H}{\overset{\|}{C}}-OH + Cu_2O\downarrow \text{ Red}$$

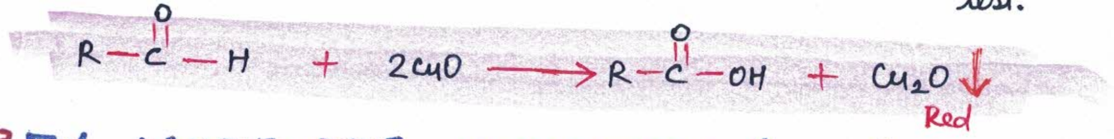
only aldehydes will give this test ketons do not give this test.

BENEDICT REAGENT

$CuSO_4$ sodium citrate $Cu(OH)_2$ CuO



citric acid It is a tricarboxylic acid & hydroxy carbo-xylic acid.
only aldehydes give the test.



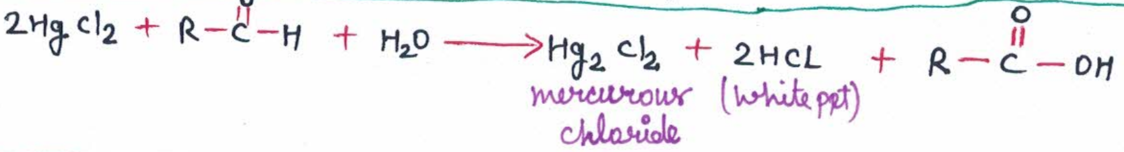
$$R-\overset{O}{\overset{\|}{C}}-H + 2CuO \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + Cu_2O\downarrow$$

Red

BY MERCURIC CHLORIDE ($HgCl_2$)

$$2HgCl_2 + H_2O \longrightarrow \underset{\text{(white ppt)}}{Hg_2Cl_2} + 2HCl + O$$

$$R-\overset{O}{\overset{\|}{C}}-H + O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH$$



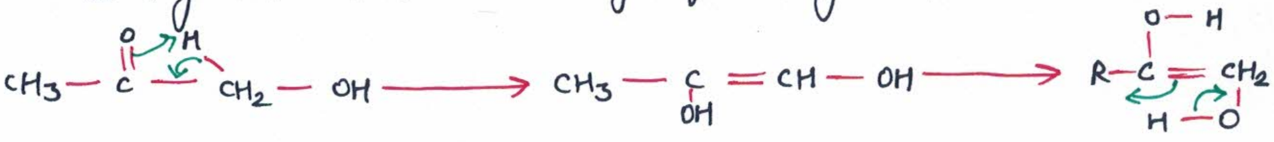
$$2HgCl_2 + R-\overset{O}{\overset{\|}{C}}-H + H_2O \longrightarrow Hg_2Cl_2 + 2HCL + R-\overset{O}{\overset{\|}{C}}-OH$$

mercurous chloride (white ppt)

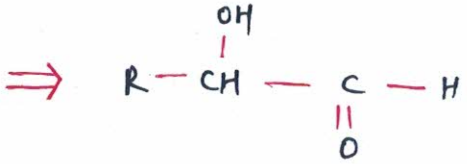
$HgCl_2$ → soluble
Hg_2Cl_2 → insoluble

only aldehydes give this test, ketons do not.

All α hydroxy ketons will give +ve test for all aldehydes test's as they can convert to aldehyde form by tautomerisation.

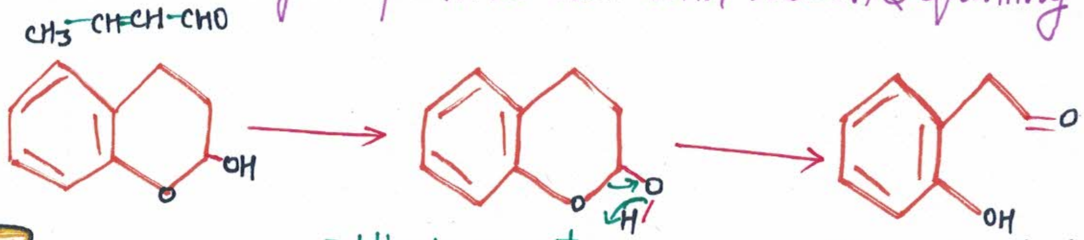


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-OH \longrightarrow CH_3-\underset{OH}{C}=CH-OH \longrightarrow R-\overset{O-H}{\overset{|}{C}}=CH_2$$

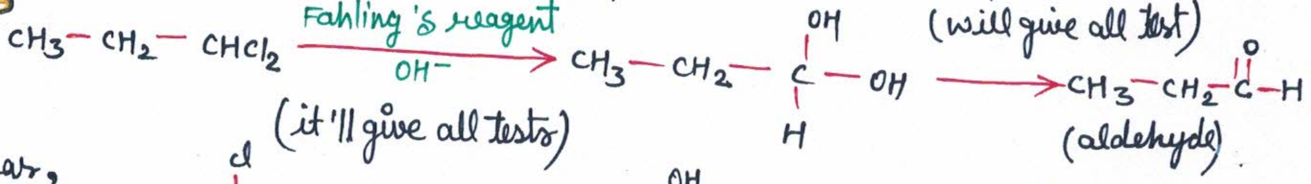


$$\Rightarrow R-\overset{OH}{\overset{|}{C}}H-\underset{O}{\underset{\|}{C}}-H$$

All hemiacetals give positive test with tollen's fahling reagent



(will give all test)

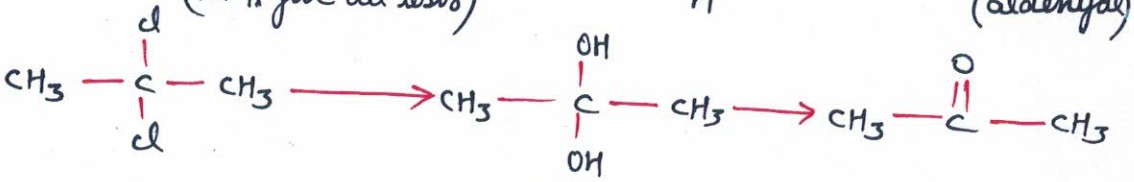


$$CH_3-CH_2-CHCl_2 \xrightarrow[OH^-]{\text{Fahling's reagent}} CH_3-CH_2-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-OH \longrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$$

(it'll give all tests)

(aldehyde).

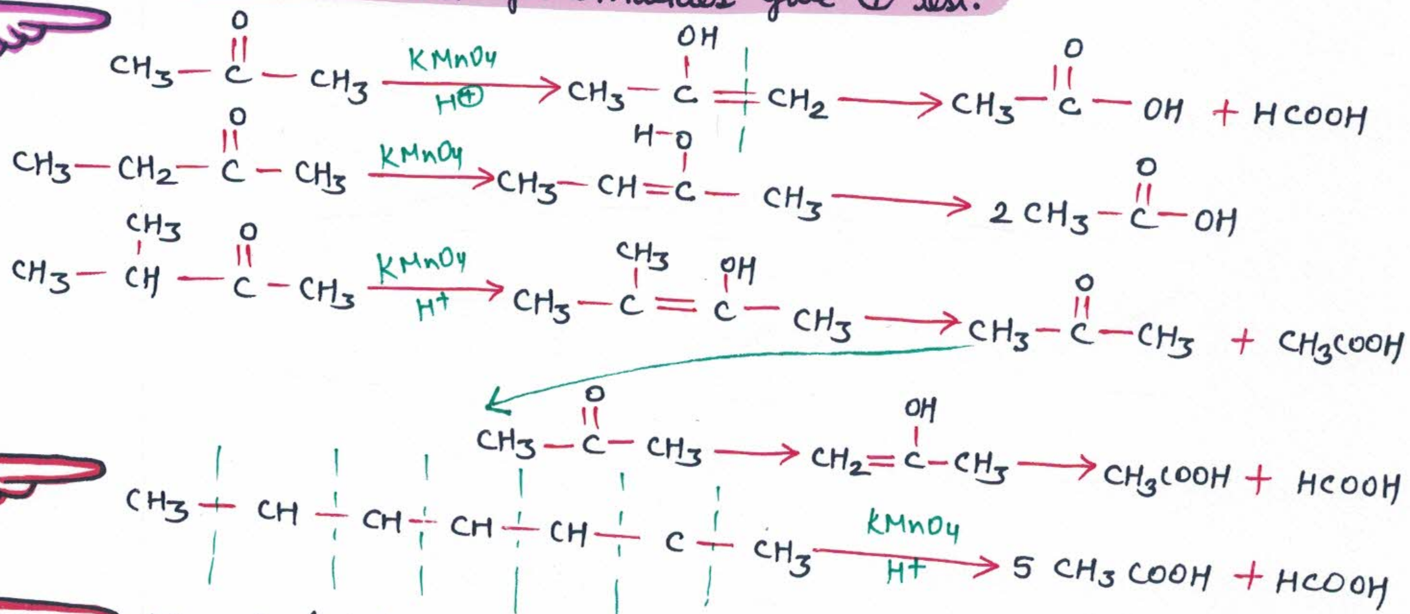
whereas,



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

(does not give any test)

Thus, all terminal gemdihalides give ⊕ test.



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H^{\oplus}]{KMnO_4} CH_3-\overset{OH}{\overset{|}{C}}=CH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + HCOOH$$

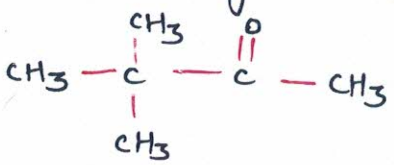
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{KMnO_4} CH_3-CH=\overset{H-O}{\overset{|}{C}}-CH_3 \longrightarrow 2\,CH_3-\overset{O}{\overset{\|}{C}}-OH$$

$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H^+]{KMnO_4} CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{OH}{\overset{|}{C}}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COOH$$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_2=\overset{OH}{\overset{|}{C}}-CH_3 \longrightarrow CH_3COOH + HCOOH$$

$$CH_3 - CH - CH - CH - CH - C - CH_3 \xrightarrow[H^+]{KMnO_4} 5\,CH_3COOH + HCOOH$$

All methyl ketons having at least one "H" will give CH_3COOH on oxidation.

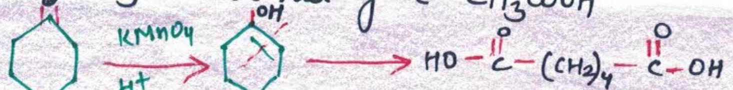


$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-CH_3$$

&

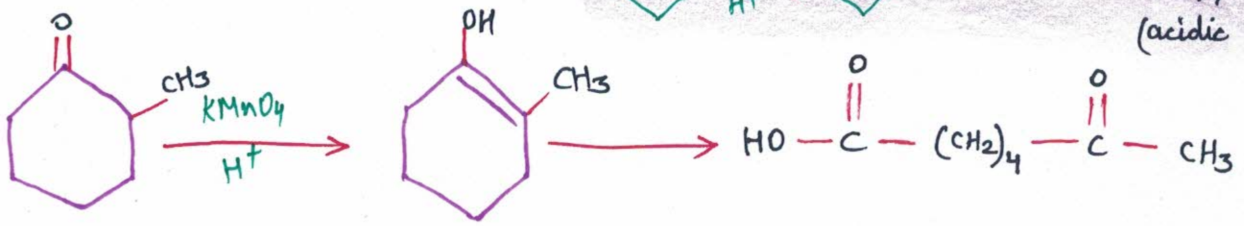
$$Ph-\overset{O}{\overset{\|}{C}}-CH_3$$

does not give CH_3COOH

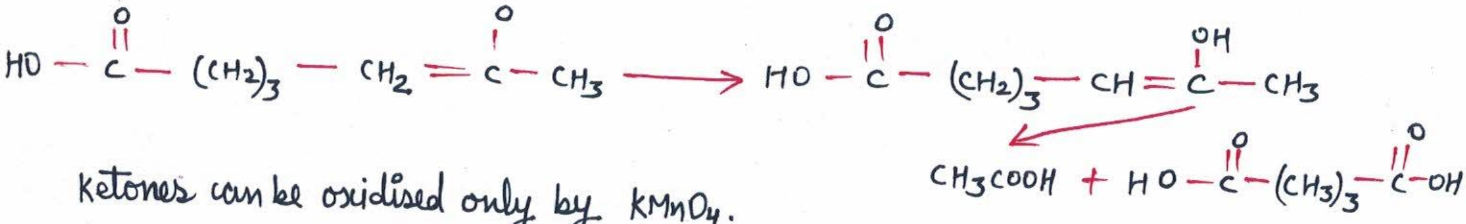


$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$$

(acidic acid)



$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-CH_3$$



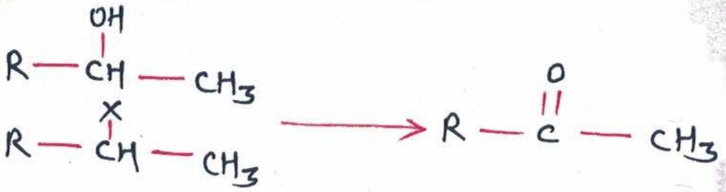
$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_3-CH_2=\overset{O}{\overset{|}{C}}-CH_3 \longrightarrow HO-\overset{O}{\overset{\|}{C}}-(CH_2)_3-CH=\overset{OH}{\overset{|}{C}}-CH_3$

$\longrightarrow CH_3COOH + HO-\overset{O}{\overset{\|}{C}}-(CH_3)_3-\overset{O}{\overset{\|}{C}}-OH$

Ketones can be oxidised only by $KMnO_4$.

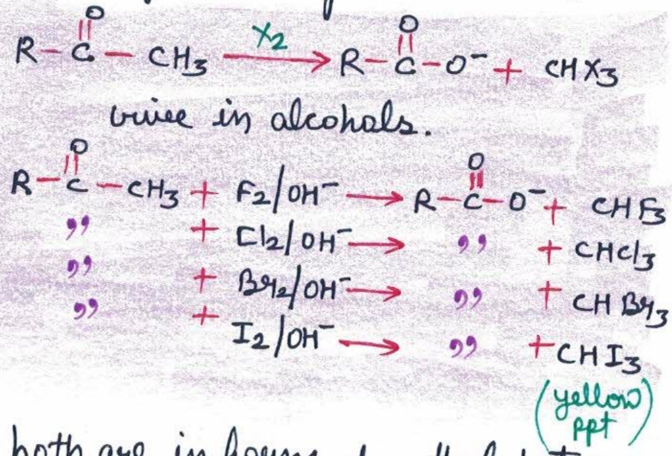
HALOFORM REACTION

All compounds which on reaction with X_2/OH^- can give methyl ketons can give haloform reactions.



$R-\overset{OH}{\overset{|}{C}H}-CH_3$

$R-\overset{X}{\overset{|}{C}H}-CH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-CH_3$



$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{X_2} R-\overset{O}{\overset{\|}{C}}-O^- + CHX_3$

wise in alcohols.

$R-\overset{O}{\overset{\|}{C}}-CH_3 + F_2/OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + CHF_3$

" $+ Cl_2/OH^- \longrightarrow$ " $+ CHCl_3$

" $+ Br_2/OH^- \longrightarrow$ " $+ CHBr_3$

" $+ I_2/OH^- \longrightarrow$ " $+ CHI_3$ (yellow ppt)

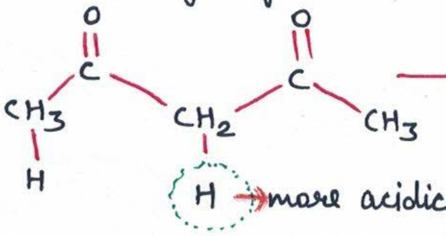
The only aldehyde which can give this reaction is acetaldehyde $CH_3-\overset{O}{\overset{\|}{C}}-H$.

Only ethyl alcohol can give this test. Because both are in form of methyl ketons.

E.g. $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \longrightarrow$ will not give this reaction.

$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow$ will give this reaction.

Methyl ketones having reactive methylene do not give this reaction as it's Hydrogen is more acidic than methyl hydrogen.



$\longrightarrow$ does not give this test.

