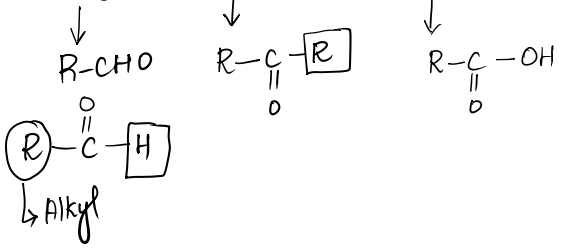
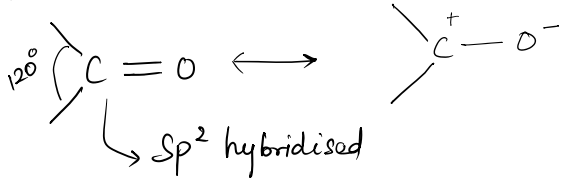
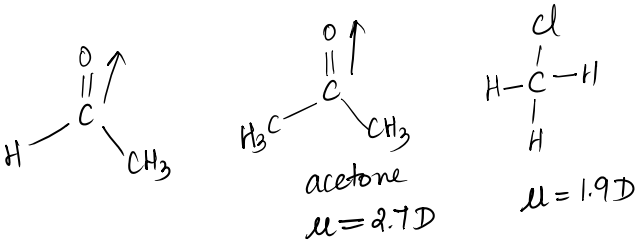
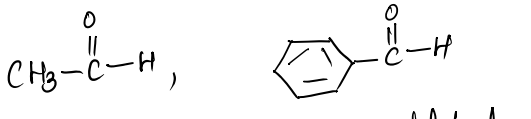
Aldehydes Ketones and Caeboxylic acids

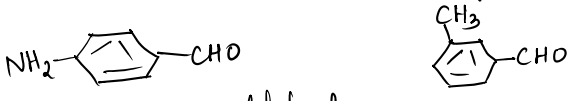


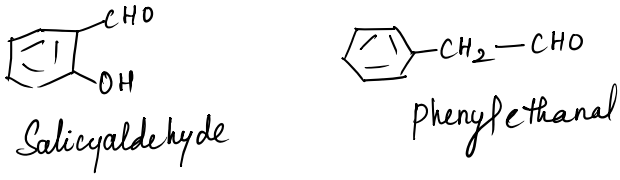




Nomenclature : Aldehyde – 'al'
Ketone – 'one'







Preparation: ⇒ Aldehyde

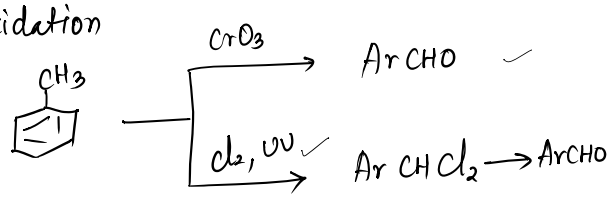
(i) Oxidation of primary alcohol.

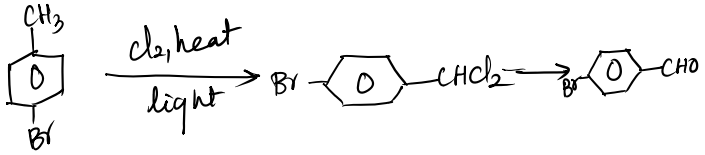
Preparation: ⇒ Aldehyde

① Oxidation of primary alcohol

$$R\text{-}CH_2OH \xrightarrow{K_2Cr_2O_7} R\text{-}CHO$$
$$\xrightarrow{PCC}$$

② Oxidation



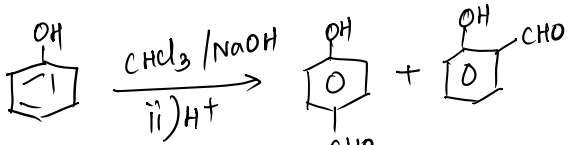


③ Redn of acid chloride (RCOCl)

$$C_6H_5COCl \xrightarrow[BaSO_4]{H_2\text{-}Pd \rightarrow \text{catalyst}} R\text{-}CHO$$
$$\hookrightarrow \text{Poi. catalyst}$$

Rosenmund's Reduction.

Reimer-Tiemann rxn:



phenol — Salicylaldehyde

$$(R-COO)_2Ca + (HCOO)_2Ca \rightarrow CaCO_3 + 2\,RCHO$$

$$CH_3\text{-}COO\text{-}Ca\text{-}CH_3COO + HCOO\text{-}Ca\text{-}HCOO \xrightarrow{-CaCO_3} CH_3CHO$$

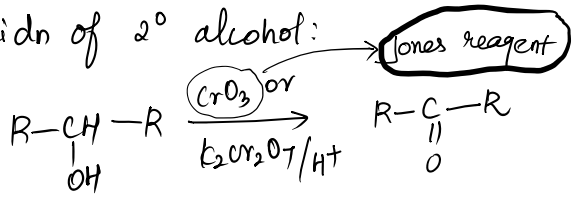
⑤ Stephen rxn

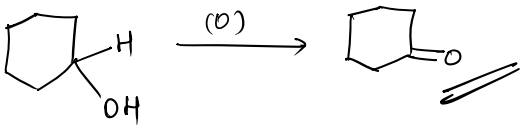
$$R\text{-}C\equiv N \xrightarrow[HCl,\ H_2O]{SnCl_2} R\text{-}CH=NH \xrightarrow{} R\text{-}CHO + NH_3$$

Preparation of ketones:

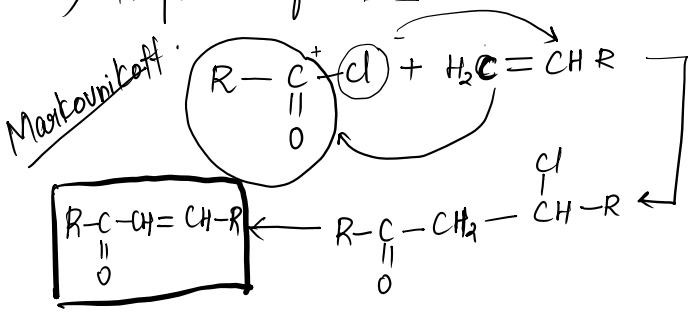
Preparation of ketones:

1) Oxidn of 2° alcohol:

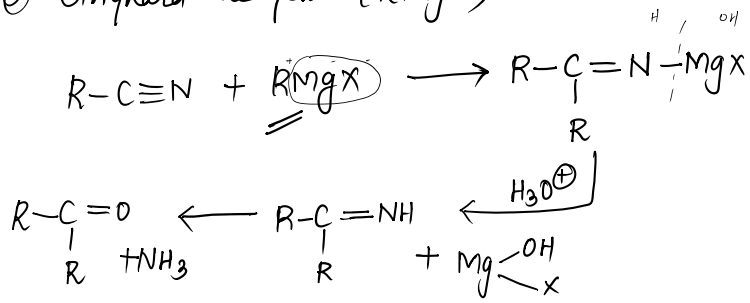




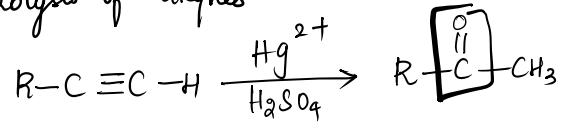
2) Acylation of alkenes:



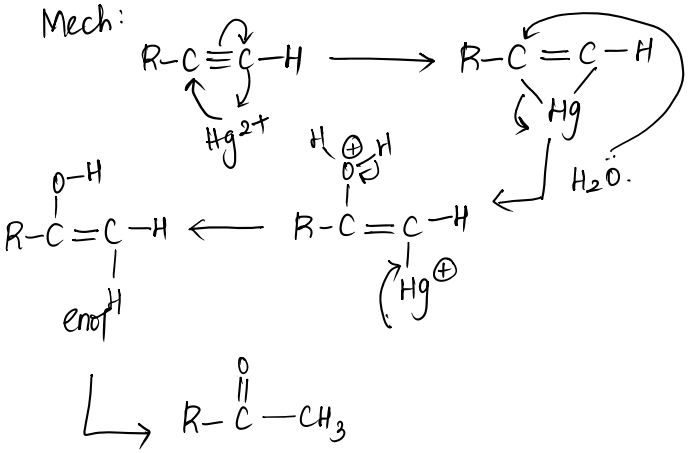
③ Grignard reagent (RMgX)



Hydrolysis of alkynes:

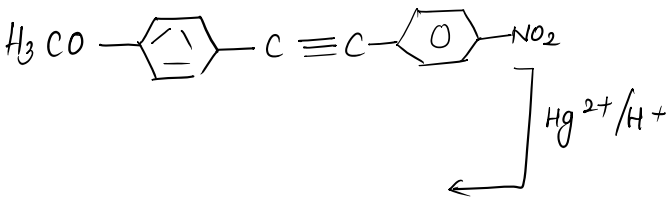


Mech:

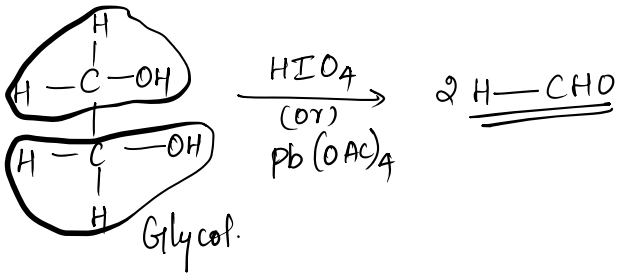


H.W

H.W

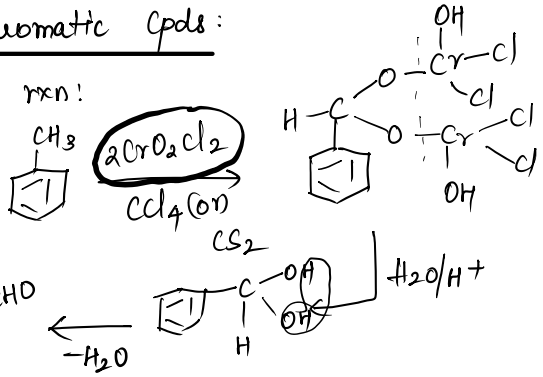


Oxidn of Vicinal diols:

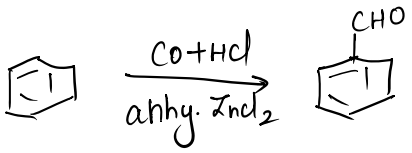


PPN of aromatic cpds:

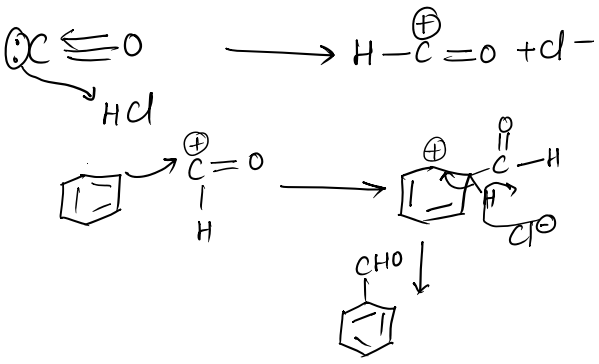
1) Etard rxn:



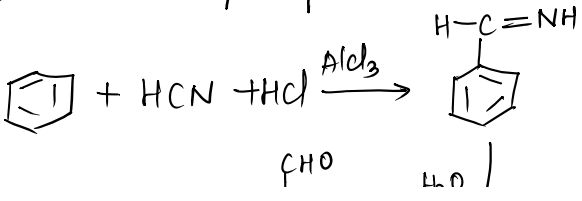
Gattermann - koch Formylation:

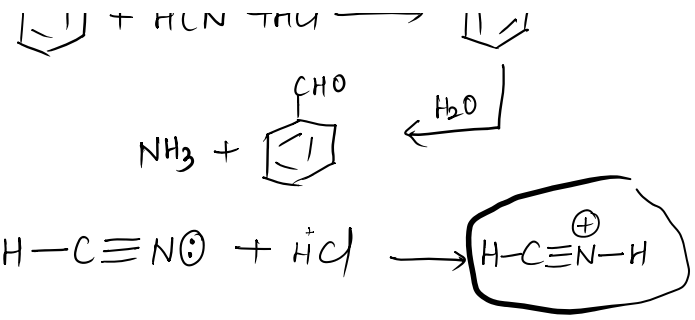


Mech

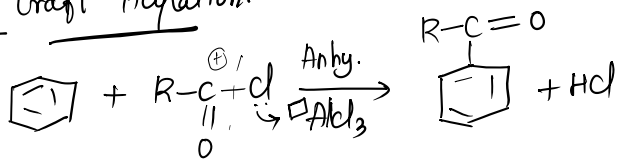


Gattermann's Aldehyde Synthesis:

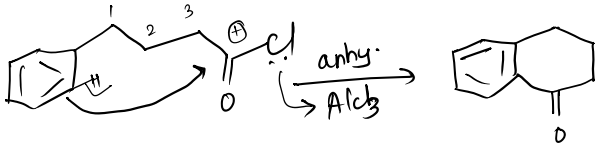




Friedal Craft Acylation:

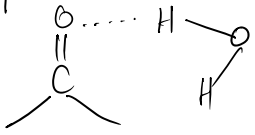


PP



Physical prop:

> Solubility: lower Car. cpd Soluble.

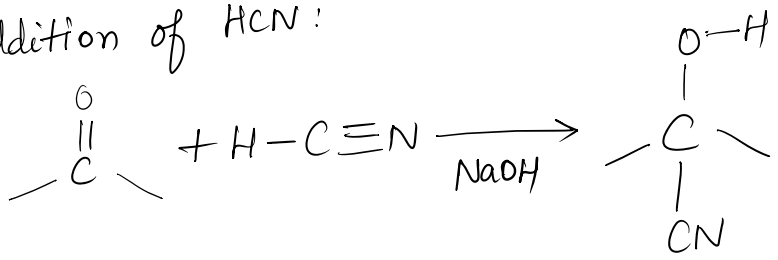


> B.pt : higher than hydrocarbons

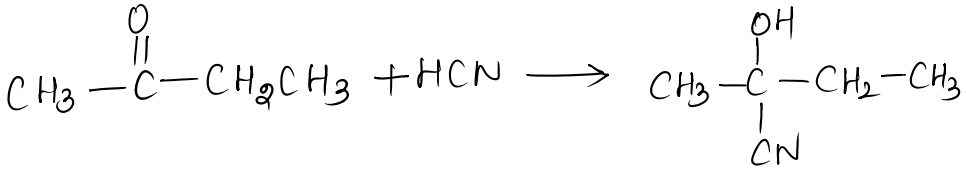
H.C < Alkyl halides < ethers < Ald < ketone < Alcohol

Chemical prop:

i) Addition of HCN:

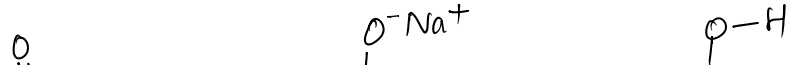


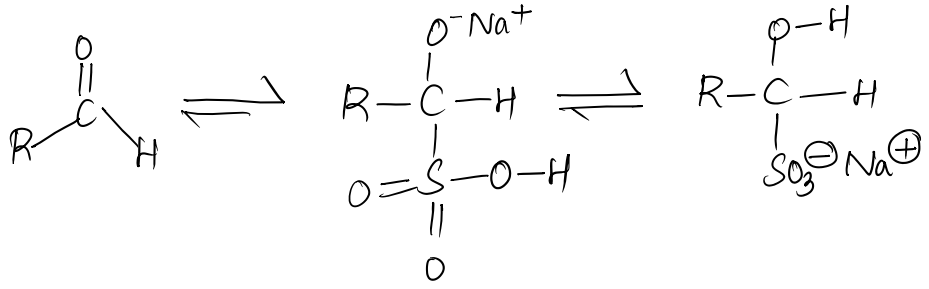
Cyanohydrin



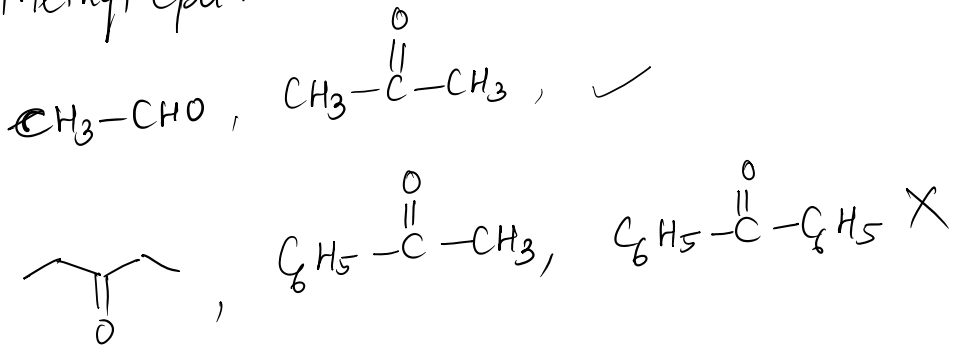
Addn of $NaHSO_3$

$$NaHSO_3 \rightarrow Na^+ + HSO_3^-$$

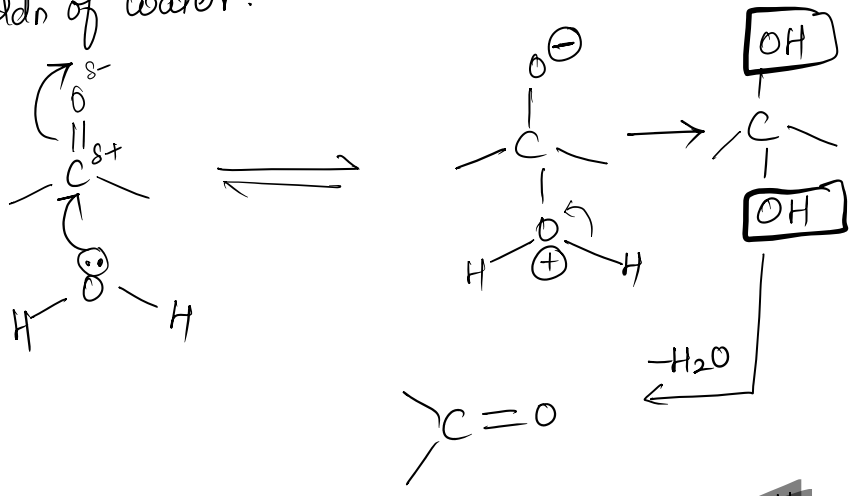




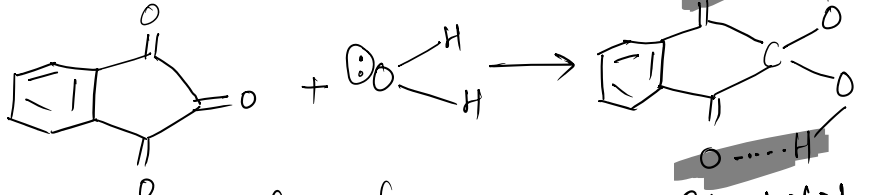
Ali. Methyl Cpd:



③ Addn of water:



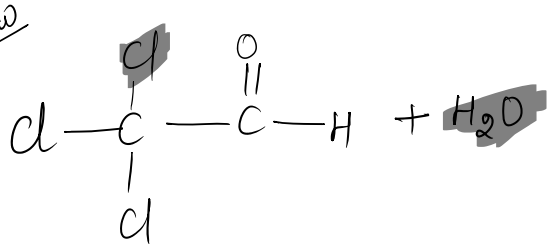
Ex:



Ninhydrin (test for protein)