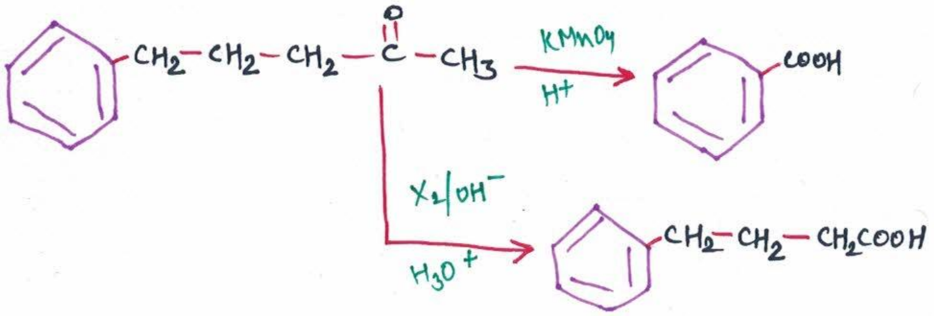
H → more acidic & hence more reactions

R>X

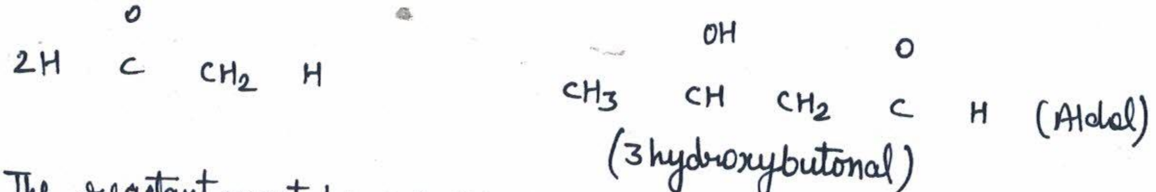
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-CH_2-COOH$

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{CaOCl_2} (CH_3-CH_2-COO^-)_2Ca \xrightarrow{H_3O^+} CH_3-CH_2-COOH$

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[H^+]{KMnO_4} 2CH_3COOH$



ALDOL CONDENSATION

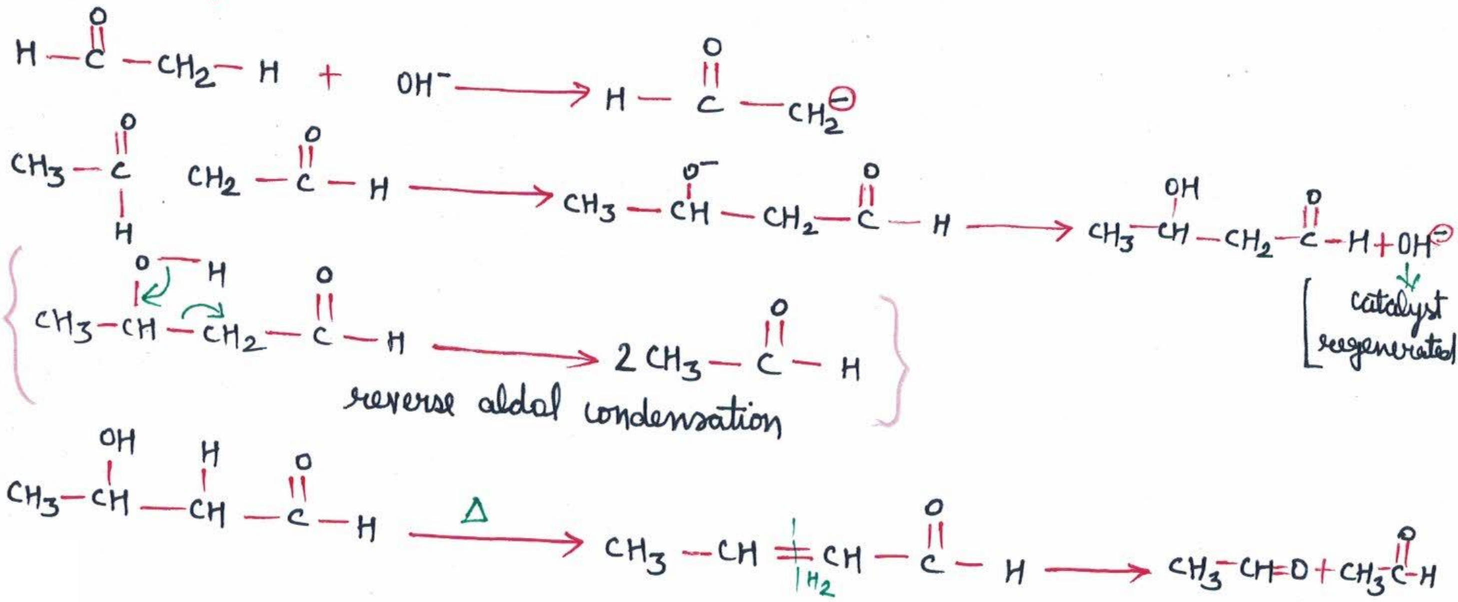


$2H\ \ \overset{O}{C}\ \ CH_2\ \ H \qquad CH_3\ \ \overset{OH}{CH}\ \ CH_2\ \ \overset{O}{C}\ \ H$ (Aldol)

(3 hydroxybutonal)

The reactant must have "α" hydragenand its reacted with dilute alkali which acts as catalyst.

MECHANISM



$H-\overset{O}{\overset{\|}{C}}-CH_2-H + OH^- \longrightarrow H-\overset{O}{\overset{\|}{C}}-CH_2^{\ominus}$

$CH_3-\underset{H}{\overset{O}{\overset{\|}{C}}}\quad CH_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{O^-}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H+OH^{\ominus}$

catalyst regenerated

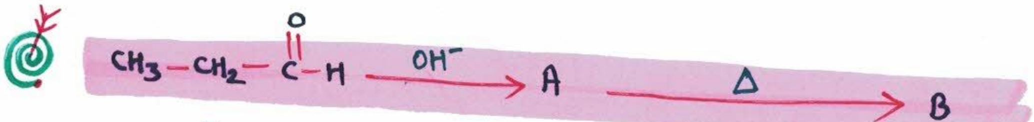
$CH_3-\overset{O-H}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow 2\,CH_3-\overset{O}{\overset{\|}{C}}-H$

reverse aldal condensation

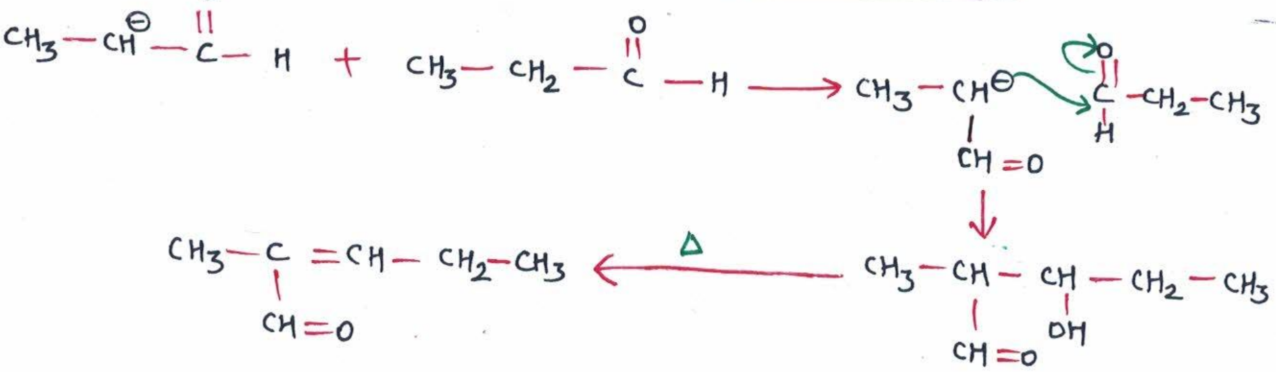
$CH_3-\overset{OH}{CH}-\overset{H}{CH}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{\Delta} CH_3-CH\underset{H_2}{\cancel{=}}CH-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-CH=O+CH_3-\overset{O}{\overset{\|}{C}}-H$

convert acetaldehyde to protonaldehyde

Done above.



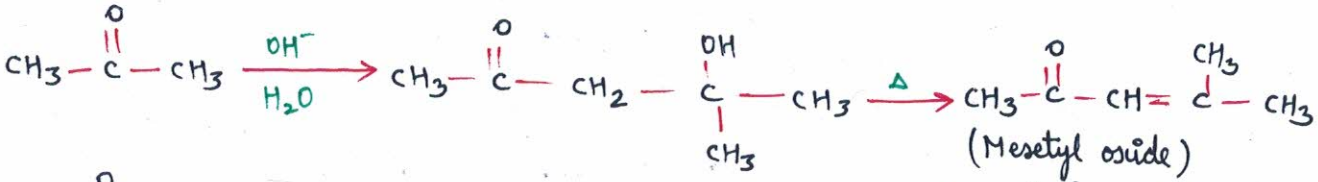
$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{OH^-} A \xrightarrow{\Delta} B$



$CH_3-\overset{\ominus}{CH}-\overset{O}{\overset{\|}{C}}-H + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\underset{CH=O}{CH^{\ominus}}\ \ \underset{H}{\overset{O}{\overset{\|}{C}}}-CH_2-CH_3$

$\downarrow$

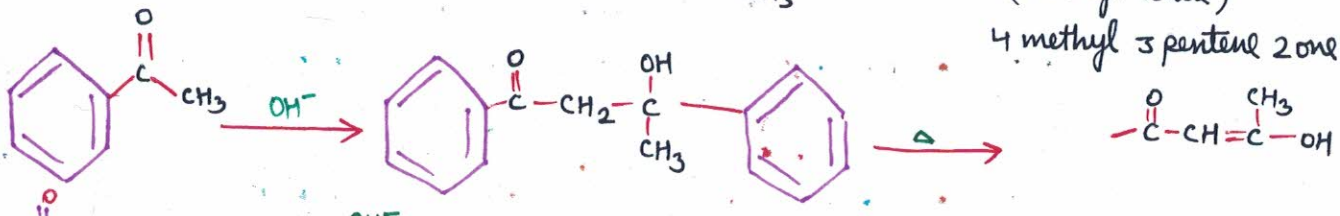
$CH_3-\underset{CH=O}{C}=CH-CH_2-CH_3 \xleftarrow{\Delta} CH_3-\underset{CH=O}{CH}-\underset{OH}{CH}-CH_2-CH_3$

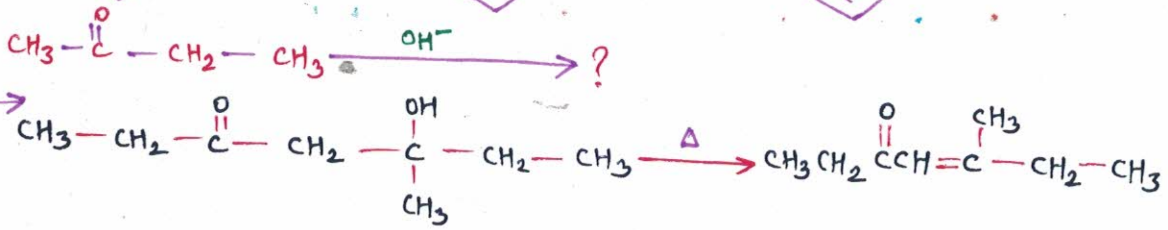


$CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[H_2O]{OH^-} CH_3-\overset{\overset{O}{||}}{C}-CH_2-\underset{CH_3}{\overset{OH}{C}}-CH_3 \xrightarrow{\Delta} CH_3-\overset{\overset{O}{||}}{C}-CH=\overset{CH_3}{C}-CH_3$

(Mesetyl oxide)

4 methyl 3 pentene 2 one

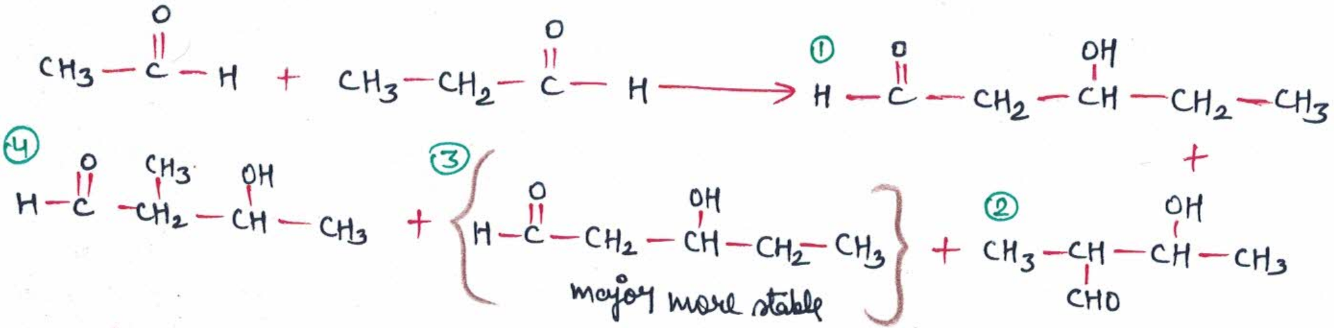


Q. 

$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 \xrightarrow{OH^-} ?$

$\rightarrow CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_2-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH_3 \xrightarrow{\Delta} CH_3CH_2\overset{\overset{O}{||}}{C}CH=\overset{CH_3}{C}-CH_2-CH_3$

CROSSED ALDOL CONDENSATION

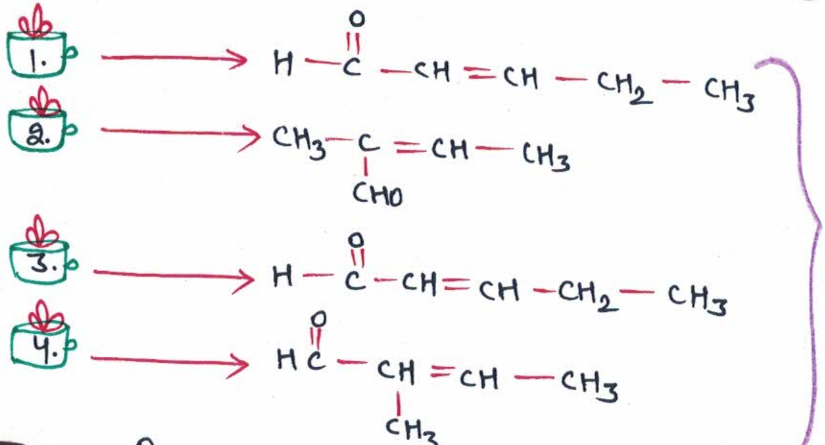


$CH_3-\overset{\overset{O}{||}}{C}-H + CH_3-CH_2-\overset{\overset{O}{||}}{C}-H \longrightarrow$ ① $H-\overset{\overset{O}{||}}{C}-CH_2-\overset{OH}{CH}-CH_2-CH_3$

$+$ ④ $H-\overset{\overset{O}{||}}{C}-\overset{CH_3}{CH_2}-\overset{OH}{CH}-CH_3 +$ ③ $\left\{H-\overset{\overset{O}{||}}{C}-CH_2-\overset{OH}{CH}-CH_2-CH_3\right\}$ $+$ ② $CH_3-\underset{CHO}{CH}-\overset{OH}{CH}-CH_3$

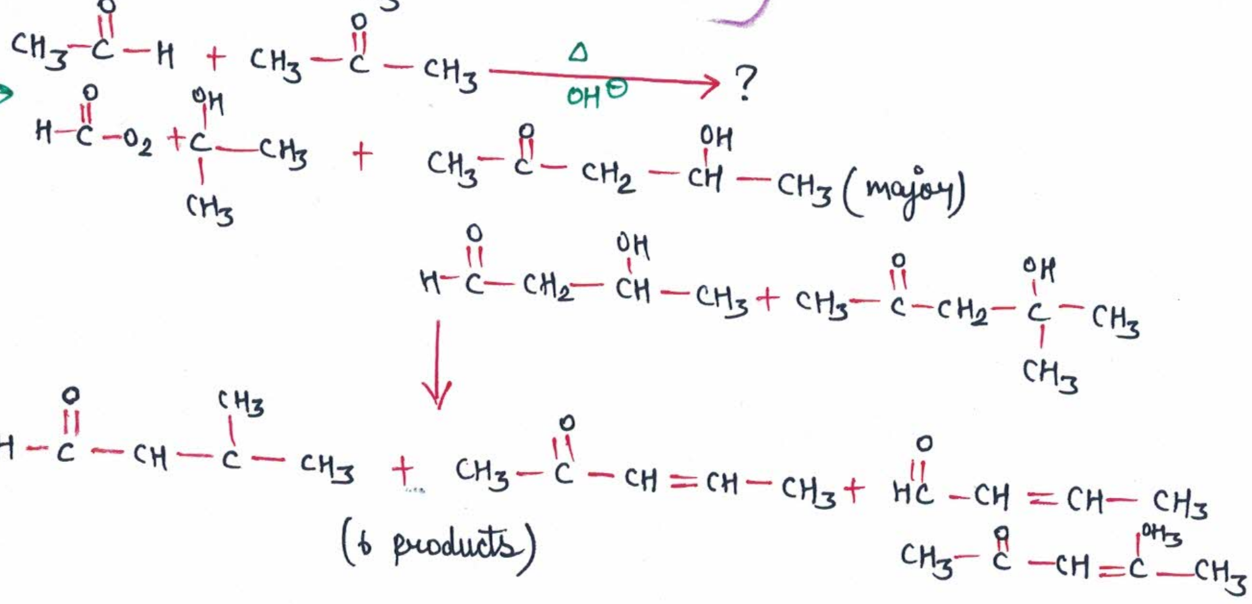
major more stable

Abey Box! It must be carboanion



1. $\longrightarrow H-\overset{\overset{O}{||}}{C}-CH=CH-CH_2-CH_3$
2. $\longrightarrow CH_3-\underset{CHO}{C}=CH-CH_3$
3. $\longrightarrow H-\overset{\overset{O}{||}}{C}-CH=CH-CH_2-CH_3$
4. $\longrightarrow H\overset{\overset{O}{||}}{C}-\underset{CH_3}{CH}=CH-CH_3$

Total 8 products (G.I) also



$CH_3-\overset{\overset{O}{||}}{C}-H + CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[OH^\ominus]{\Delta} ?$

$\rightarrow H-\overset{\overset{O}{||}}{C}-O_2 + \underset{CH_3}{\overset{OH}{C}}-CH_3 + CH_3-\overset{\overset{O}{||}}{C}-CH_2-\overset{OH}{CH}-CH_3$ (major)

$H-\overset{\overset{O}{||}}{C}-CH_2-\overset{OH}{CH}-CH_3 + CH_3-\overset{\overset{O}{||}}{C}-CH_2-\underset{CH_3}{\overset{OH}{C}}-CH_3$