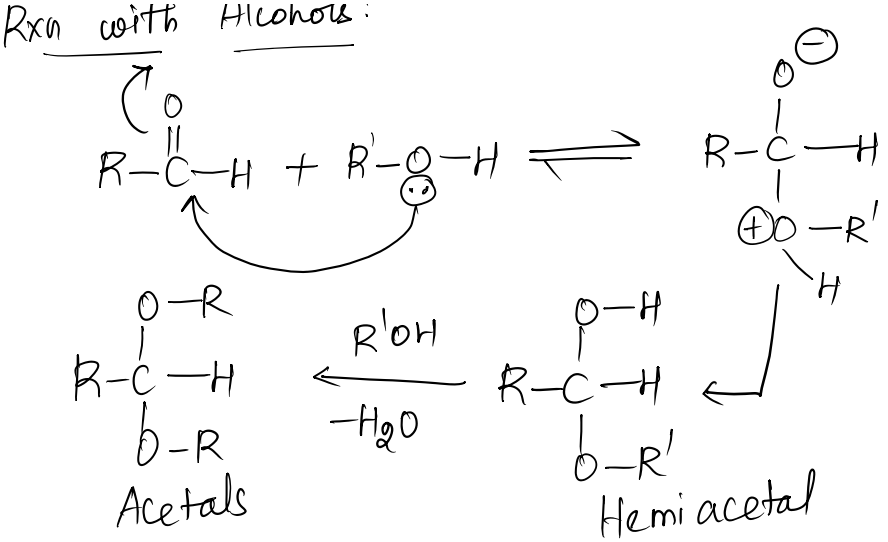
Stability

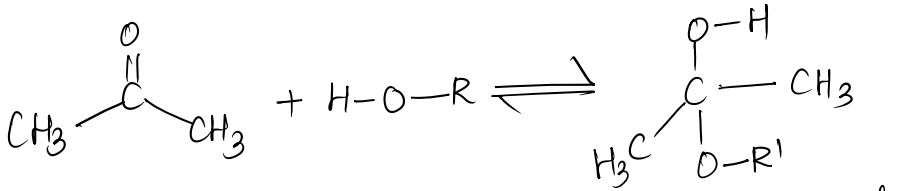
H.W

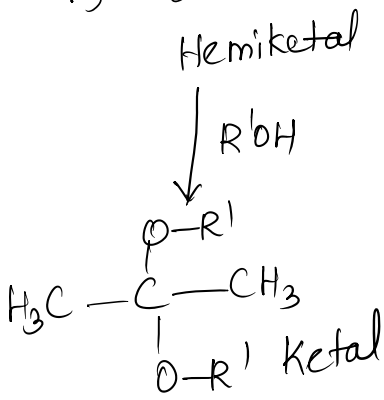


Rxn with Alcohols:

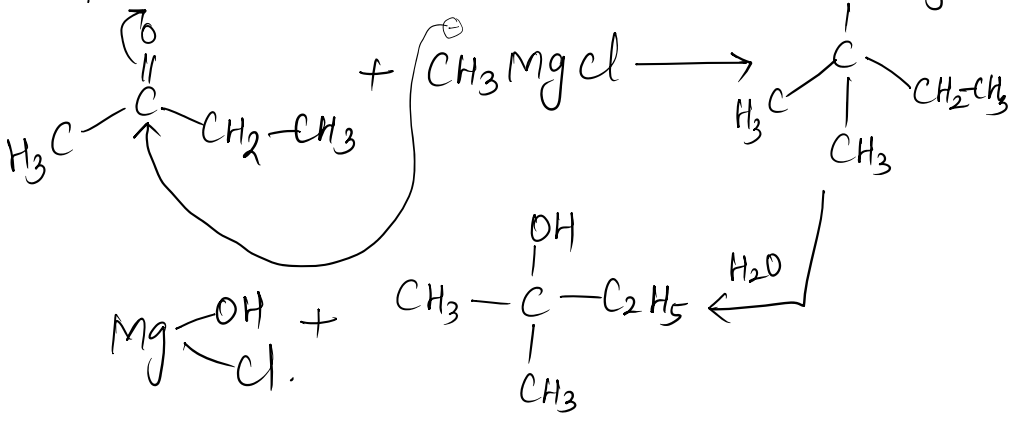
Rxn with Hiconols:



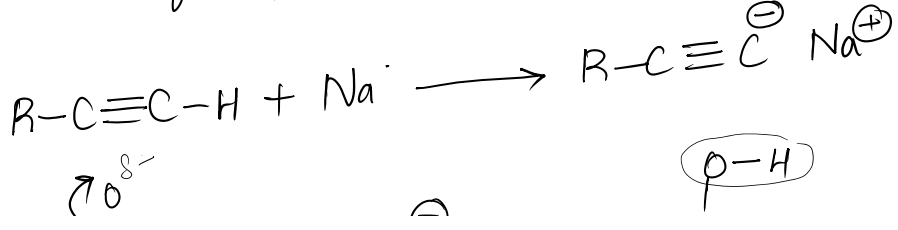


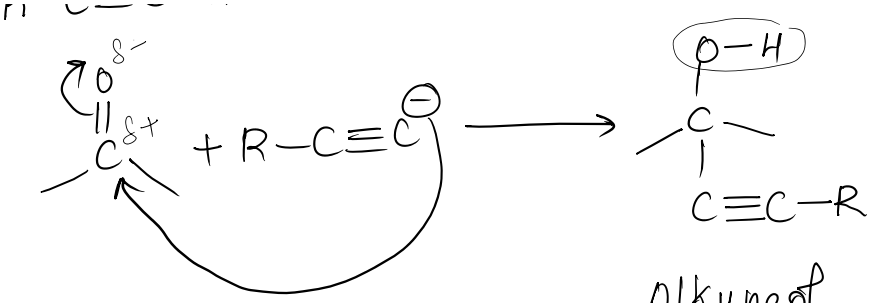


Grignard reagent:



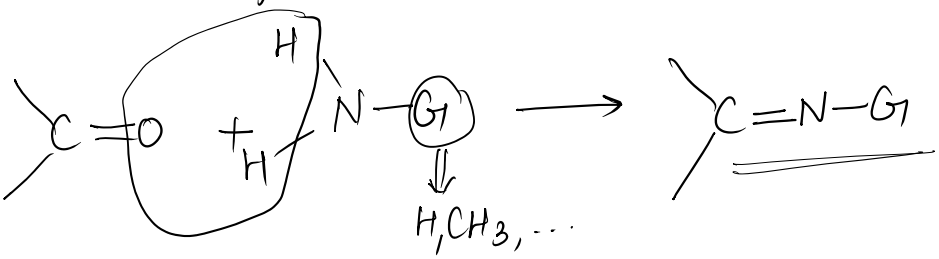
Addition of Teminal Alkynes:

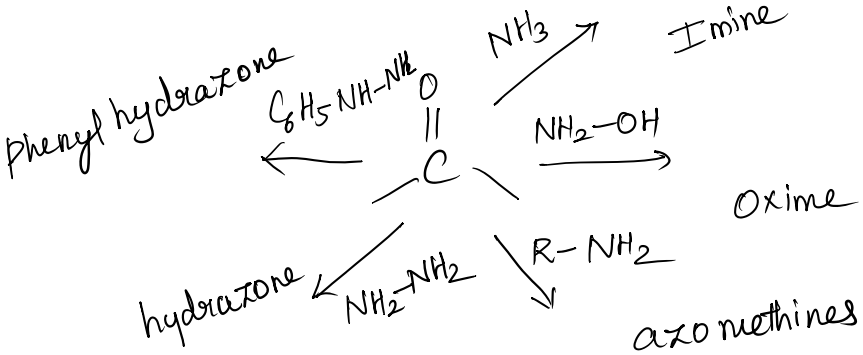


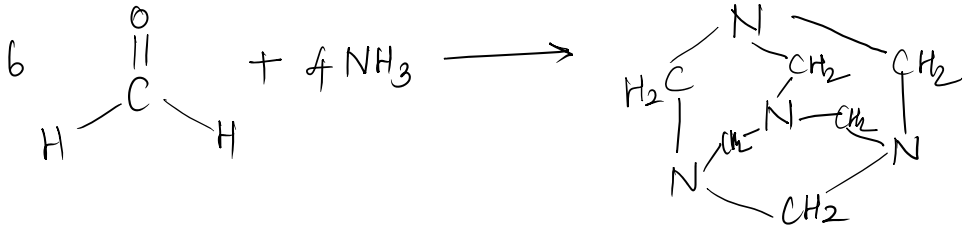


Alkynol

Addn followed by Elimn:



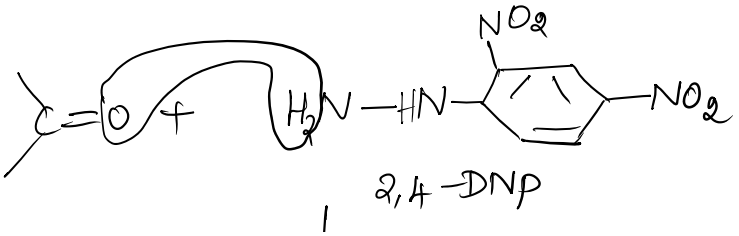




Urotrophine

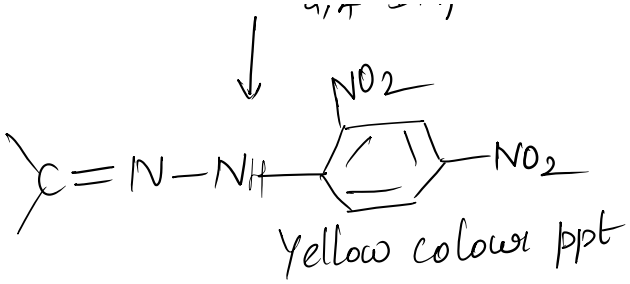
2,4-DNP test → dinitrophenyl hydrazine (Brady's reagent)

→ Test for carbonyl cpd.