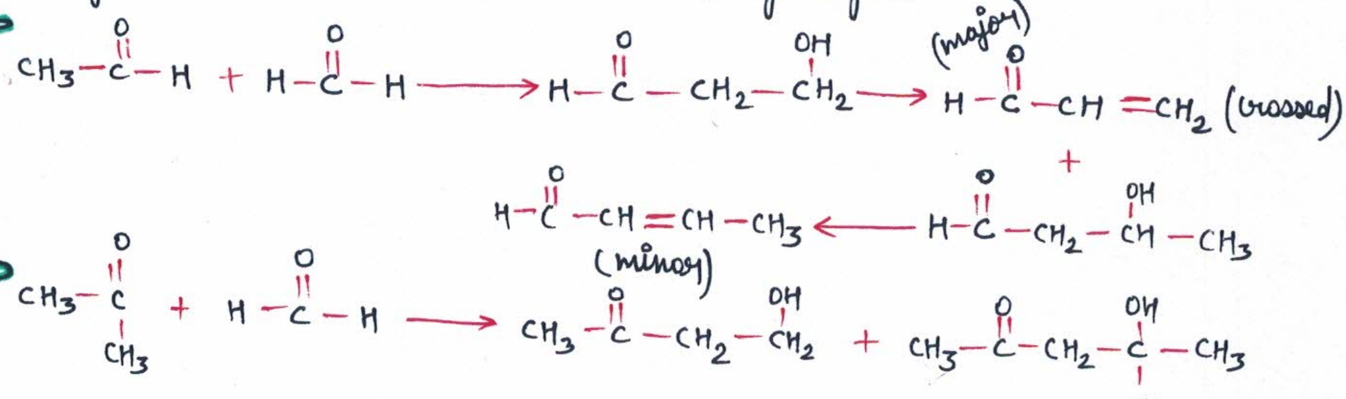
$\downarrow$

$H-\overset{\overset{O}{||}}{C}-CH-\overset{CH_3}{C}-CH_3 + CH_3-\overset{\overset{O}{||}}{C}-CH=CH-CH_3 + H\overset{\overset{O}{||}}{C}-CH=CH-CH_3$

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

(6 products)

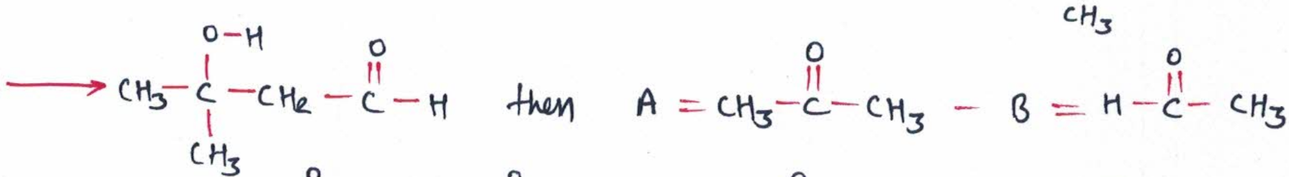
In the previous reactions, $CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{|}{C}}-CH_3$ is major because, $CH_3-\overset{O}{\overset{|}{C}}-CH_3$ will undergo nucleophilic addition and has 6 α hydrogen.



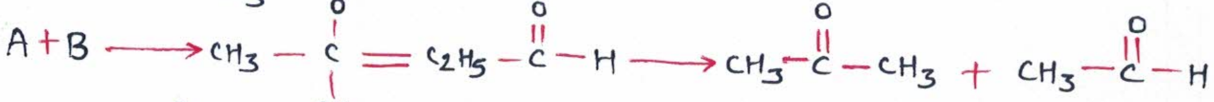
$$CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}H_2} \longrightarrow \overset{\text{(major)}}{H-\overset{O}{\overset{\|}{C}}-CH=CH_2} \text{ (crossed)}$$

$$+ \quad \underset{\text{(minor)}}{H-\overset{O}{\overset{\|}{C}}-CH=CH-CH_3} \longleftarrow H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}H}-CH_3$$

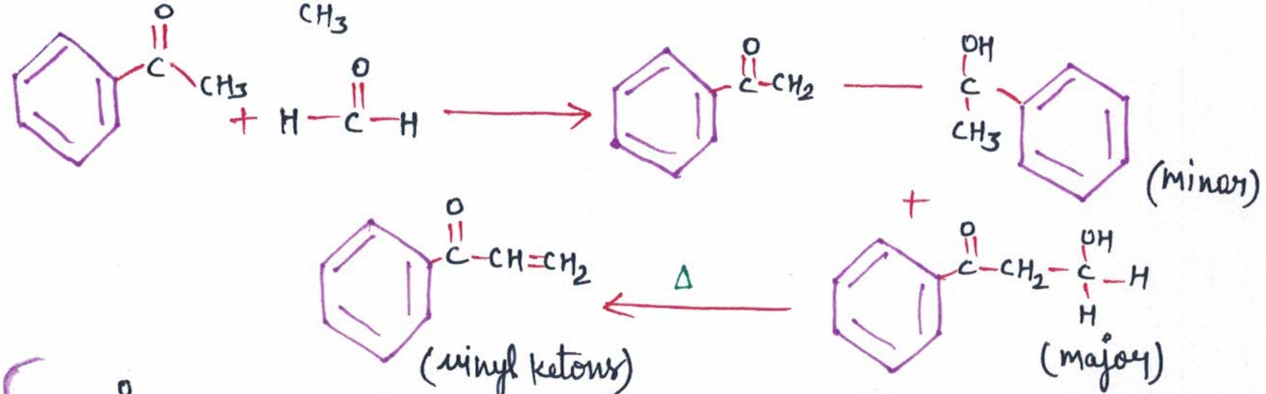
$$CH_3-\underset{CH_3}{\underset{|}{\overset{O}{\overset{\|}{C}}}} + H-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}H_2} + CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$$

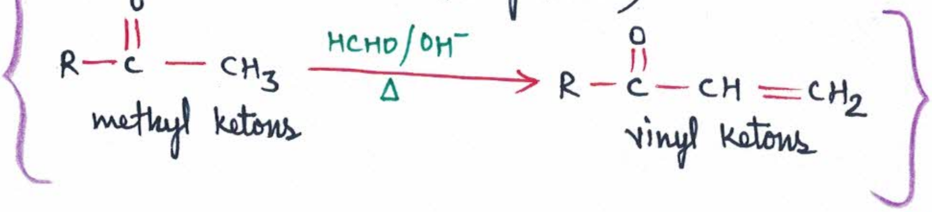


If $A+B \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{O-H}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-H$ then $A = CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ – $B = H-\overset{O}{\overset{\|}{C}}-CH_3$



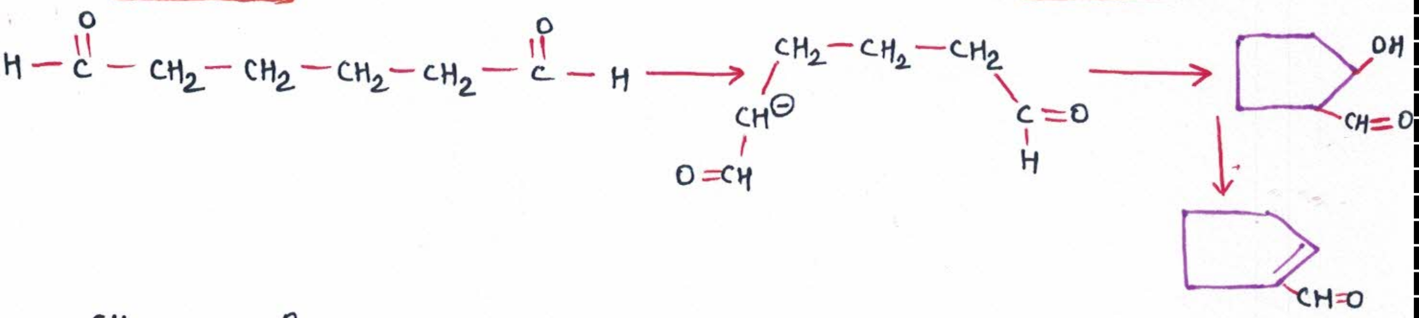
$$A+B \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{O}{\overset{|}{C}}}}=C_2H_5-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-H$$

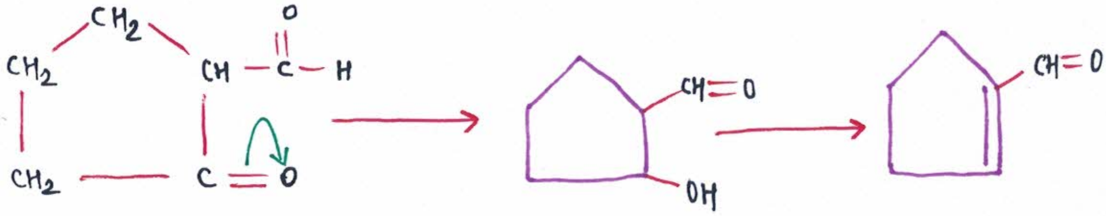


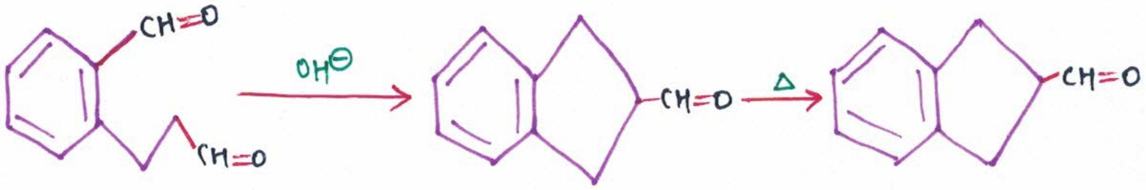


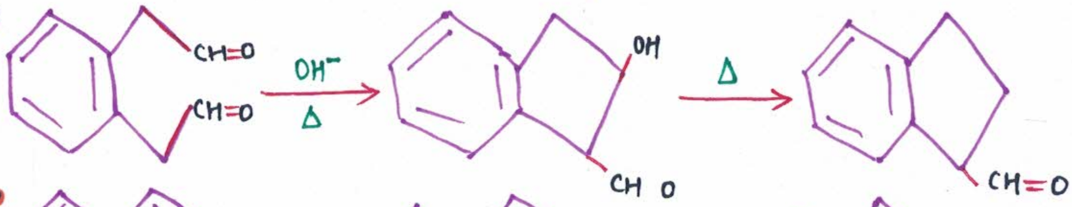
$$\left\{ \underset{\text{methyl ketone}}{R-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[\Delta]{HCHO/OH^-} \underset{\text{vinyl ketone}}{R-\overset{O}{\overset{\|}{C}}-CH=CH_2} \right\}$$

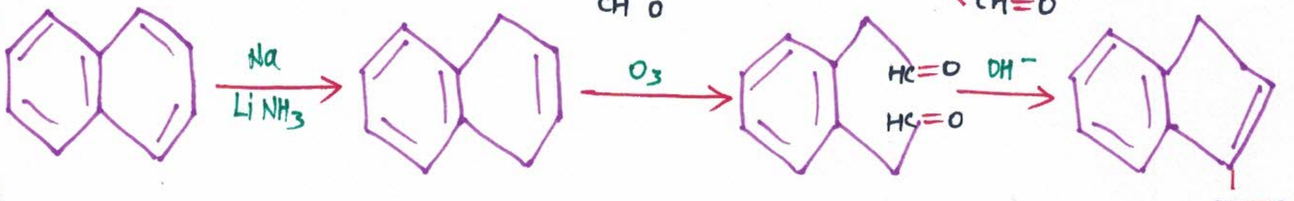
Intramolecular Aldol Condensation

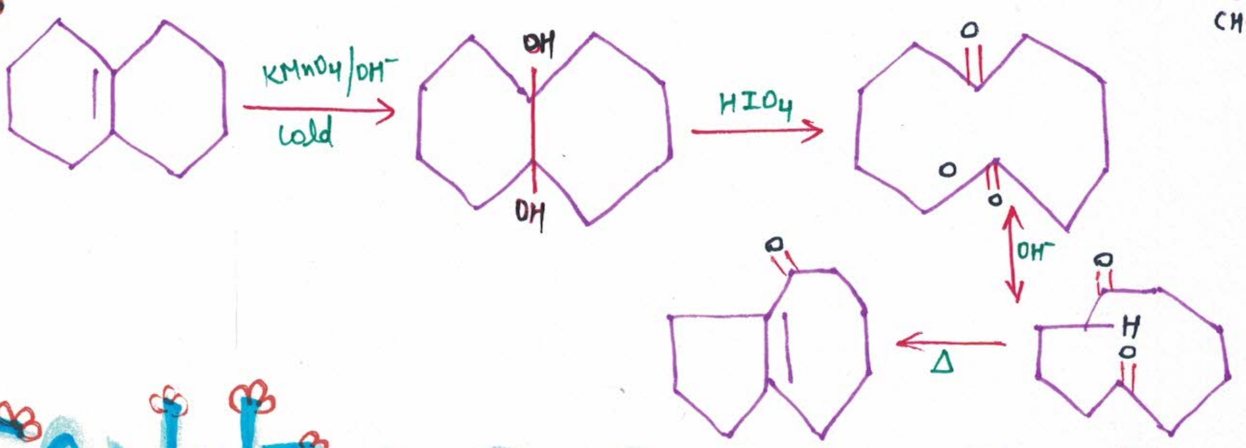




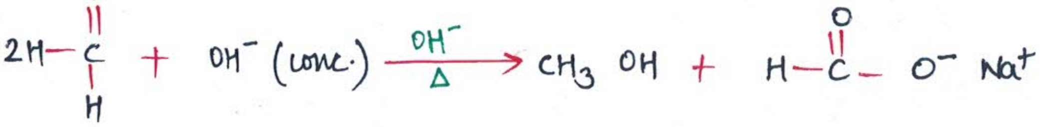




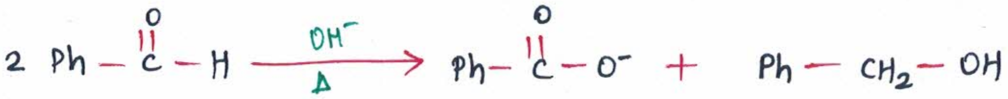




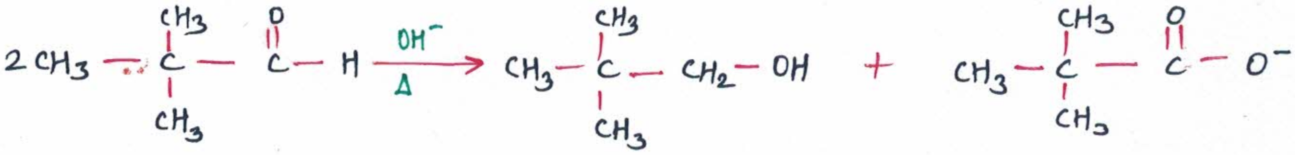
CANNIZZARRO REACTION



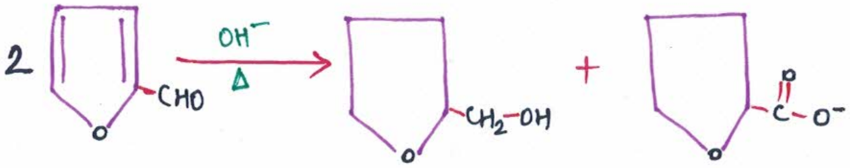
$$2\mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}} + OH^-\ (conc.) \xrightarrow[\Delta]{OH^-} CH_3\ OH + \mathrm{H}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-O^-\ Na^+$$



$$2\ Ph-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{OH^-} Ph-\overset{O}{\overset{\|}{C}}-O^- + Ph-CH_2-OH$$



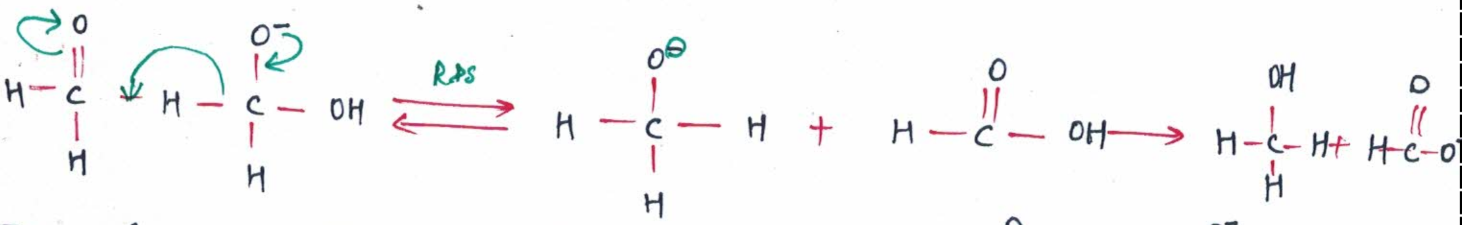
$$2\,CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{OH^-} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-OH + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-O^-$$



MECHANISM

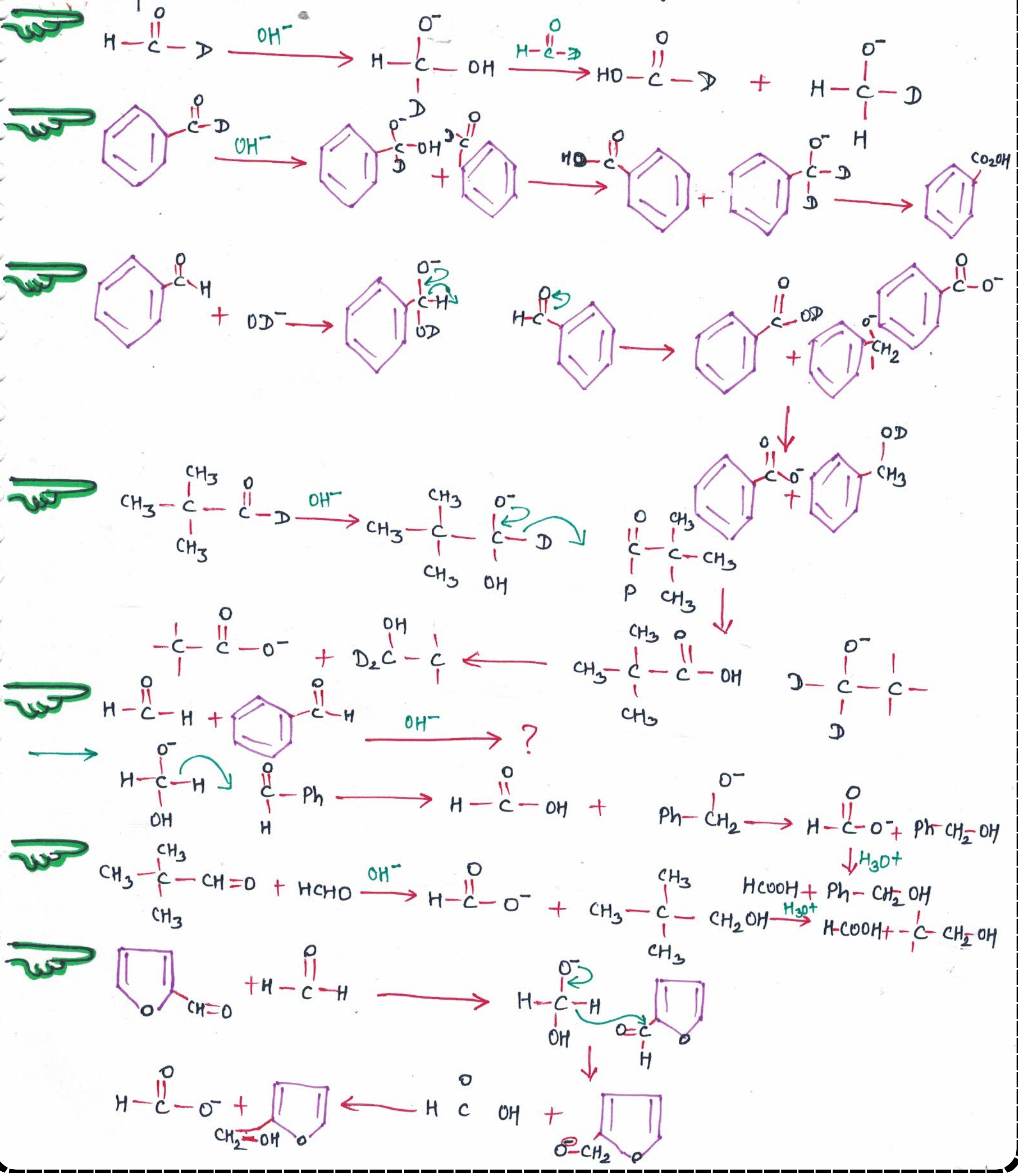
It should have no "α" hydrogen.

$$\mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}} + OH^- \longrightarrow \mathrm{H}-\underset{\mathrm{H}}{\overset{O^-}{\overset{|}{\mathrm{C}}}}-OH$$

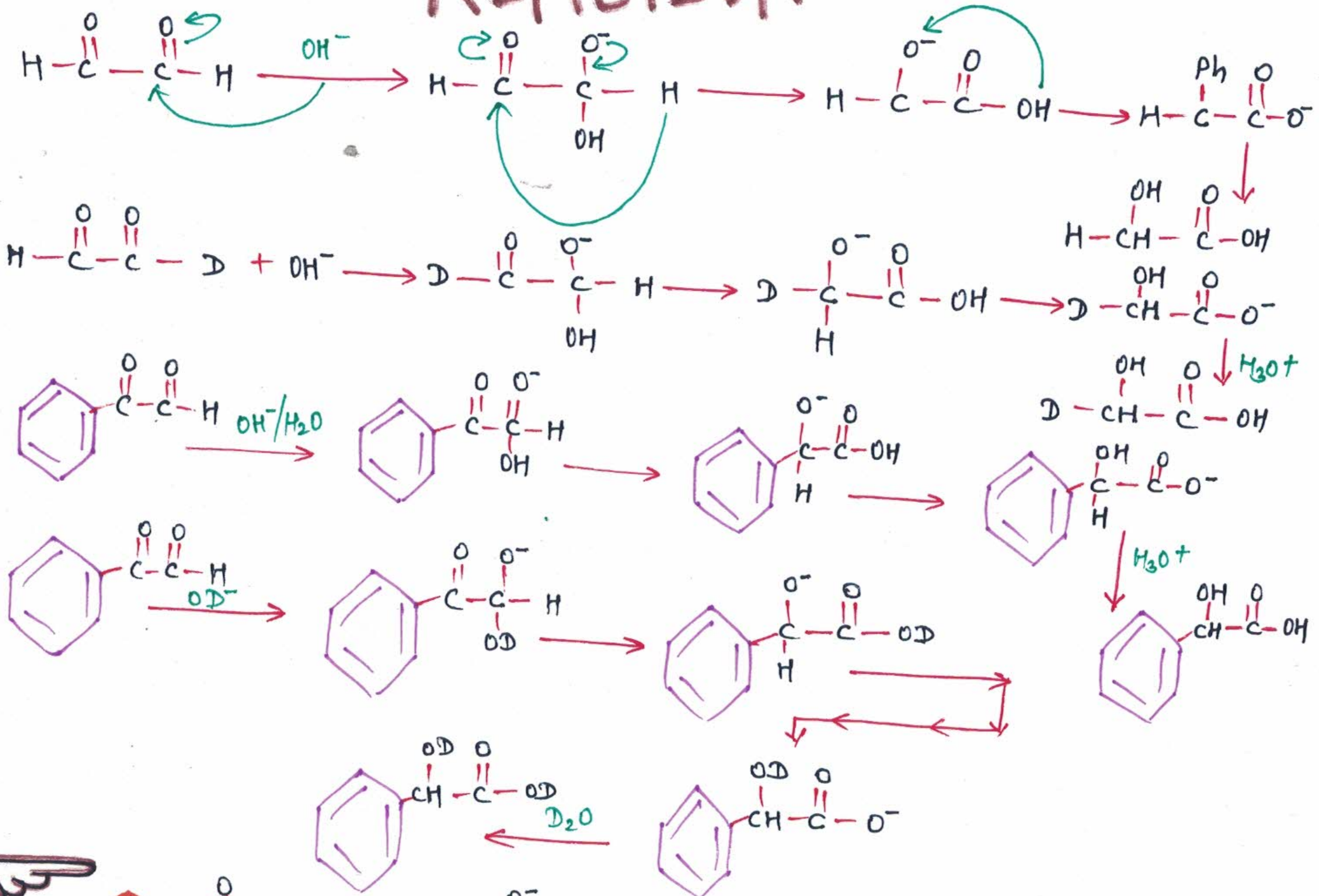


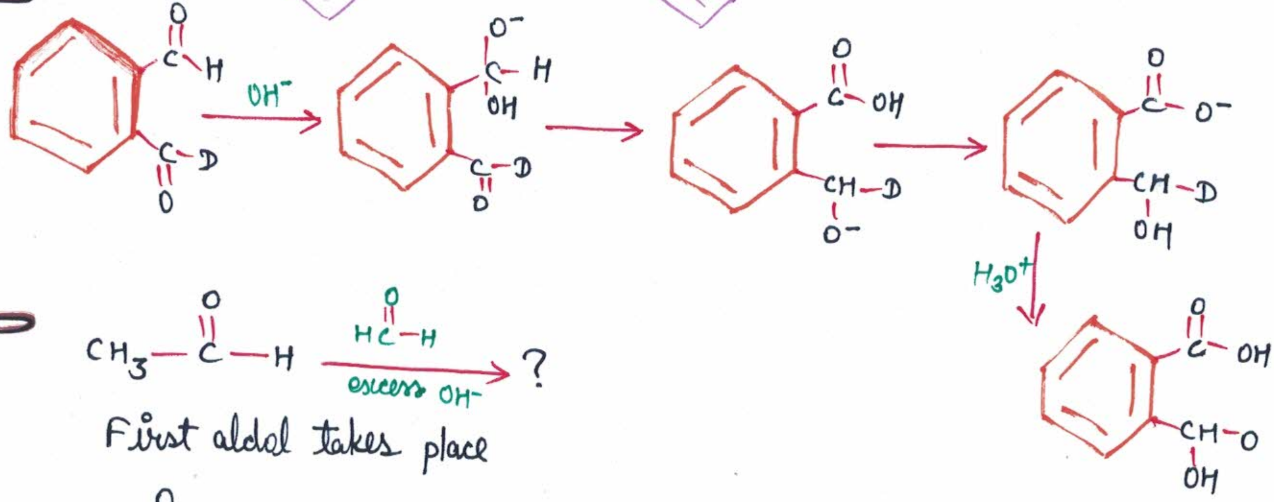
It cannizzaro reaction, OH⁻ is a reactant. Rate $\propto \left[H-\overset{\overset{O}{||}}{C}-H\right]\left[H-\overset{O^-}{\underset{H}{C}}-OH\right]$

It is 3rd order kinetics. It occurs at high concⁿ & high temp. aldol occurs at mild temp.



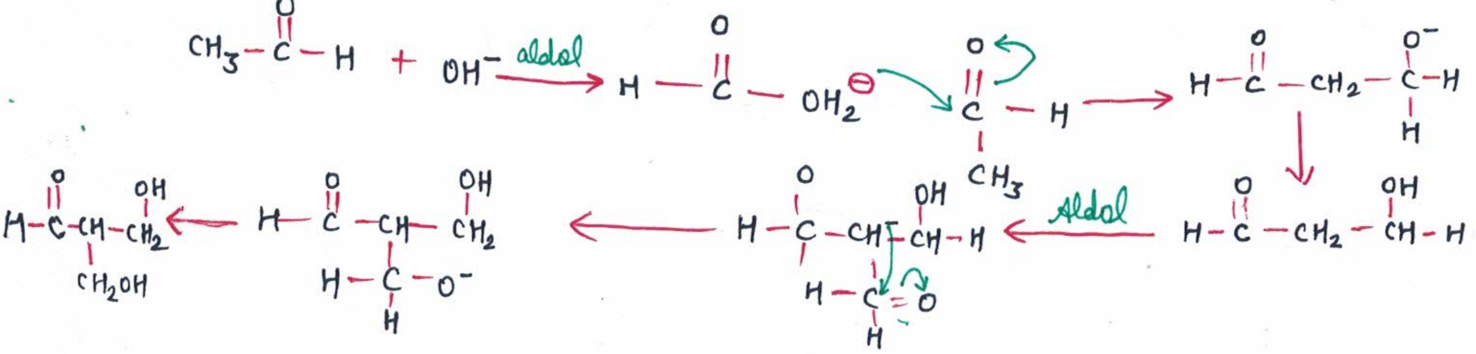
INTRAMOLECULAR CANNIZARO REACTION

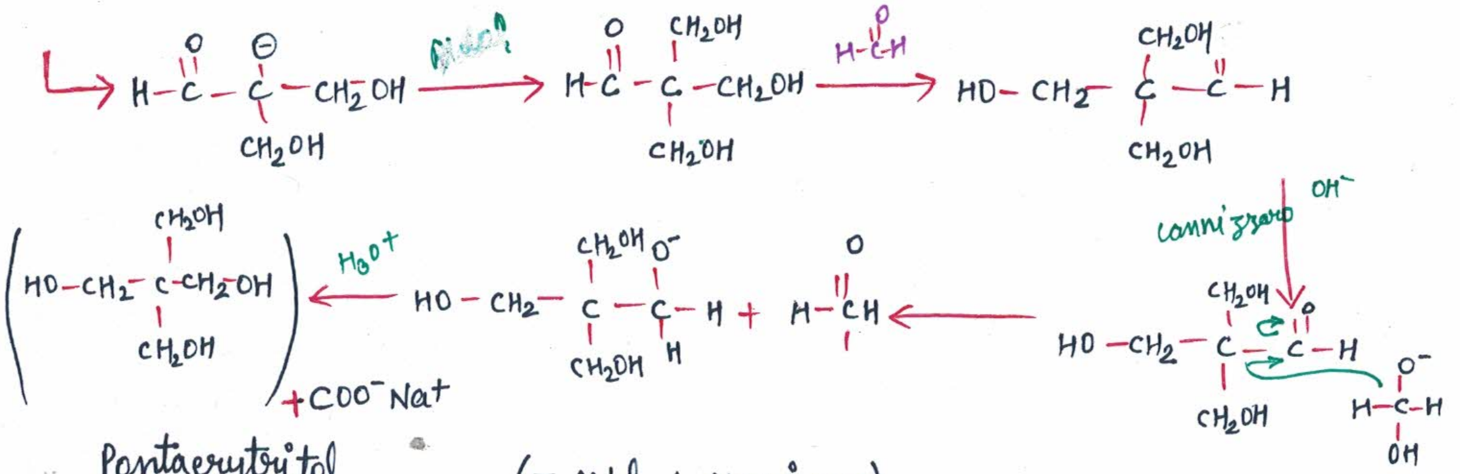




$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{excess } OH^-]{H\overset{O}{\overset{\|}{C}}-H} ?$

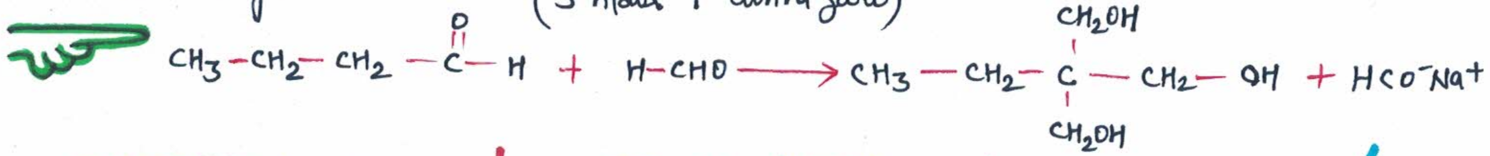
First aldol takes place





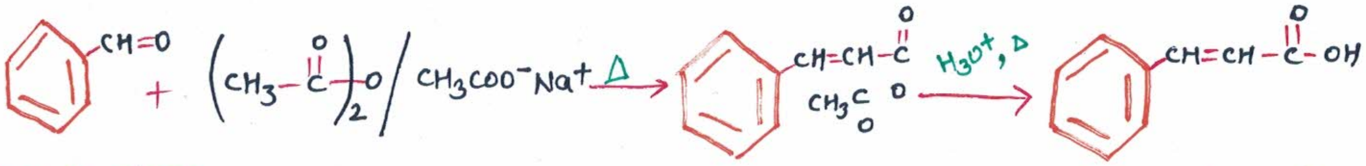
Pentaerythritol

(3 Aldol 1 cannizaro)



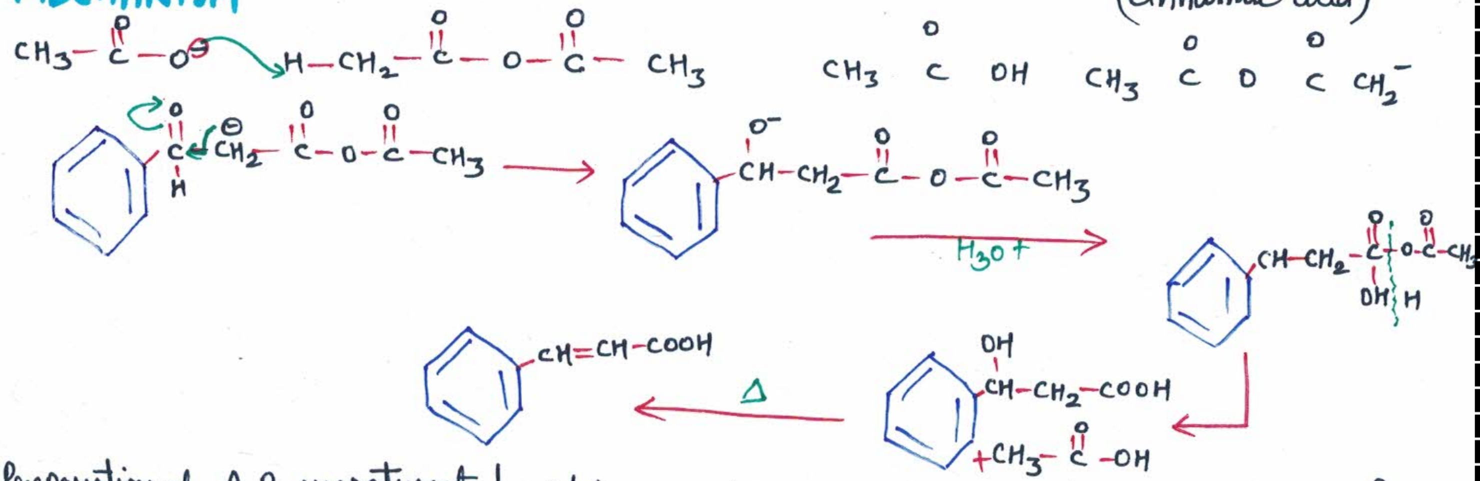
$$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H + H-CHO \rightarrow CH_3-CH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2-OH + HCO^-Na^+$$