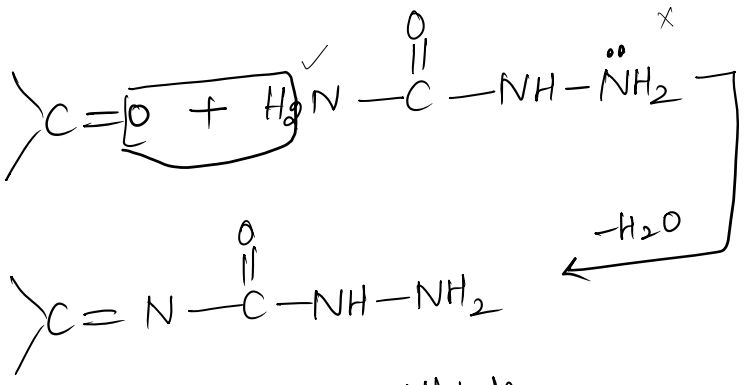


2,4-DNP

1

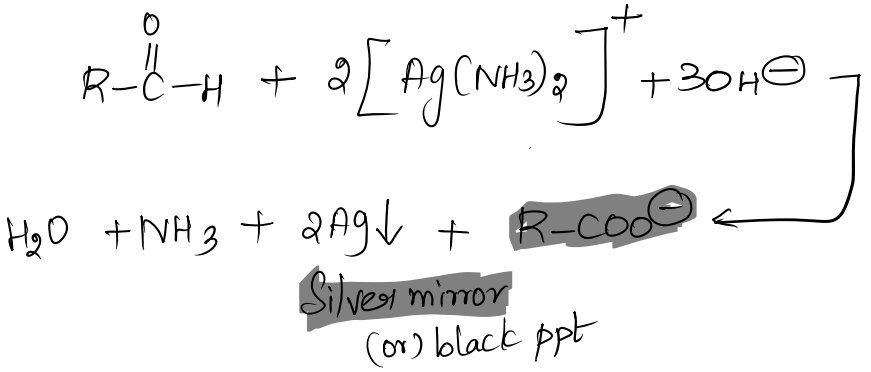


Semicarbazide:



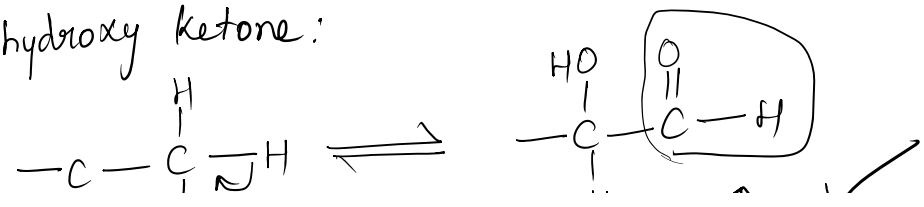
③ Schiff's base → Aldehyde → Pink
→ ketone → No change

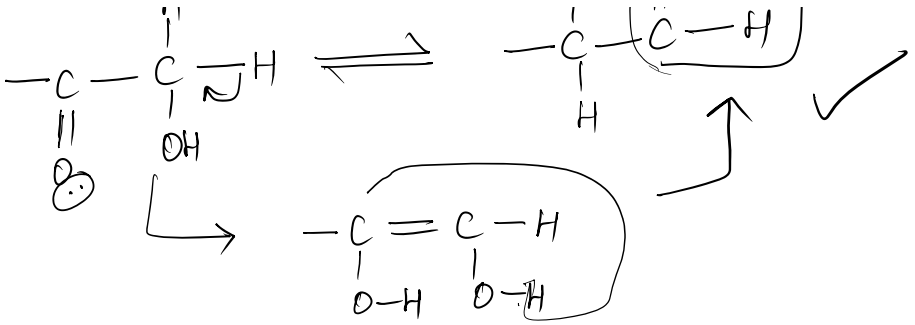
④ Tollens' reagent: Ammoniacal $AgNO_3$
→ Oxidising agent

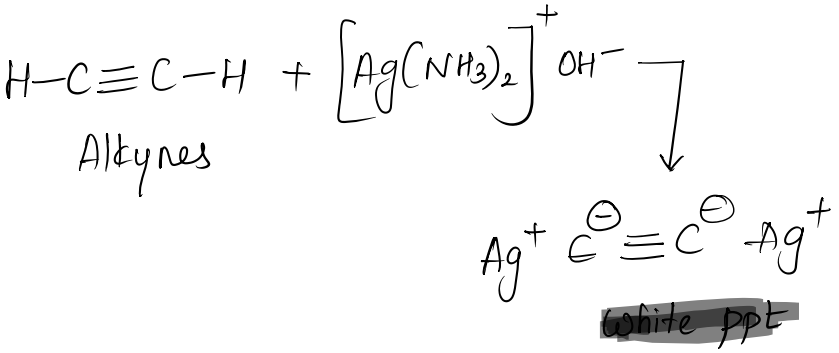


Not for ketones - Only for aldehydes
(Ali (or) Aro)

α-hydroxy ketone:



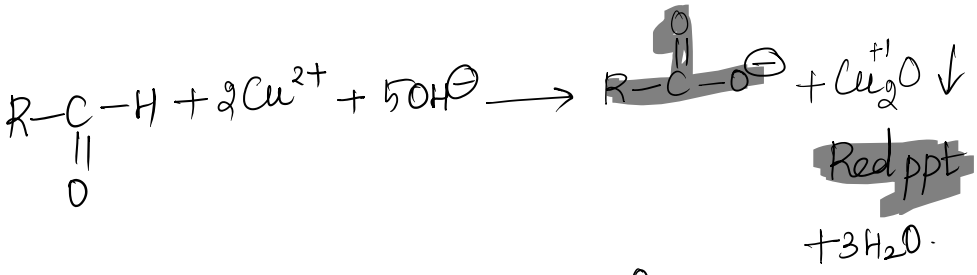




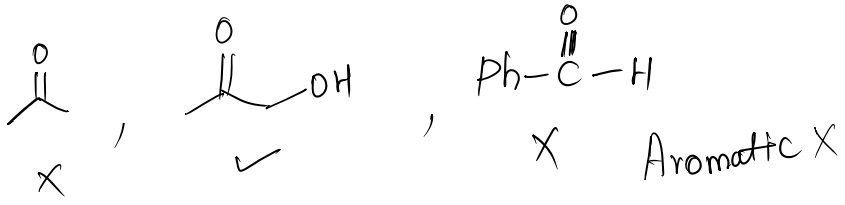
Alkynes

White ppt

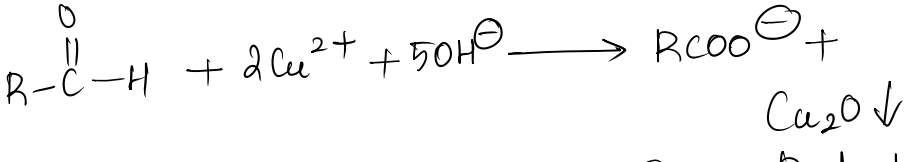
④ Fehling test : — Feh A —
Feh B



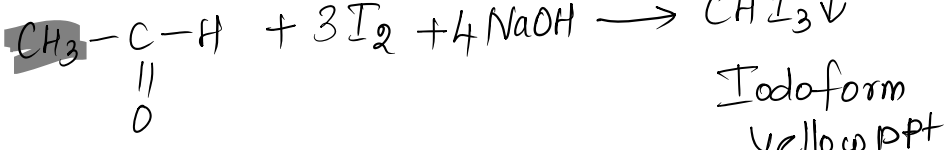
Red ppt



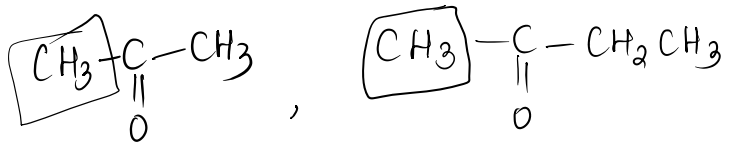
Benedict's Solution : Cupric citrate



Haloform rxn : methyl grp with 



$\overset{O}{\overset{\|}{}}$ → Iodoform yellow ppt



Oxidation:

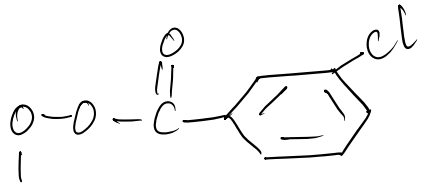
i) $R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[(or)\ K_2Cr_2O_7/H^+]{KMnO_4/H^+} R-COOH$

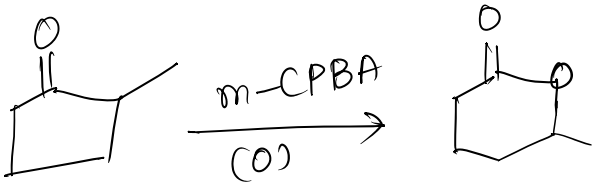
ii) $R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{KMnO_4/H^+} R-COOH + R'COOH$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{(O)} CH_3COOH + HCOOH$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2CH_3 \longrightarrow CH_3COOH + CH_3CH_2COOH$

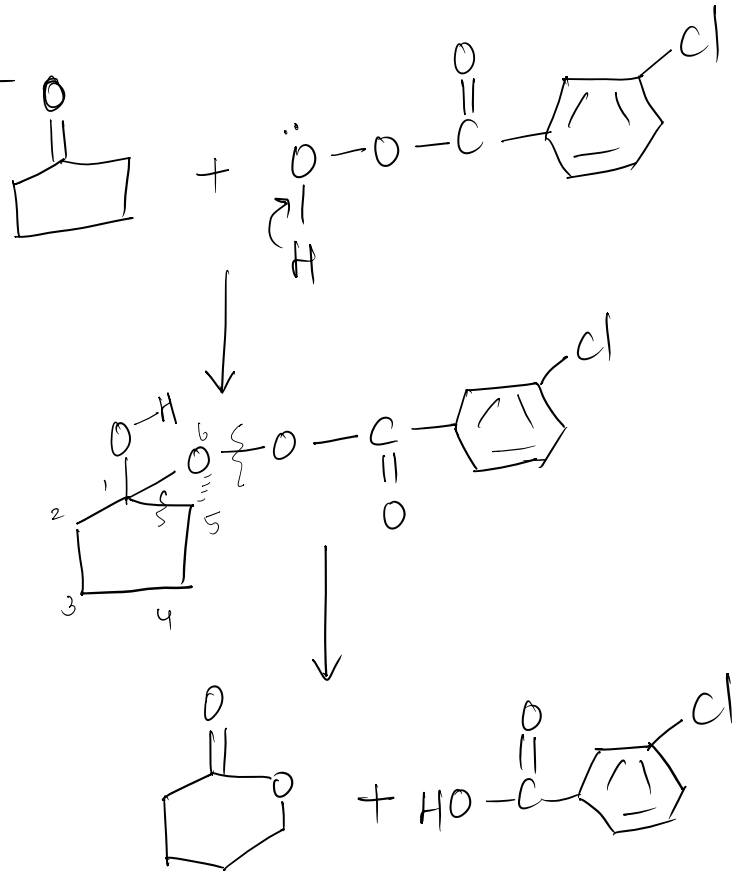
iv) Baeyer-Villiger Oxidn:



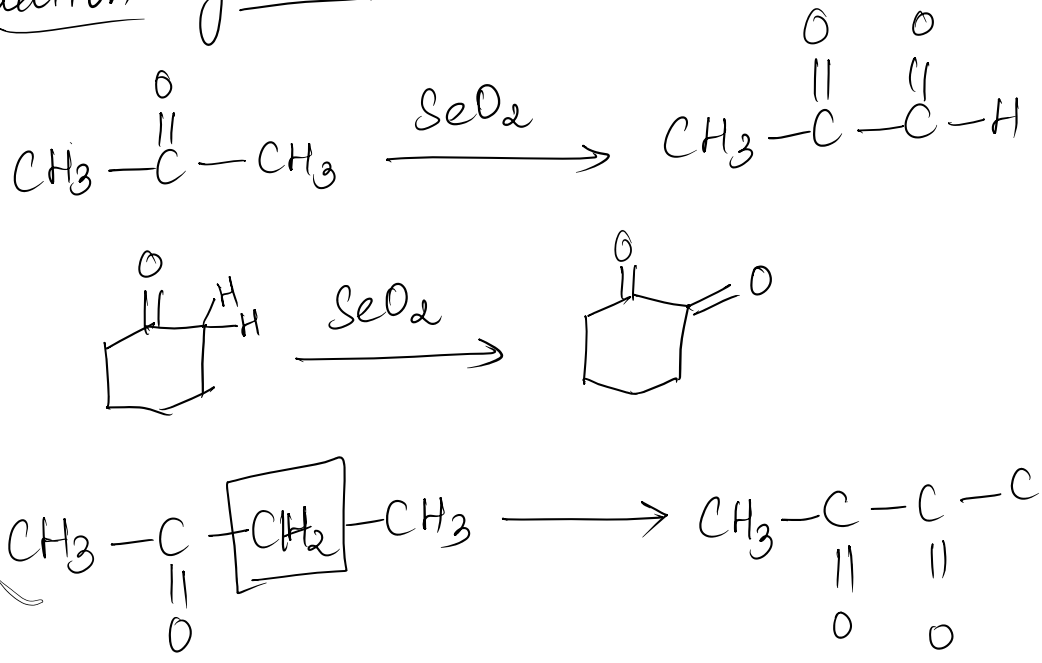


Mech:

Mech:

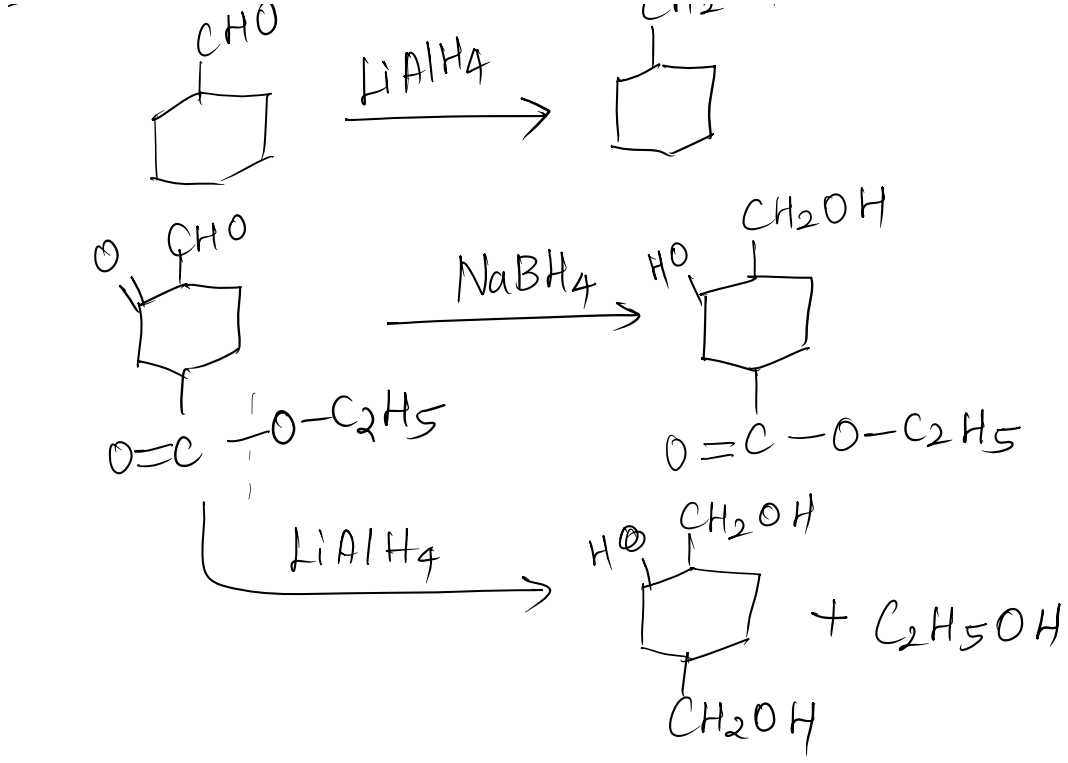


Oxidation by SeO_2:



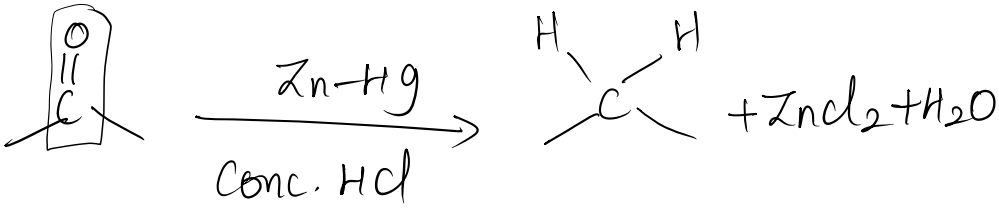
More Substituted Carbon is more preferred.

Reduction:



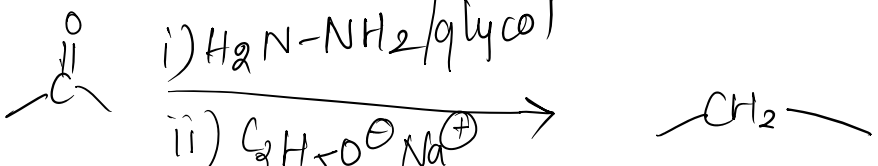
Reduction to hydrocarbon:

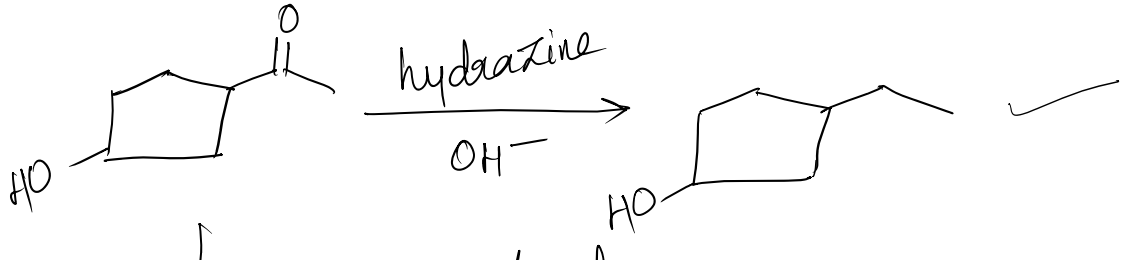
a) Clemmenson Redn:



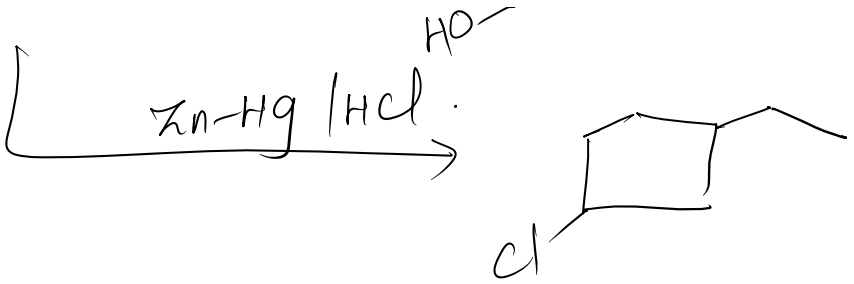
For acid sensitive grp clemmensen can't be used

b) Wolff-kischner redn.





hν



· Red P + HI

$$R-\overset{O}{\overset{\|}{C}}-H + 4HI \xrightarrow{\text{Red P}} R-CH_3 + H_2O + 2I_2$$

Bouveault - Blanc redn:

$$C_6H_5-CHO + C_6H_5CHO \xrightarrow[H_2O]{C_2H_5OH/Na} C_6H_5-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-C_6H_5$$

i) $CH_3-\overset{O}{\overset{\|}{C}}-H + Br_2 \xrightarrow{CH_3COOH} \underset{Br}{CH_2}-CHO$

Aldol. Condensation: α-hydrogen is important

$$2\,CH_3CHO \underset{}{\overset{\text{dil. NaOH}}{\rightleftharpoons}} CH_3-\underset{OH}{CH}-CH_2-CHO$$

Aldol.