PERKIN CONDENSATION

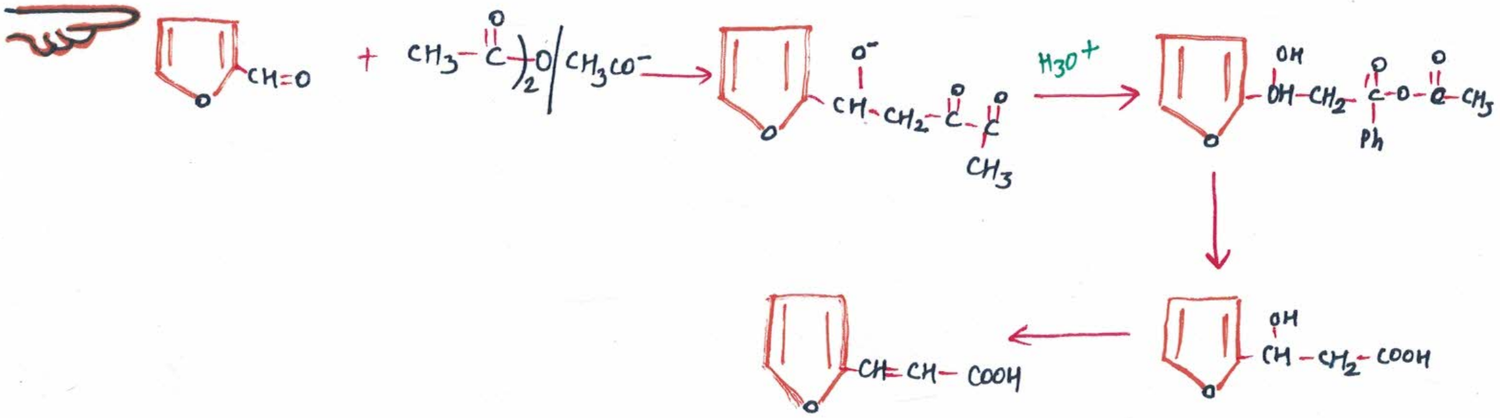


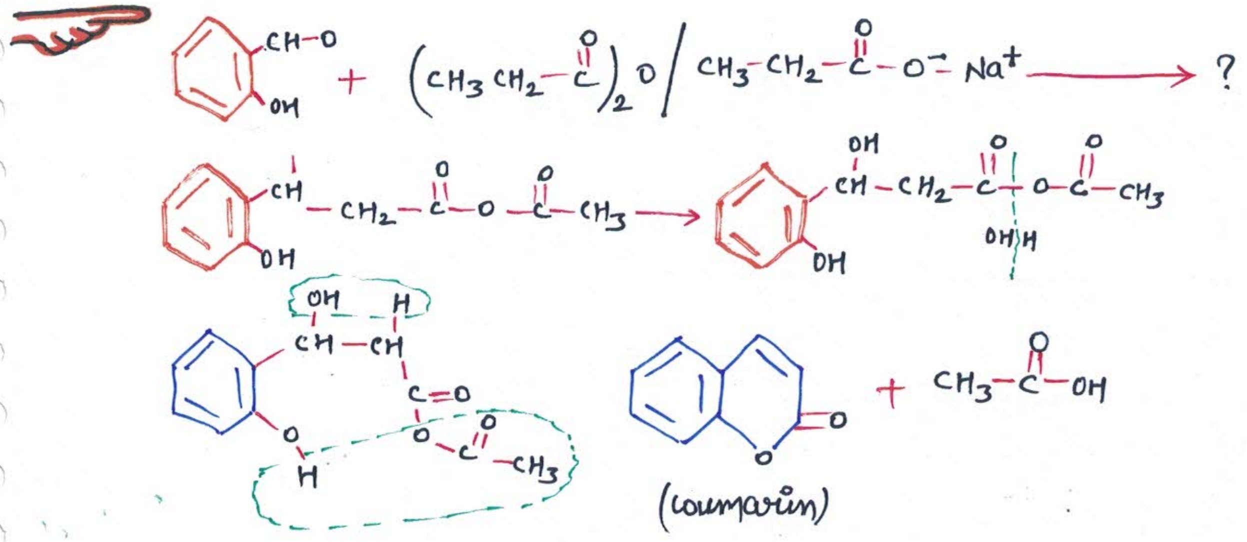
(cinnamic acid)

MECHANISM



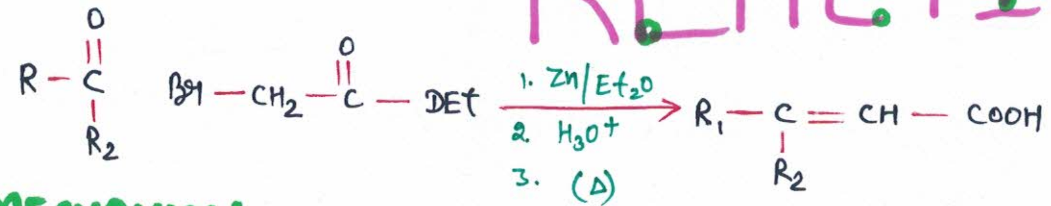
Preparation of A,B unsaturated acid by reaction of aromatic aldehyde with $(CH_3-\overset{O}{\overset{\|}{C}})_2O$ is Perkin's condensation.





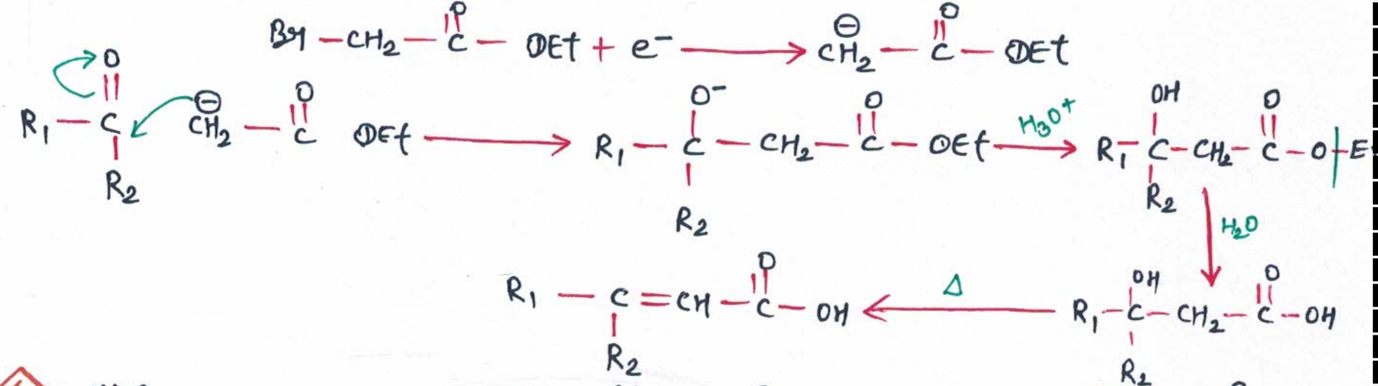
(coumarin)

REFORMATING REACTION



$$R-\overset{O}{\overset{\|}{C}}-R_2 \quad Br-CH_2-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[\text{2. } H_3O^+ \quad \text{3. } (\Delta)]{\text{1. } Zn/Et_2O} R_1-\underset{R_2}{\underset{|}{C}}=CH-COOH$$

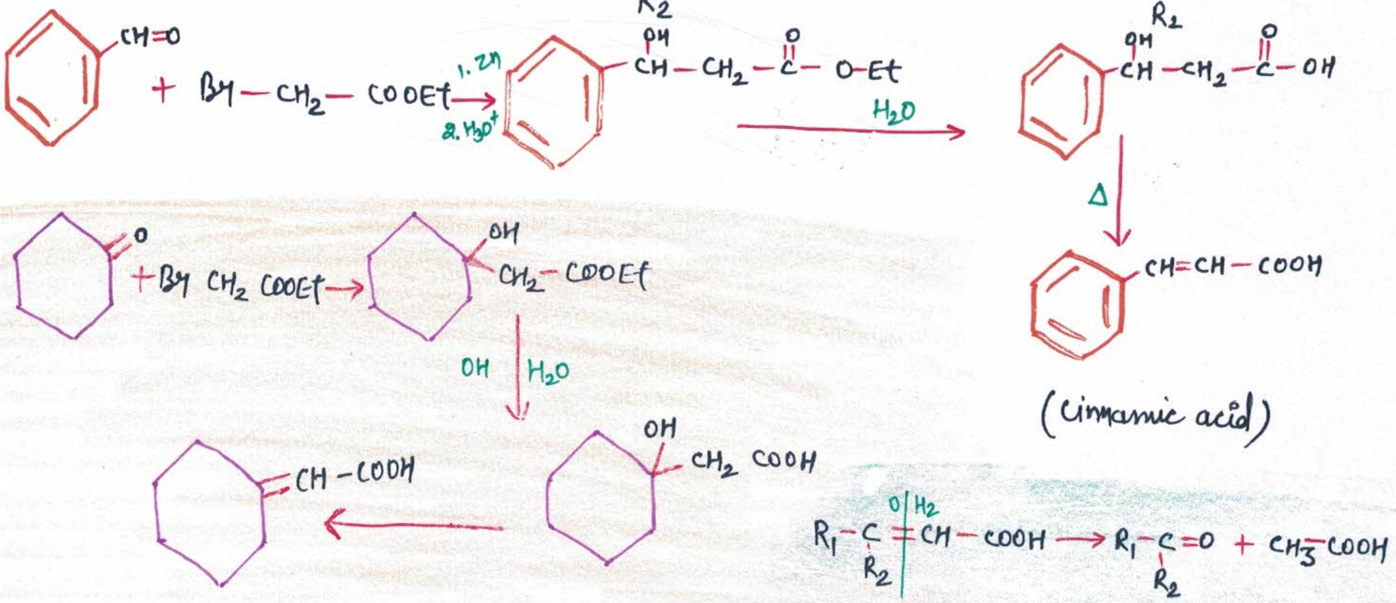
MECHANISM - $Zn \longrightarrow Zn^{+2} + 2e^-$



$$Br-CH_2-\overset{O}{\overset{\|}{C}}-OEt + e^- \longrightarrow \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-OEt$$

$$R_1-\underset{R_2}{\underset{|}{\overset{O}{\overset{\|}{C}}}} \quad \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}\;OEt \longrightarrow R_1-\underset{R_2}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{H_3O^+} R_1-\underset{R_2}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-O-Et$$

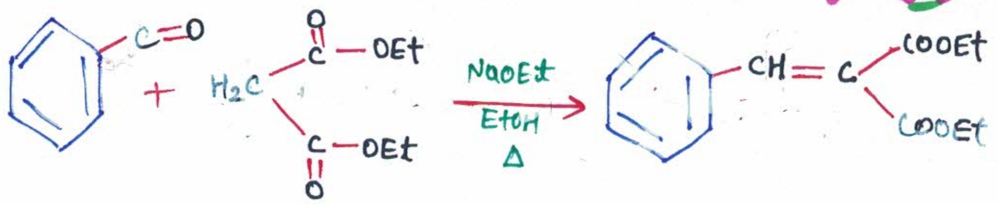
$$\xrightarrow{H_2O} R_1-\underset{R_2}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} R_1-\underset{R_2}{\underset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-OH$$



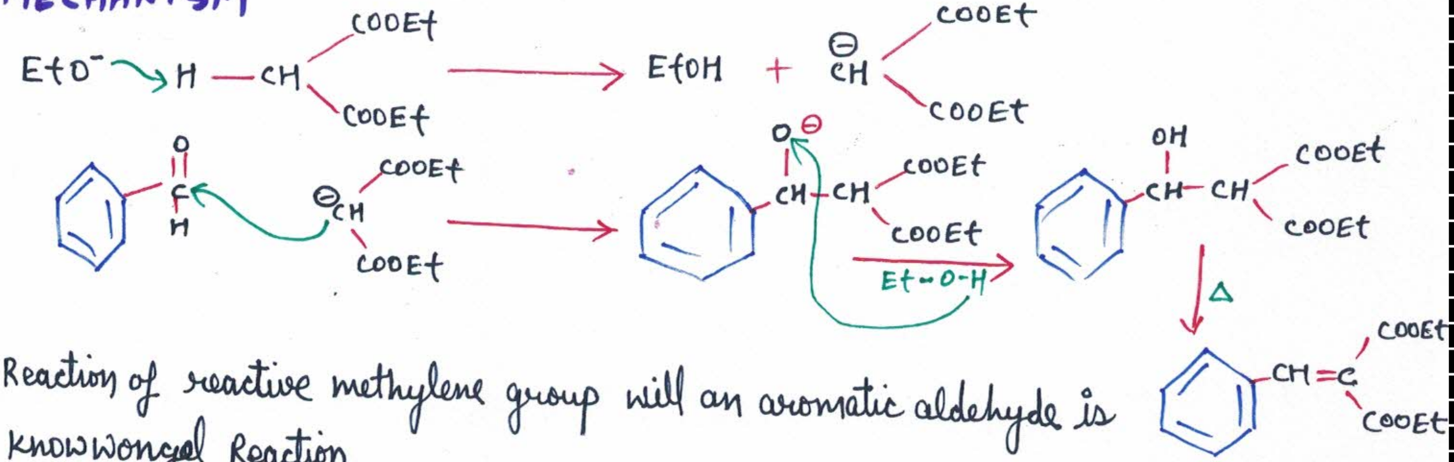
(cinnamic acid)

$$R_1-\underset{R_2}{\underset{|}{C}}\overset{O\,|\,H_2}{=}CH-COOH \longrightarrow R_1-\underset{R_2}{\underset{|}{C}}=O + CH_3COOH$$

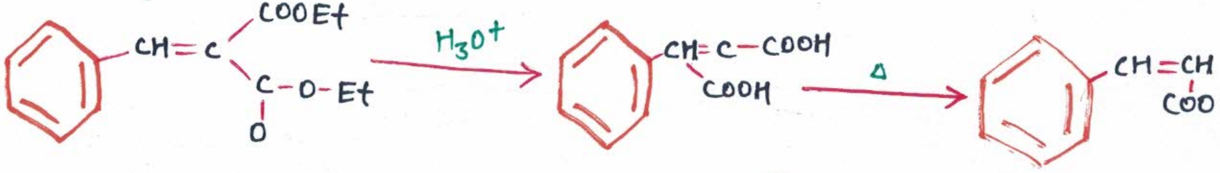
KNOWWONGAL REACTION



MECHANISM

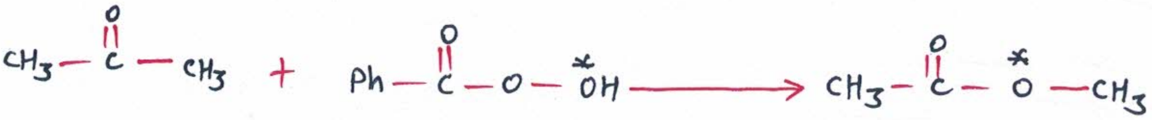


Reaction of reactive methylene group will an aromatic aldehyde is knowwongal Reaction.

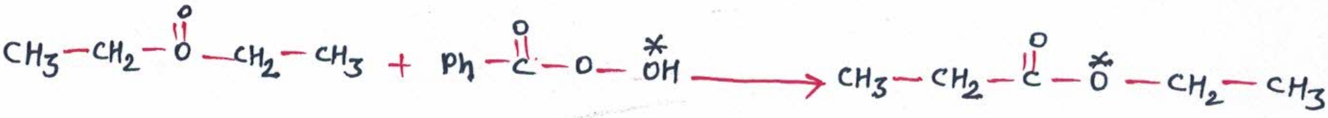


BAYER VILLIGOR REACTION (OXIDATION)

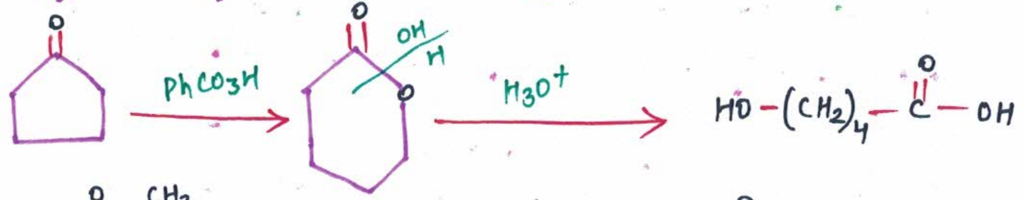
$R_1-\overset{O}{\overset{\parallel}{C}}-R_2 + Ph-\overset{O}{\overset{\parallel}{C}}-O-\overset{*}{O}-H \longrightarrow R_1-\overset{O}{\overset{\parallel}{C}}-\overset{*}{O}-R_2$



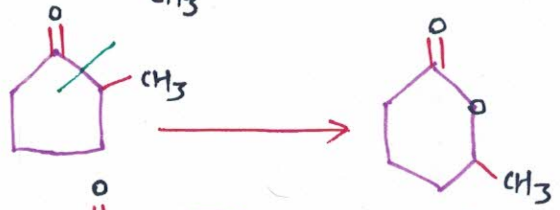
$CH_3-\overset{O}{\overset{\parallel}{C}}-CH_3 + Ph-\overset{O}{\overset{\parallel}{C}}-O-\overset{*}{O}H \longrightarrow CH_3-\overset{O}{\overset{\parallel}{C}}-\overset{*}{O}-CH_3$



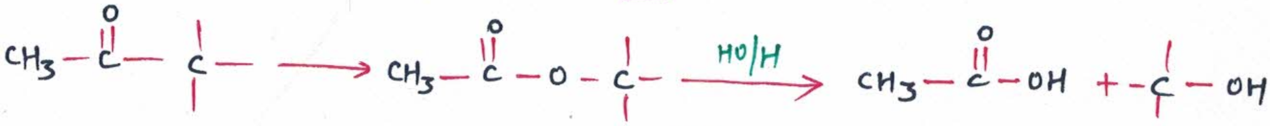
$CH_3-CH_2-\overset{O}{\overset{\parallel}{C}}-CH_2-CH_3 + Ph-\overset{O}{\overset{\parallel}{C}}-O-\overset{*}{O}H \longrightarrow CH_3-CH_2-\overset{O}{\overset{\parallel}{C}}-\overset{*}{O}-CH_2-CH_3$



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

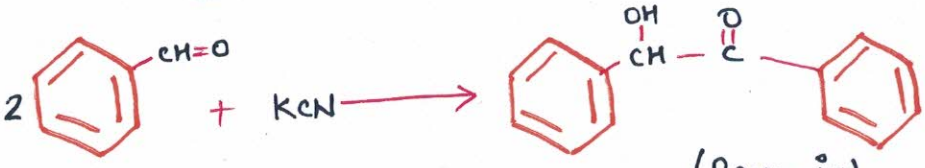


O in introduced near the more bulky group



$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{|}{\underset{|}{C}}- \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{|}{\underset{|}{C}}- \xrightarrow{HO/H} CH_3-\overset{O}{\overset{\|}{C}}-OH + -\overset{|}{\underset{|}{C}}-OH$$

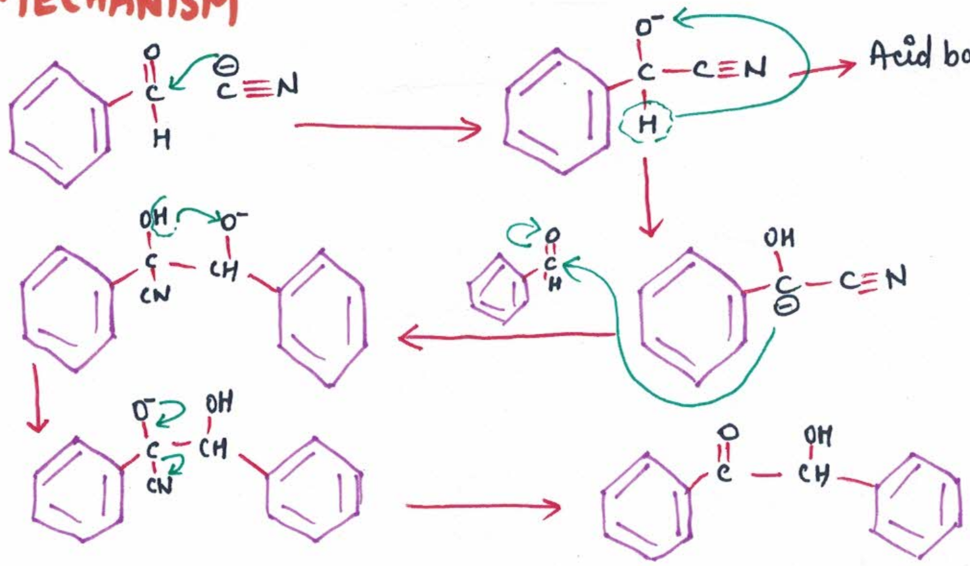
Benzoin Condensation



(Benzoin)

only aromatic aldehydes undergo it.

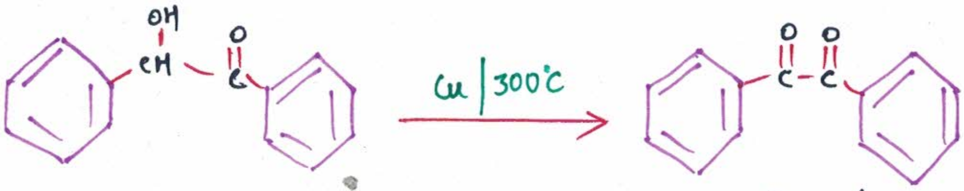
MECHANISM



Acid base reaction occurs

In aliphatic aldehydes, as KCN is basic salt and in $CH_3-\overset{O^-}{\underset{CN}{C}}-H$, H cannot migrate as it is not acidic, so instead of benzoic aldol condensation takes place.

$H\overset{O}{C}CH_3$ KCN $H\overset{O}{C}CH_2^-$



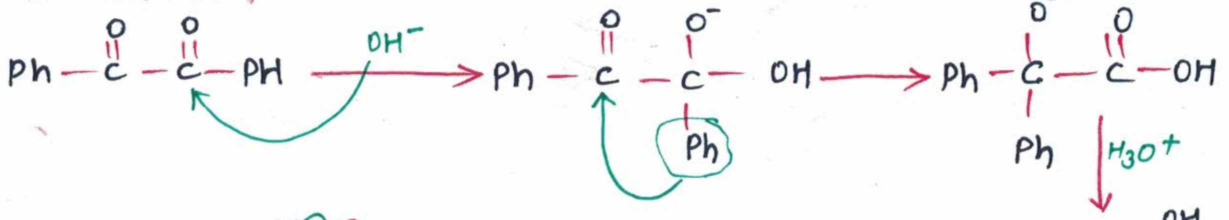
Benzil

Benzil - Benzilic acid rearrangement

$Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow[2.\ H_3O^+]{1.\ OH^-\ \Delta} Ph-\overset{OH}{\overset{\|}{\underset{Ph}{C}}}-COOH$ (Benzalic acid)

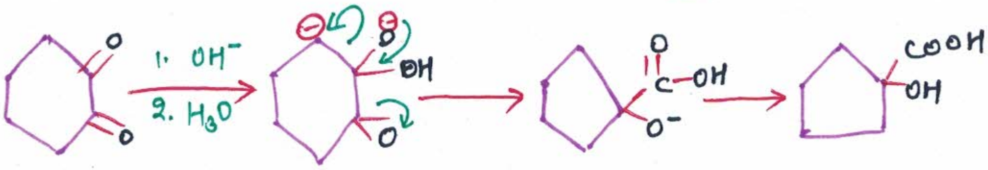
(2, Hydroxy, 2,2 diphenyl ethanoic acid)

MECHANISM



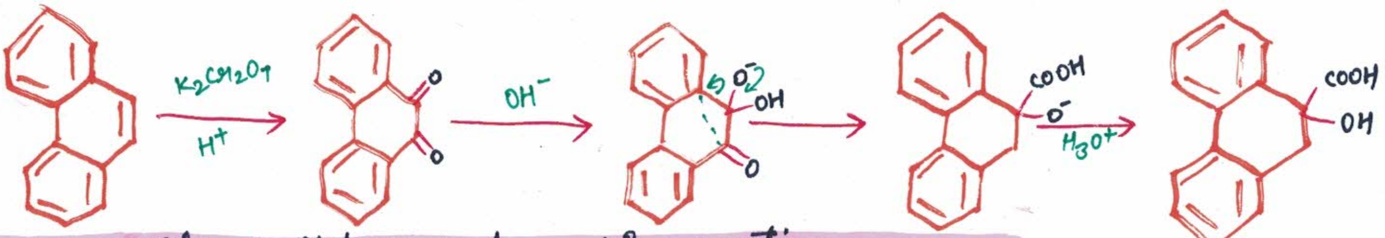
$Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-PH \xrightarrow{OH^-} Ph-\overset{O}{\overset{\|}{C}}-\overset{O^-}{\underset{Ph}{C}}-OH \longrightarrow Ph-\overset{O^-}{\underset{Ph}{C}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{H_3O^+}$

$Ph-\overset{OH}{\underset{Ph}{C}}-COOH$



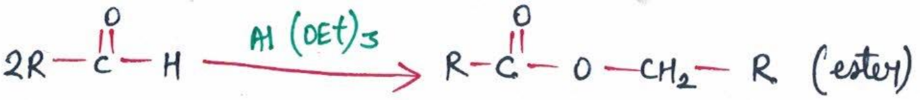
α hydroxy carboxylic acids are formed.

$\xrightarrow{KCN}$ Benzoin $\xrightarrow{Cu/300°C}$ Benzil $\xrightarrow{OH^-}$ Benzilic acid



only α diketones undergo this reaction

Tischenko Reaction



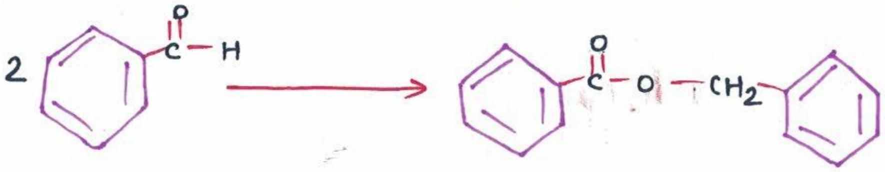
$2R-\overset{O}{\overset{||}{C}}-H \xrightarrow{Al(OEt)_3} R-\overset{O}{\overset{||}{C}}-O-CH_2-R$ (ester)

It is disproportion reaction.

As now $Al(OEt)_3$ is amphoteric, even if α hydrogen is present, aldol condensation will not take place.

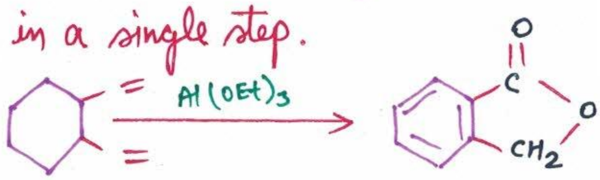
So, each & every aldehyde will give this reaction.

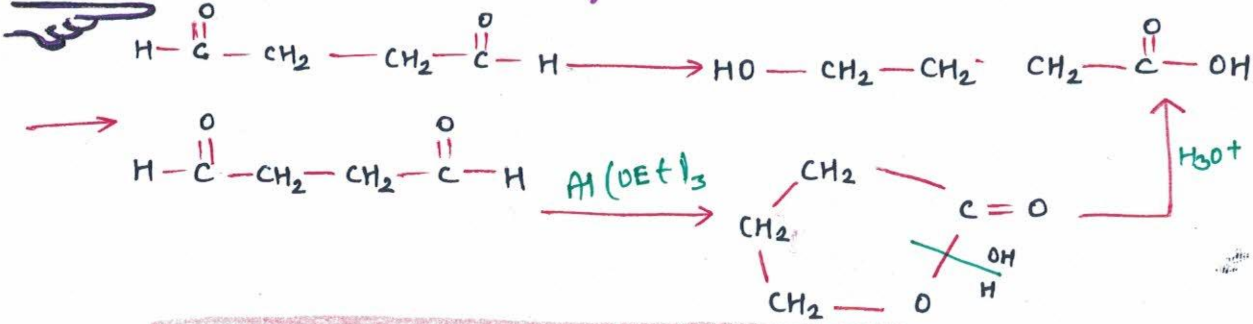
$2\,CH_3-\overset{O}{\overset{||}{C}}-H \longrightarrow CH_3-\overset{O}{\overset{||}{C}}-O-CH_2-CH_3$

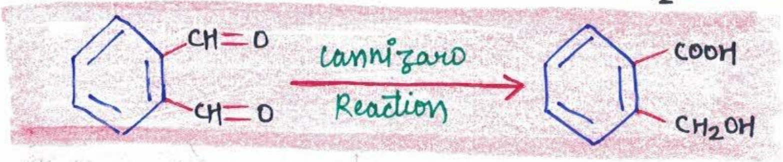


Q. Convert aldehyde into ester in a single step.

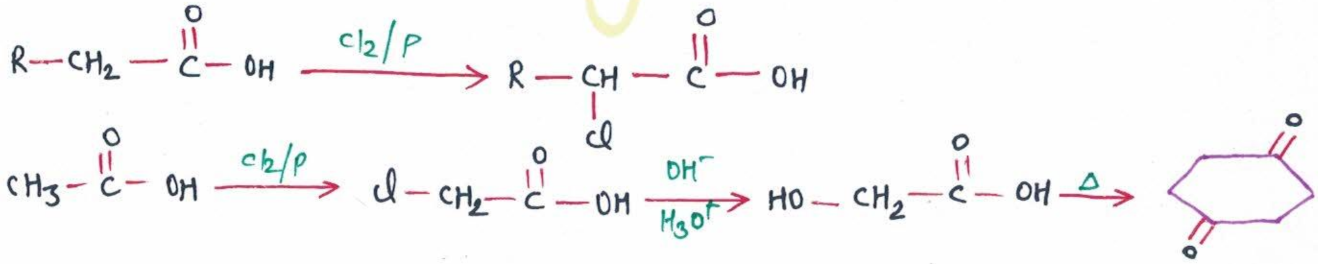
→ Tischenko Reaction



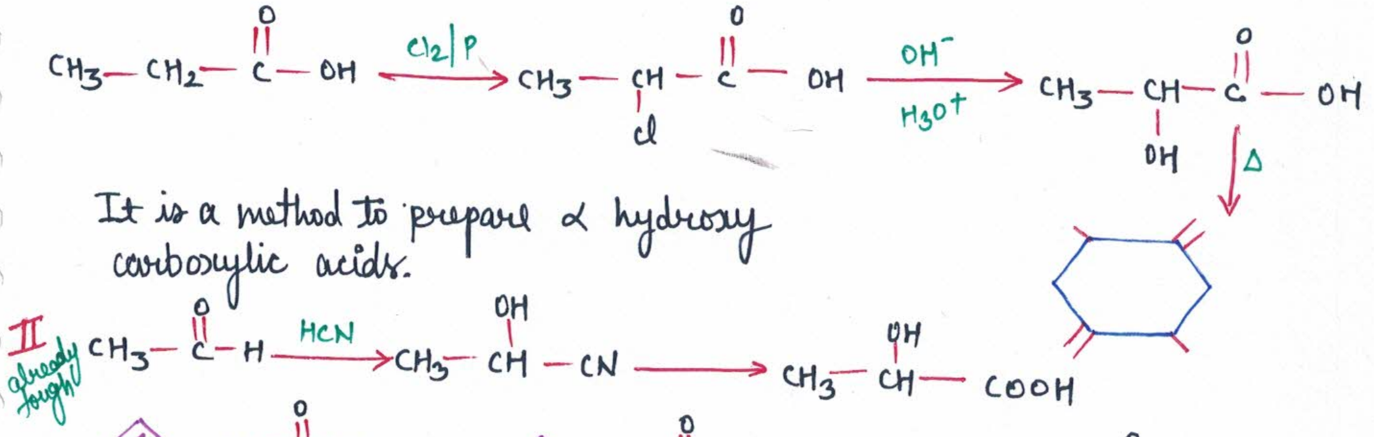




HELL VOLHARD Zilinisky Reaction (HVZ)



$R-CH_2-\overset{O}{\overset{||}{C}}-OH \xrightarrow{Cl_2/P} R-\underset{Cl}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-OH$

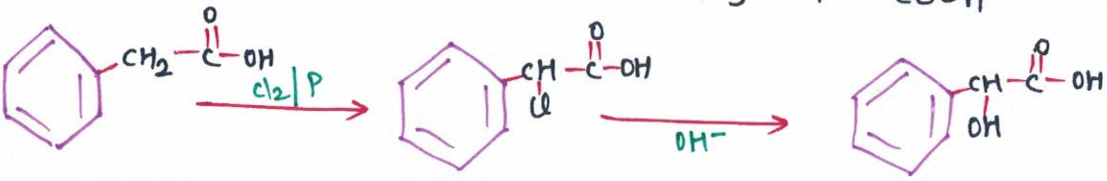


$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{Cl_2|P} CH_3-\underset{Cl}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[H_3O^+]{OH^-} CH_3-\underset{OH}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{\Delta}$$

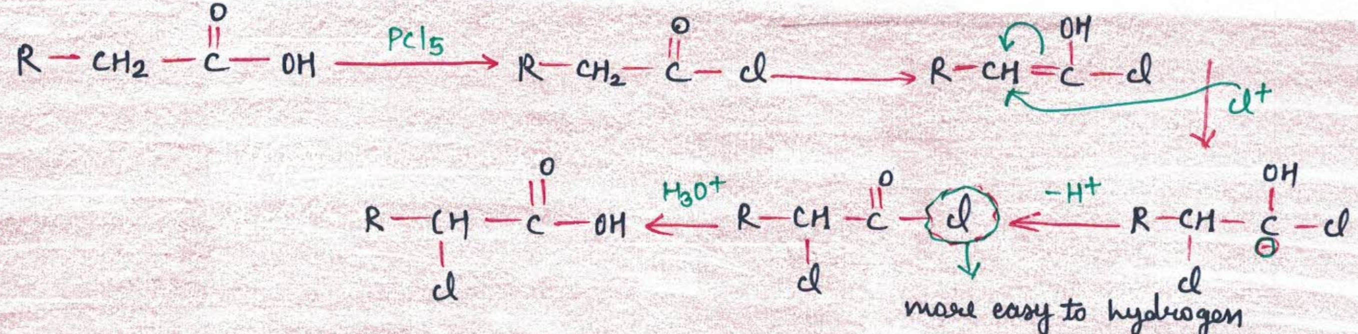
It is a method to prepare α hydroxy carboxylic acids.