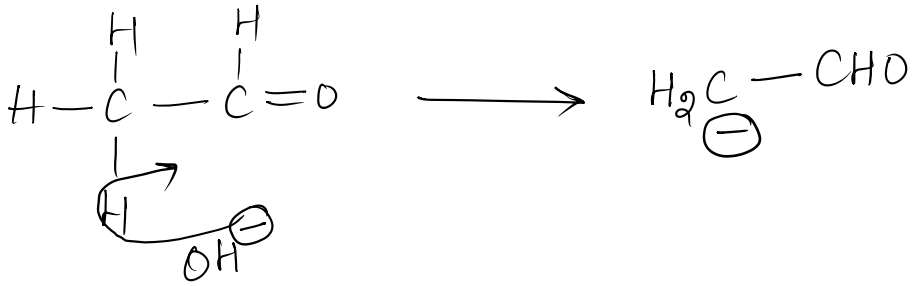
$\downarrow \Delta$

$$\checkmark\ CH_3-\overset{\beta}{C}H=\overset{\alpha}{C}H-CHO$$

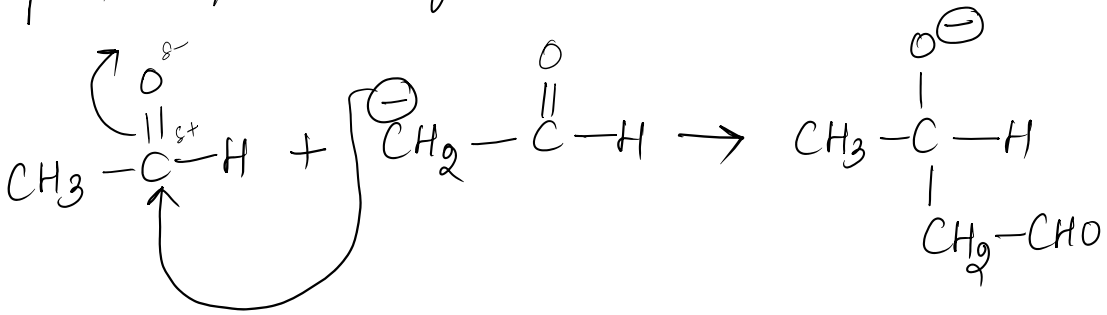
α,β-unsat. aldehyde

Mech:

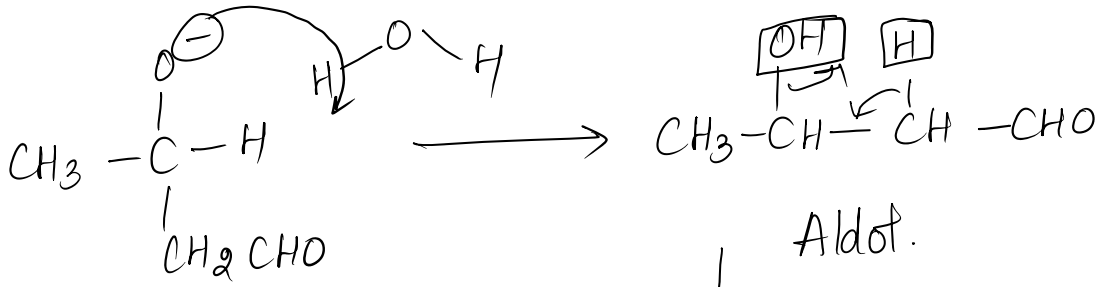
Step: 1 Formn of Carboanion:



Step: 2 Attack of nucleophile



Step 3: Abstraction of $H^{\oplus}$



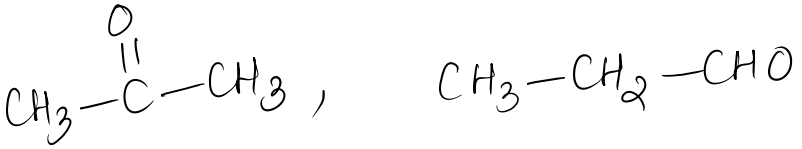
Aldol.

Δ

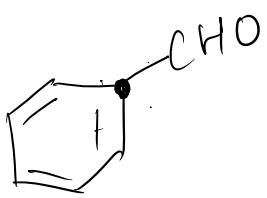
$CH_3-CH=CH-CHO$ $\leftarrow -H_2O$

α,β - Unsat.

Crotonaldehyde.

W.U 

C_6H_5CHO ✗



Cross - Aldol Condensation :

$$C_6H_5CHO + CH_3CHO \rightleftharpoons C_6H_5-\underset{\underset{CH_2-CHO}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

Claisen-Schmidt

$$C_6H_5-CH=CH-CHO \xleftarrow{\Delta}$$

$$CH_3-\overset{\overset{O}{||}}{C}-CH_3 + \underset{B}{CH_3CHO} \longrightarrow (4)$$

A

A-B B-B

B-A A-A.

Intramolecular Aldol :

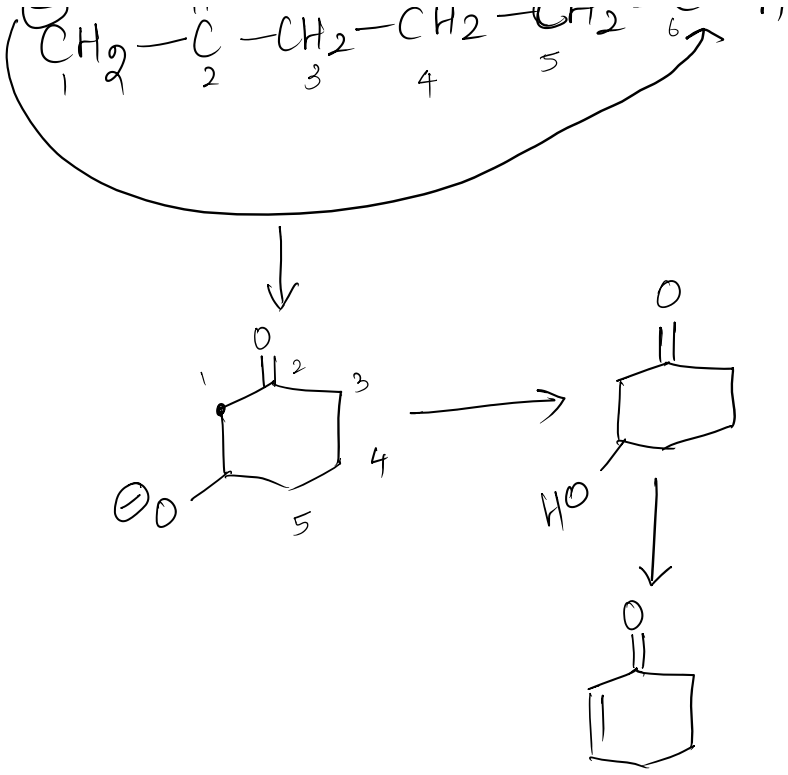
$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{||}}{C}-H \xrightleftharpoons{dil.NaOH}$$

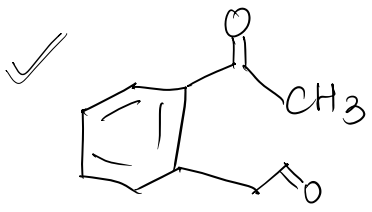
Mech:

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

$\ominus OH$

$$\overset{\ominus}{C}H_2-\underset{2}{\overset{\overset{O}{||}}{C}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{\overset{\overset{O}{||}}{C}}-H$$

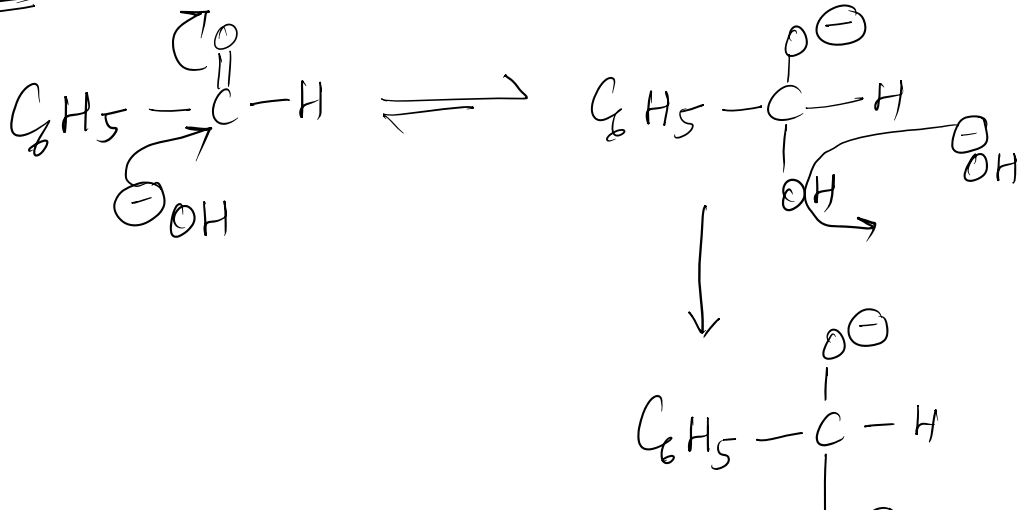


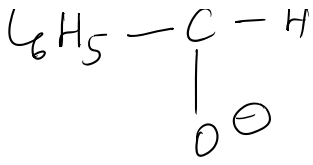


Cannizzaro Rxn: No α-Hydrogens.