II already tough

$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{HCN} CH_3-\overset{OH}{\overset{|}{CH}}-CN \longrightarrow CH_3-\overset{OH}{\overset{|}{CH}}-COOH$$

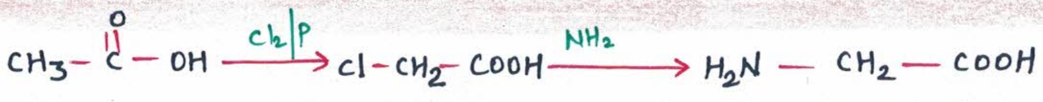


MECHANISM



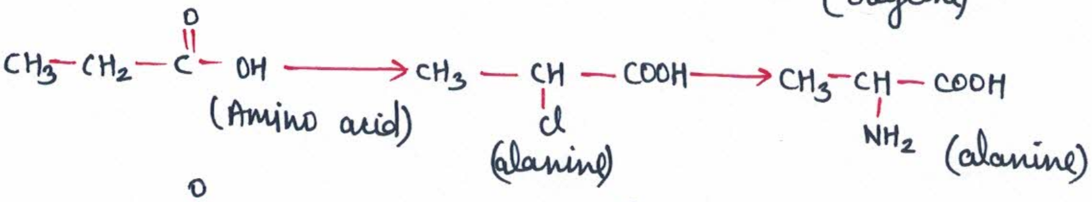
$$R-CH_2-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{PCl_5} R-CH_2-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow R-CH=\overset{OH}{\overset{|}{C}}-Cl \xrightarrow{Cl^+} R-\underset{Cl}{\underset{|}{CH}}-\overset{OH}{\overset{|}{\underset{\ominus}{C}}}-Cl \xrightarrow{-H^+} R-\underset{Cl}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{H_3O^+} R-\underset{Cl}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-OH$$

more easy to hydrogen



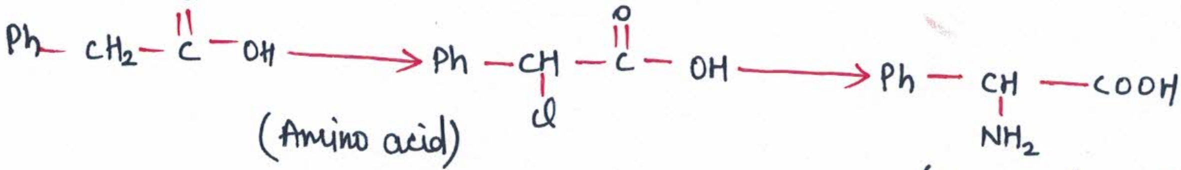
$$CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{Cl_2|P} Cl-CH_2-COOH \xrightarrow{NH_2} H_2N-CH_2-COOH$$

(Glycine)



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH \longrightarrow CH_3-\underset{Cl}{\underset{|}{CH}}-COOH \longrightarrow CH_3-\underset{NH_2}{\underset{|}{CH}}-COOH$$

(Amino acid) (alanine) (alanine)

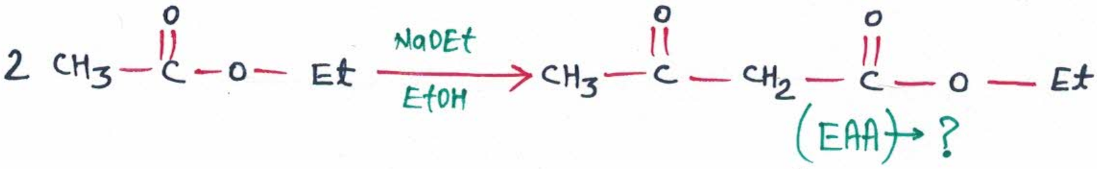


$$Ph-CH_2-\overset{\overset{O}{\|}}{C}-OH \longrightarrow Ph-\underset{Cl}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-OH \longrightarrow Ph-\underset{NH_2}{\underset{|}{CH}}-COOH$$

(Amino acid) (Phenyl glycine)

By this method we can prepare amino acids.

CLAISEN'S CONDENSATION



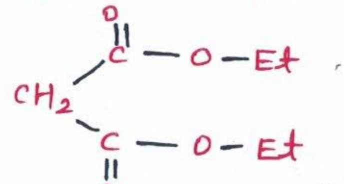
$$2\ CH_3-\overset{\overset{O}{\|}}{C}-O-Et \xrightarrow[EtOH]{NaOEt} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-Et$$

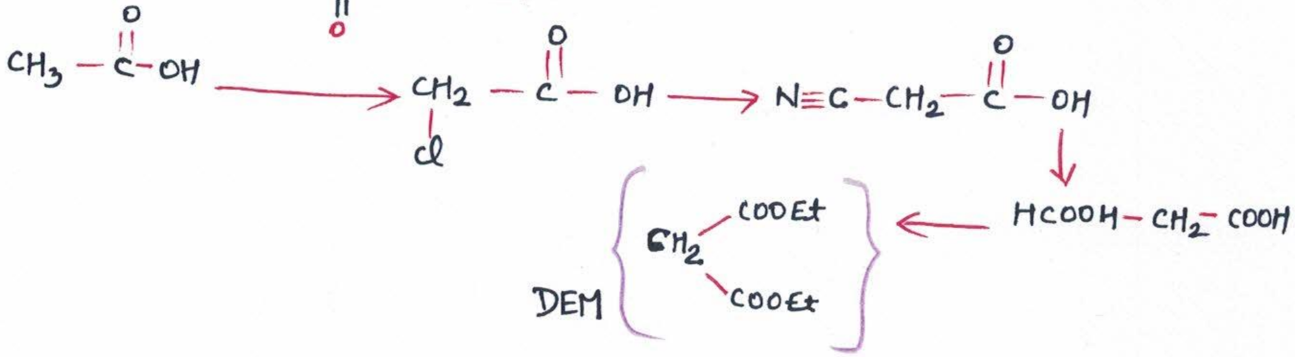
(EAA) → ?

only esters having α hydrogen can undergo this reaction.

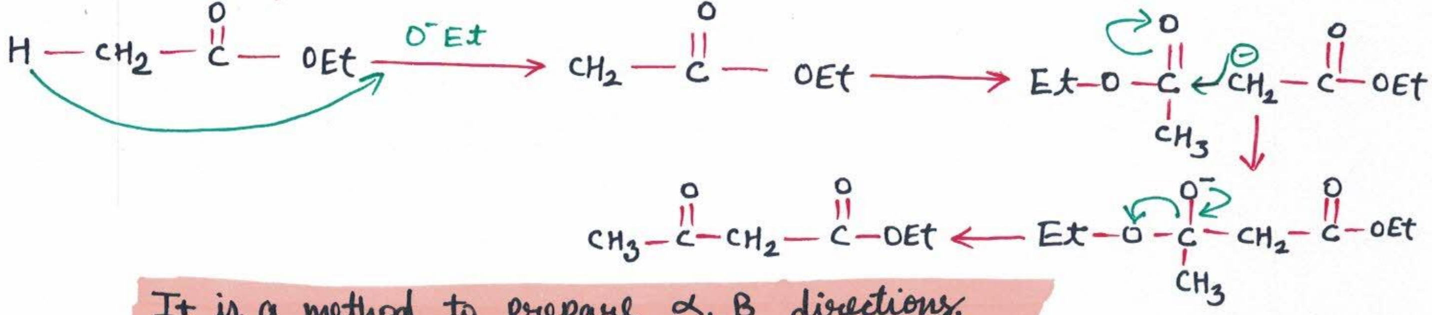
Convert CH_3COOH into DEM.

DEM =



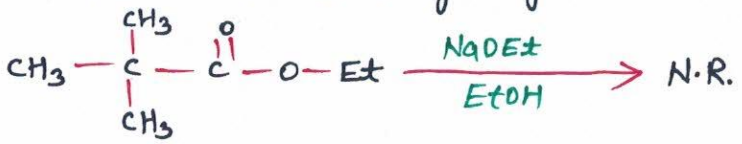


MECHANISM

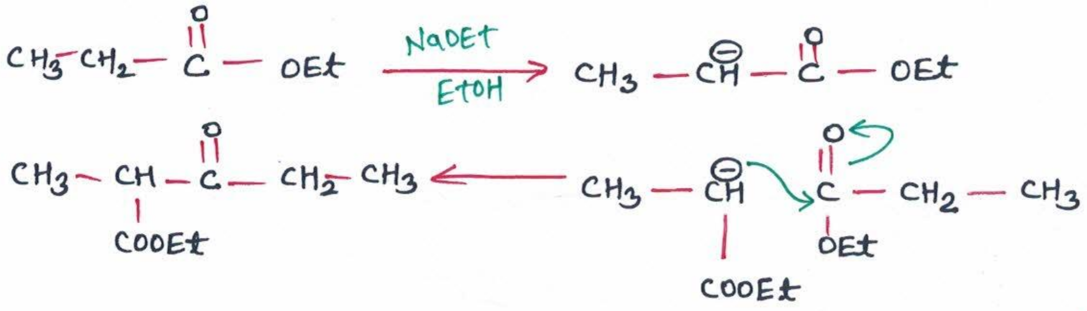


It is a method to prepare α, β directions.

These esters which do not have α hydrogen will not undergo this reaction.

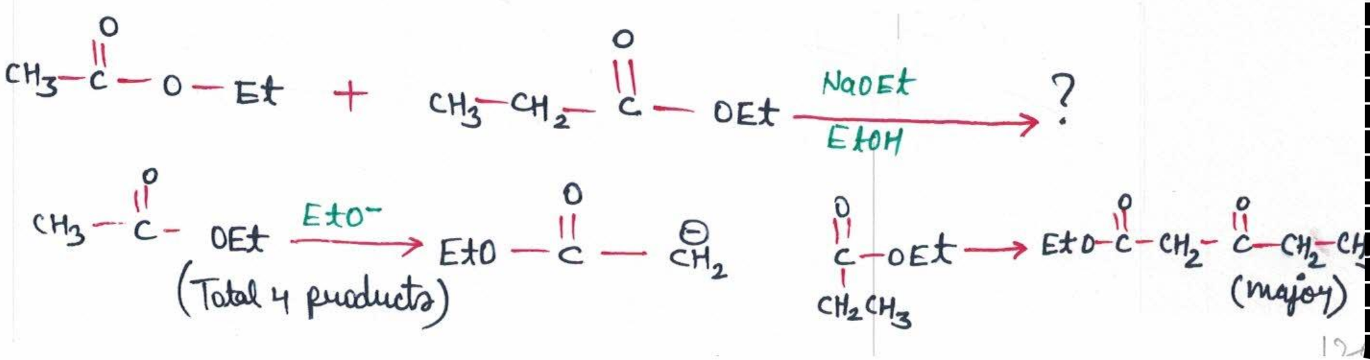


$$(CH_3)_3C-COOEt \xrightarrow[EtOH]{NaOEt} N.R.$$



$$CH_3CH_2COOEt \xrightarrow[EtOH]{NaOEt} CH_3-\overset{\ominus}{C}H-COOEt$$

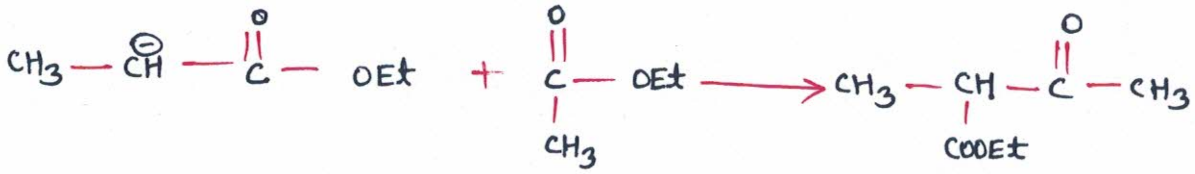
CROSSED CLAISEN's CONDENSATION



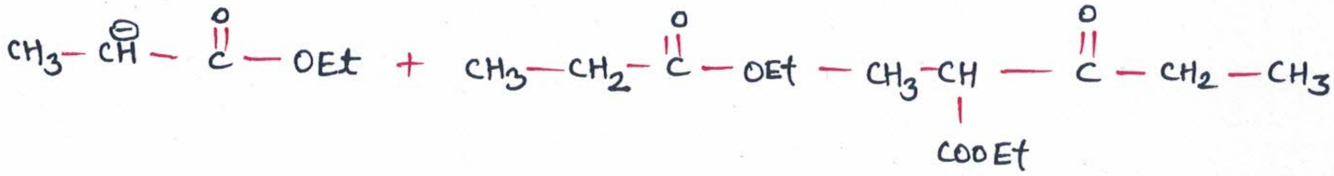
$$CH_3COOEt + CH_3CH_2COOEt \xrightarrow[EtOH]{NaOEt} ?$$

(Total 4 products)

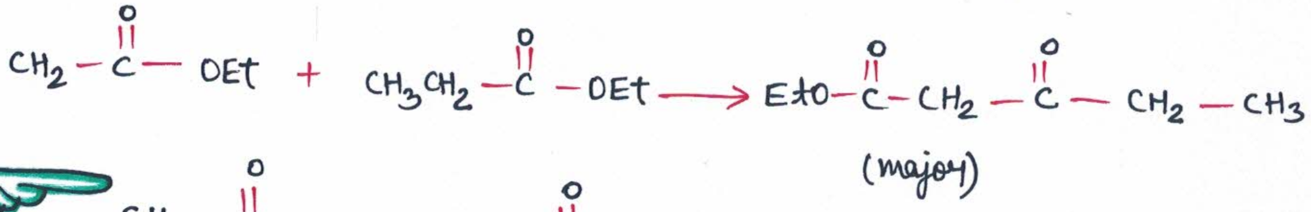
(major)



$CH_3-\overset{\ominus}{CH}-\overset{O}{\overset{\|}{C}}-OEt + \underset{CH_3}{\underset{|}{\overset{O}{\overset{\|}{C}}}}-OEt \longrightarrow CH_3-\underset{COOEt}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$

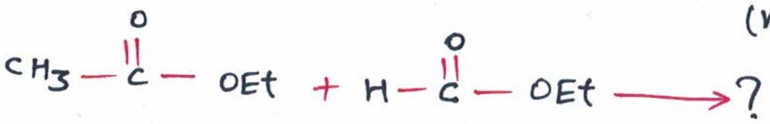


$CH_3-\overset{\ominus}{CH}-\overset{O}{\overset{\|}{C}}-OEt + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OEt - CH_3-\underset{COOEt}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

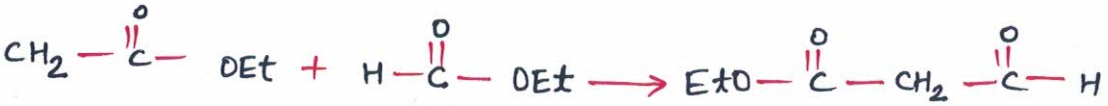


$CH_2-\overset{O}{\overset{\|}{C}}-OEt + CH_3CH_2-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow EtO-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

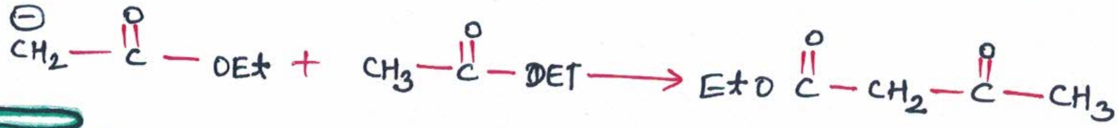
(major)



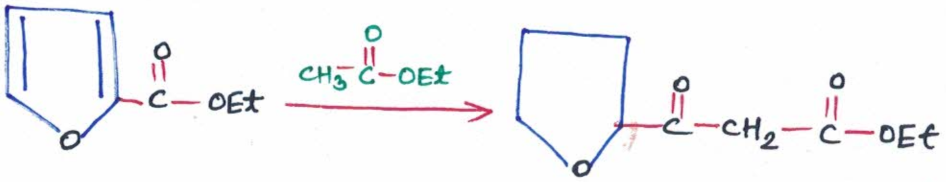
$CH_3-\overset{O}{\overset{\|}{C}}-OEt + H-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow ?$



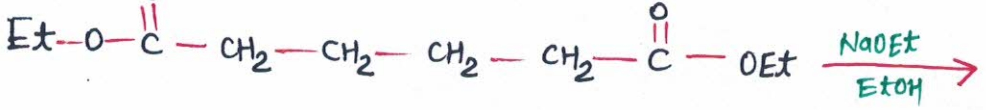
$CH_2-\overset{O}{\overset{\|}{C}}-OEt + H-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow EtO-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$



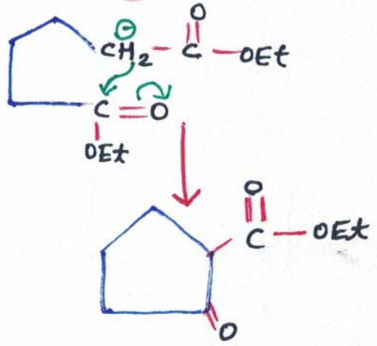
$\overset{\ominus}{CH_2}-\overset{O}{\overset{\|}{C}}-OEt + CH_3-\overset{O}{\overset{\|}{C}}-OEt \longrightarrow EtO\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

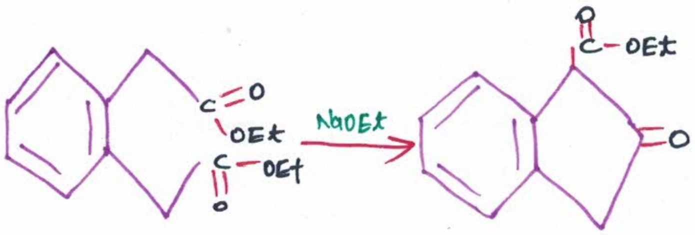


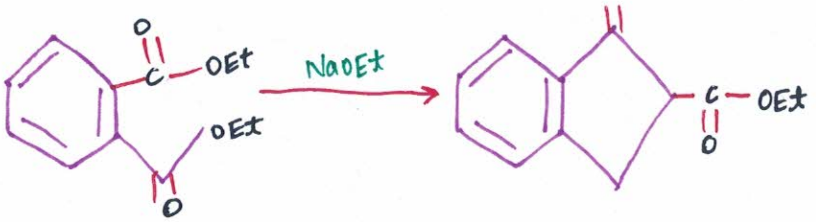
Intramolecular claisen's Condensation



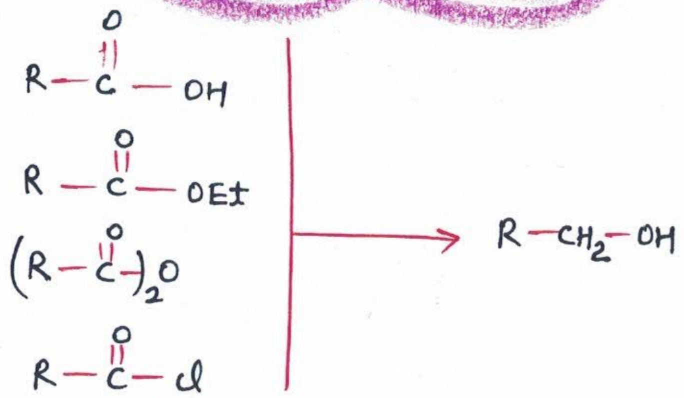
$Et-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[EtOH]{NaOEt}$





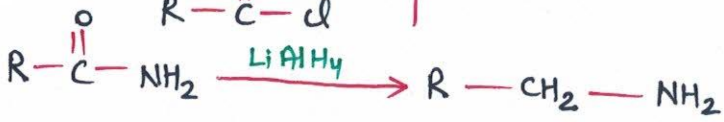


IMPORTANT POINT

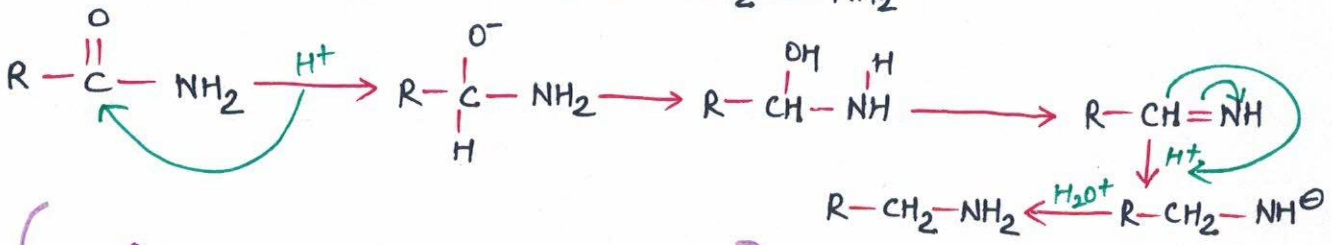


$$\left.\begin{array}{l} R-\overset{O}{\overset{\|}{C}}-OH \\ R-\overset{O}{\overset{\|}{C}}-OEt \\ (R-\overset{O}{\overset{\|}{C}})_2O \\ R-\overset{O}{\overset{\|}{C}}-Cl \end{array}\right] \longrightarrow R-CH_2-OH$$

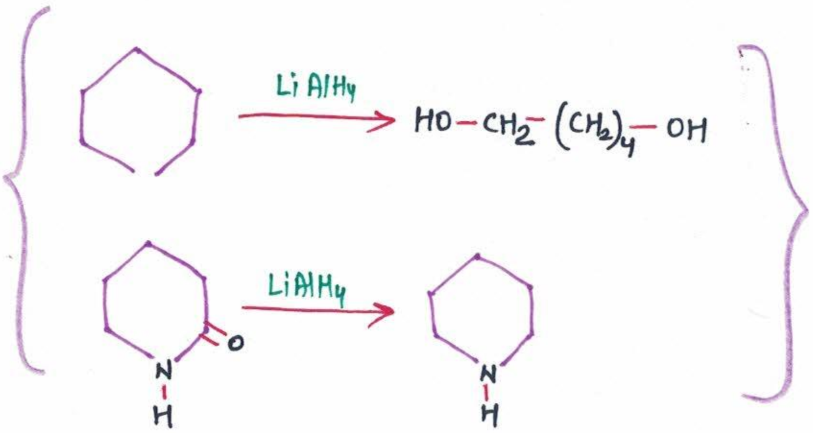
But

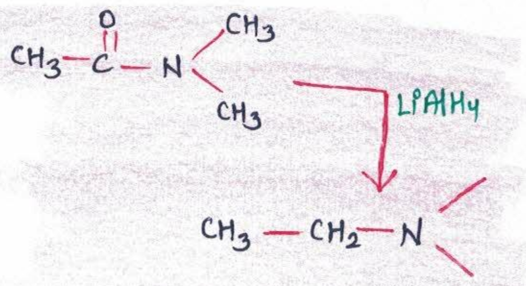


$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} R-CH_2-NH_2$$



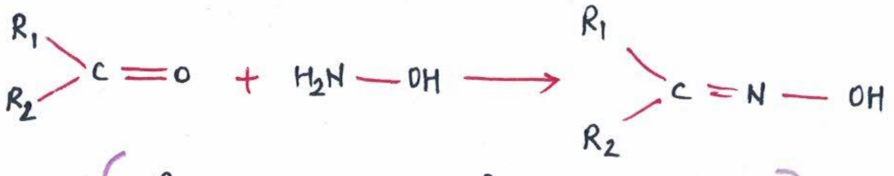
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H^+} R-\overset{O^-}{\underset{H}{C}}-NH_2 \longrightarrow R-\overset{OH}{CH}-\overset{H}{NH} \longrightarrow R-CH=NH \xrightarrow{H^+} R-CH_2-NH^{\ominus} \xrightarrow{H_2O^+} R-CH_2-NH_2$$



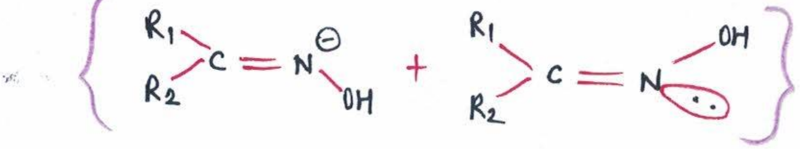


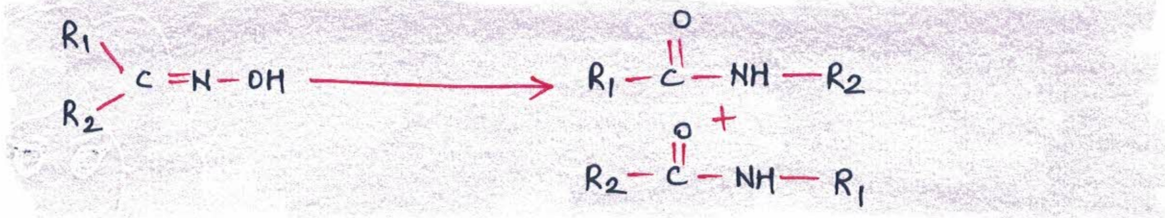
$$CH_3-\overset{O}{\overset{\|}{C}}-N(CH_3)_2 \xrightarrow{LiAlH_4} CH_3-CH_2-N<$$

BACKMANN REARRANGEMENT

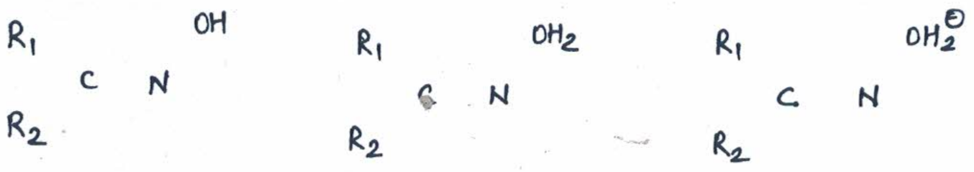


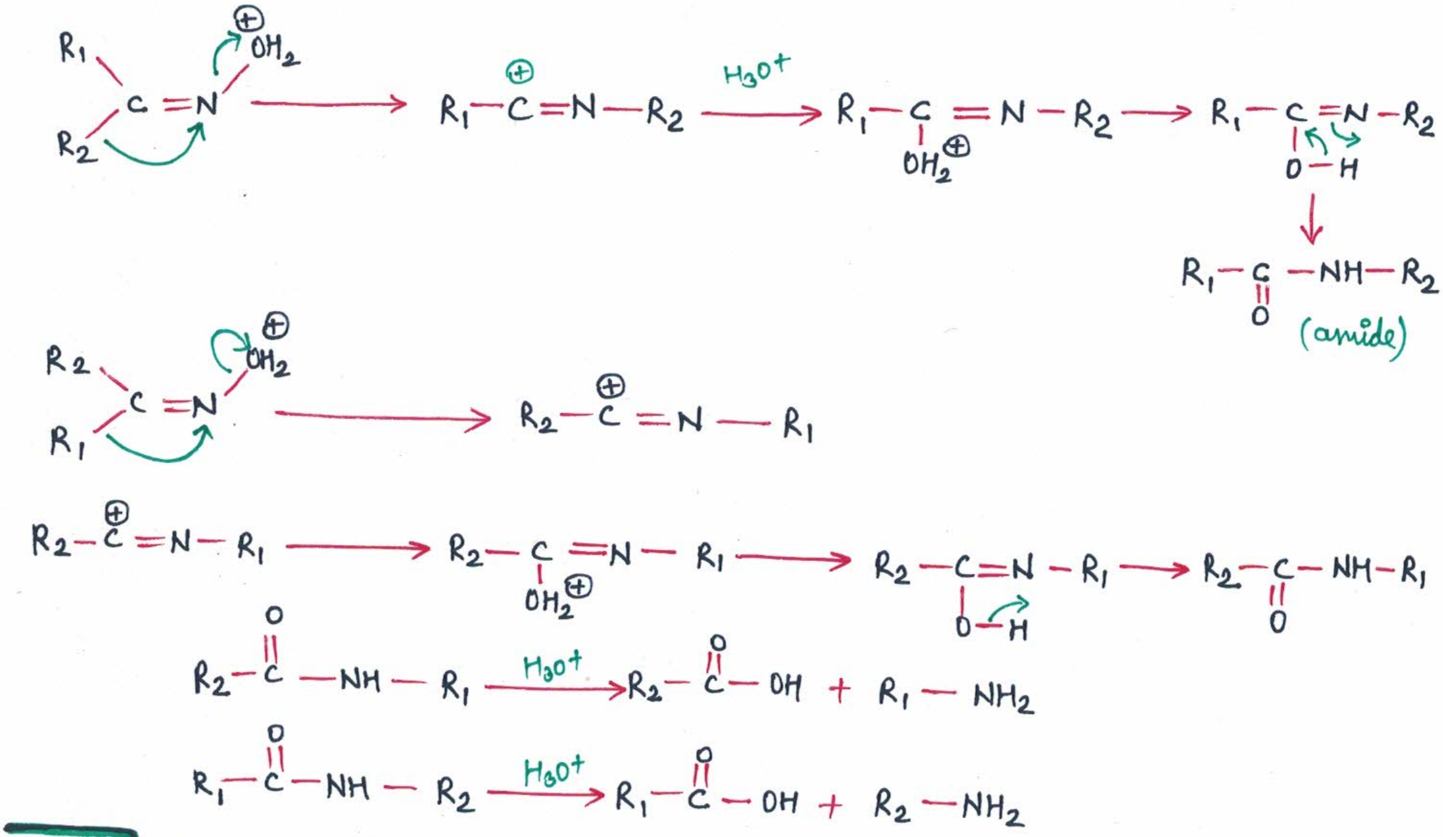
$$\overset{R_1}{\underset{R_2}{>}}C=O + H_2N-OH \longrightarrow \overset{R_1}{\underset{R_2}{>}}C=N-OH$$





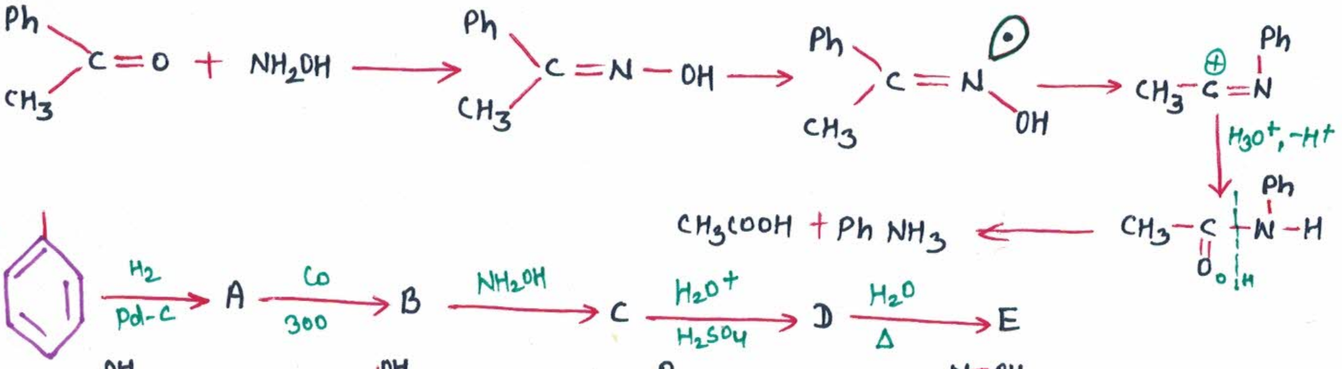
Always group trans to oxime will migrate.

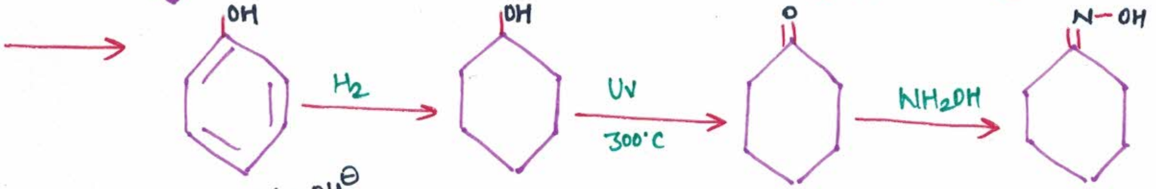


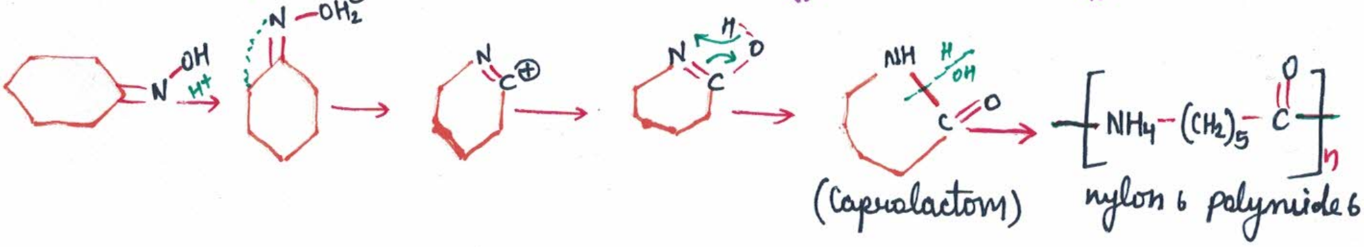


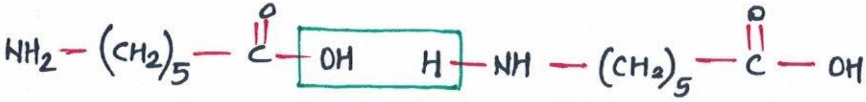
$$R_2-C(=O)-NH-R_1 \xrightarrow{H_3O^+} R_2-C(=O)-OH + R_1-NH_2$$

$$R_1-C(=O)-NH-R_2 \xrightarrow{H_3O^+} R_1-C(=O)-OH + R_2-NH_2$$





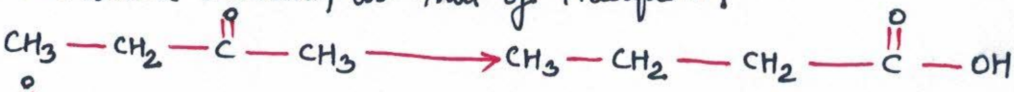




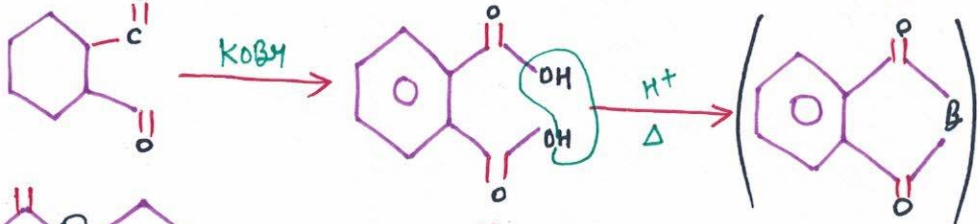
$NH_2-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\boxed{OH \quad H}-NH-(CH_2)_5-\overset{O}{\overset{\|}{C}}-OH$

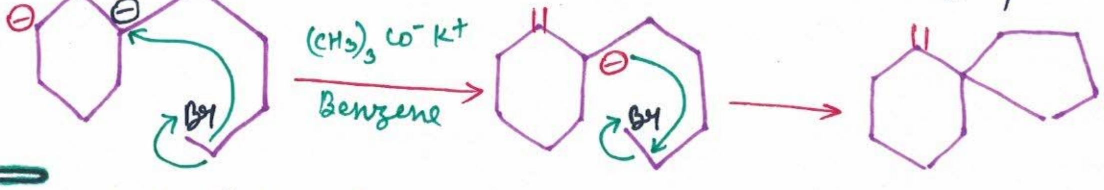
KoBr does the same reaction as that of Haloform

E.g.

1. 

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

2. 



Hydride Shift is faster than methyl shift.