$$2C_6H_5-CHO \xrightleftharpoons{NaOH} C_6H_5COO^-Na^+ + C_6H_5CH_2OH$$

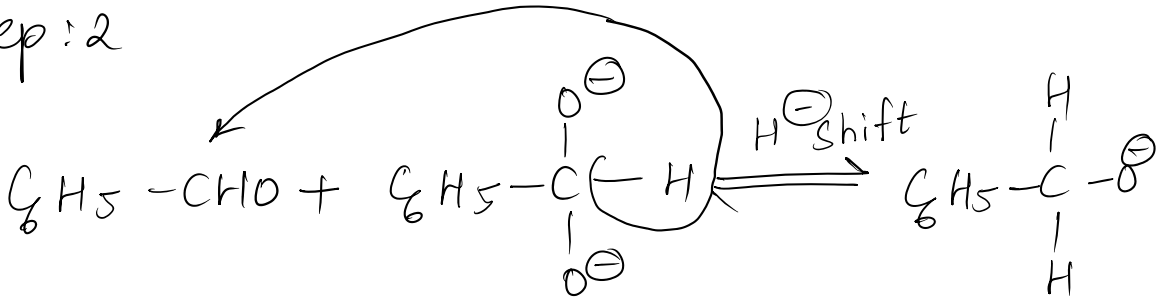
Mech:

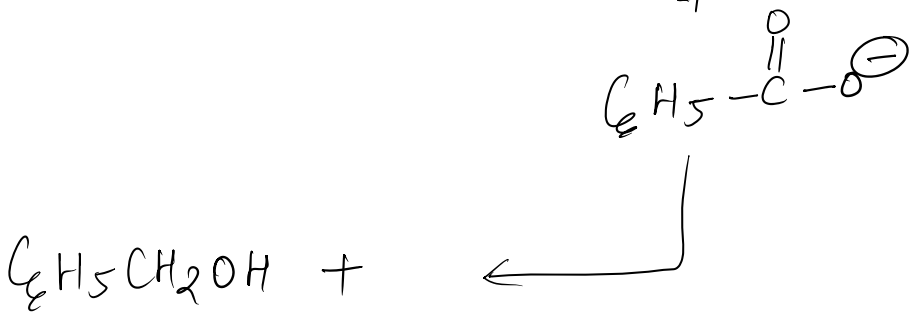


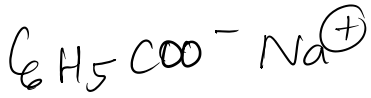


dianion.

Step : 2



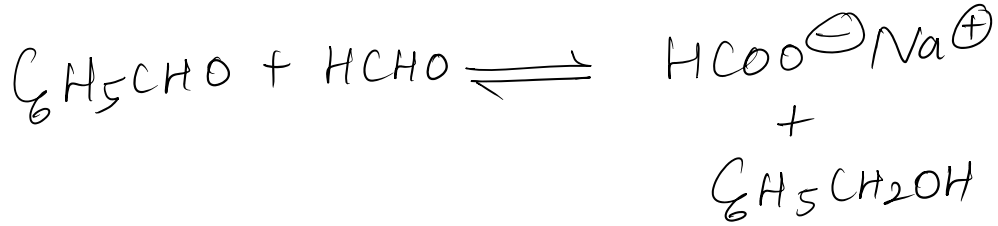




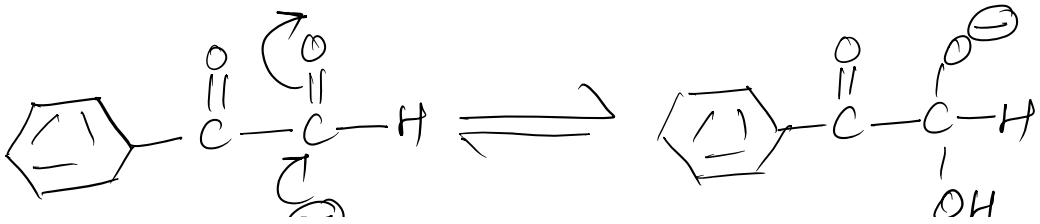
$$Rate = k[C_6H_5CHO]^2[OH^-]^2$$

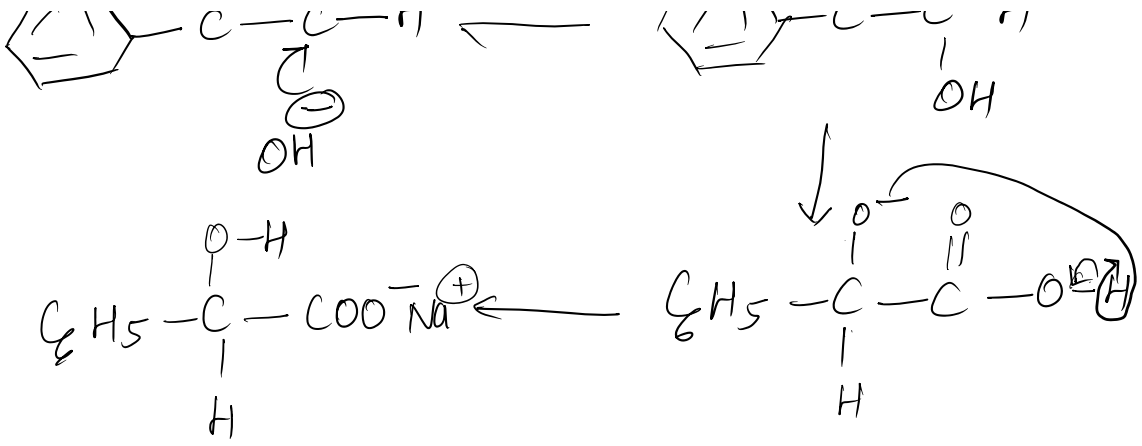
Order = 4

Crossed Cannizzaro:



Intramolecular Cannizzaro rxn:

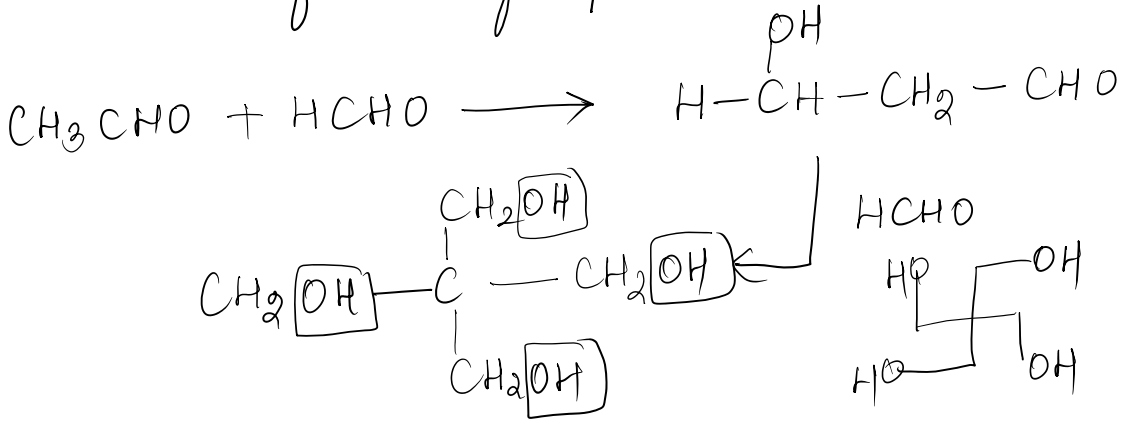




Eq:

$$CH_3CHO + HCHO \xrightarrow[\text{excess}]{\text{Conc. NaOH}} A \qquad (4)$$

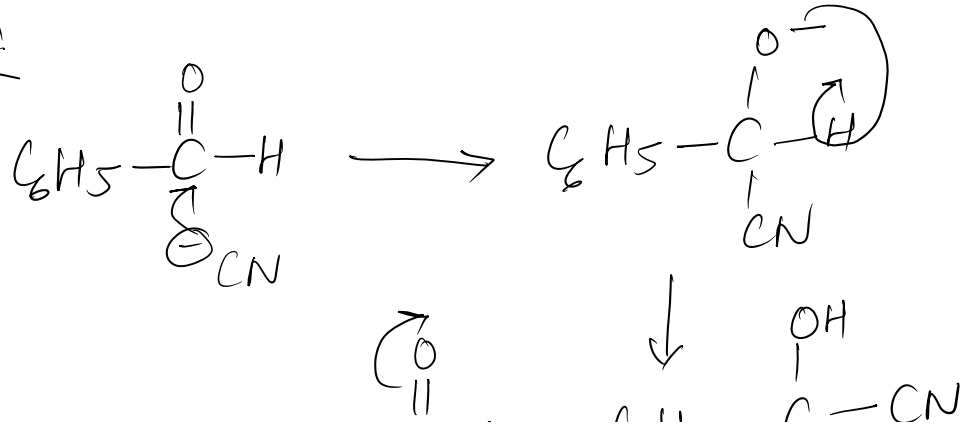
no. of OH groups in A ?

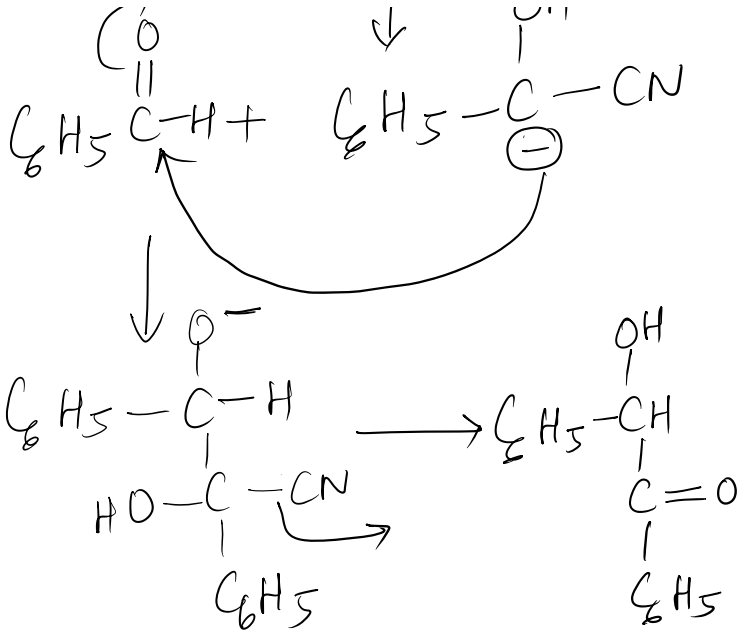


Benzoin Condensation:

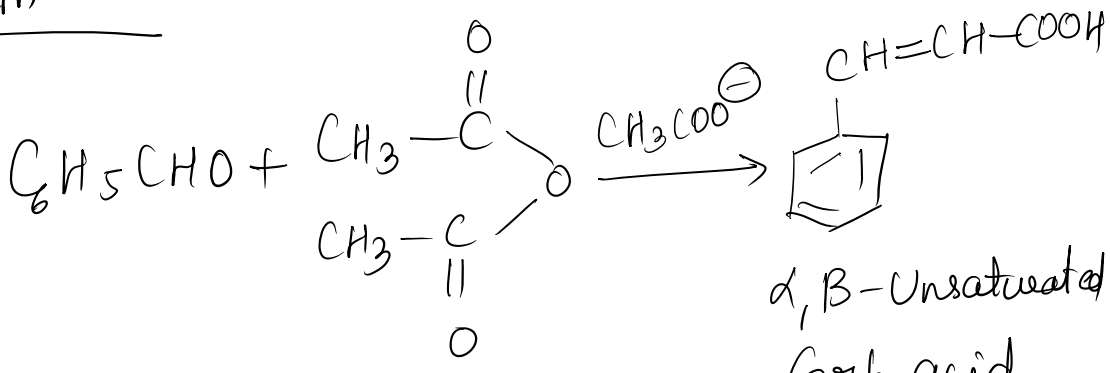
$$C_6H_5CHO \underset{\text{or KCN}}{\overset{NaCN}{\rightleftharpoons}} C_6H_5-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{C}-C_6H_5$$

Mech:

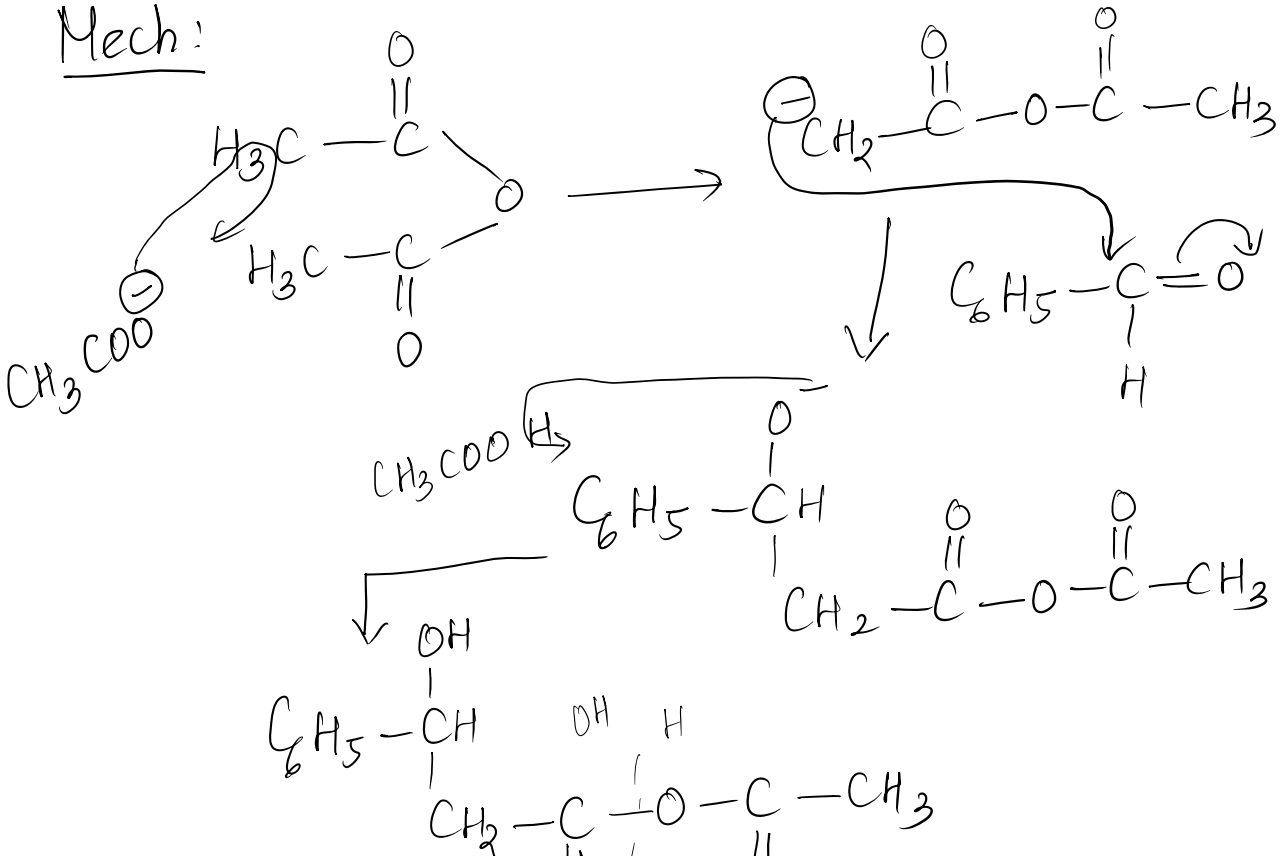


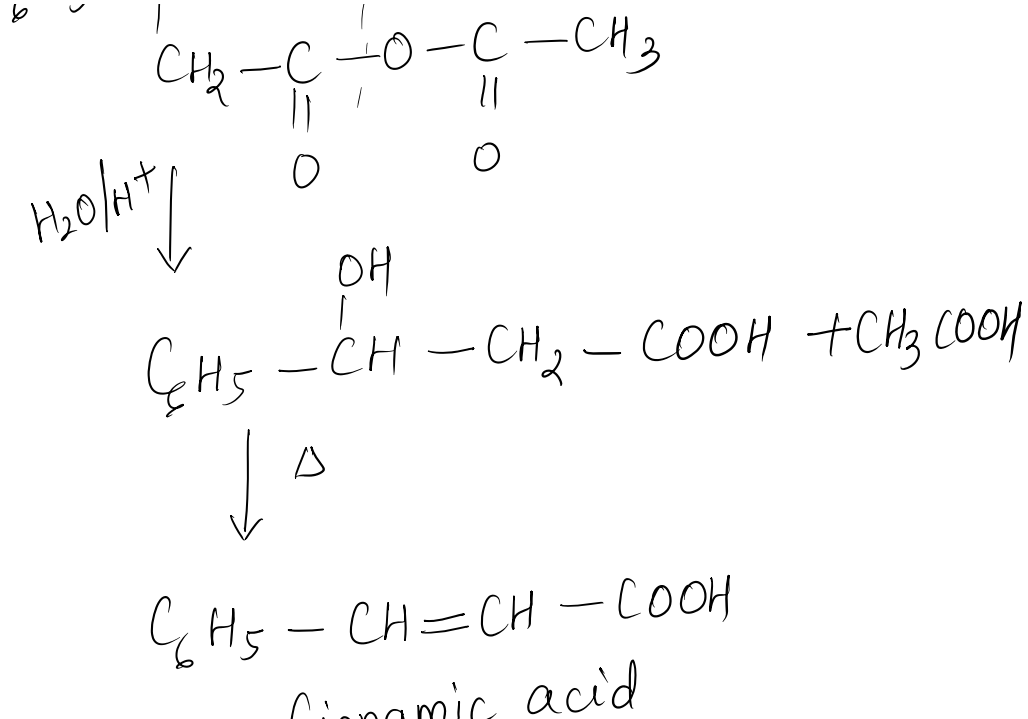


Perkin rxn:

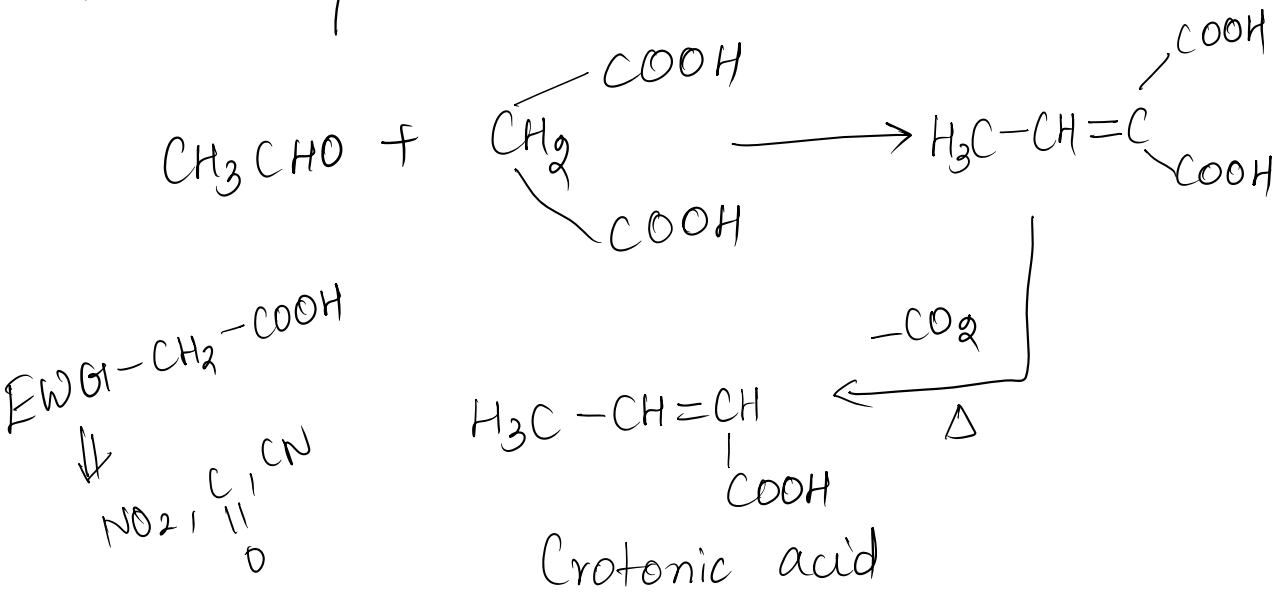


Mech:

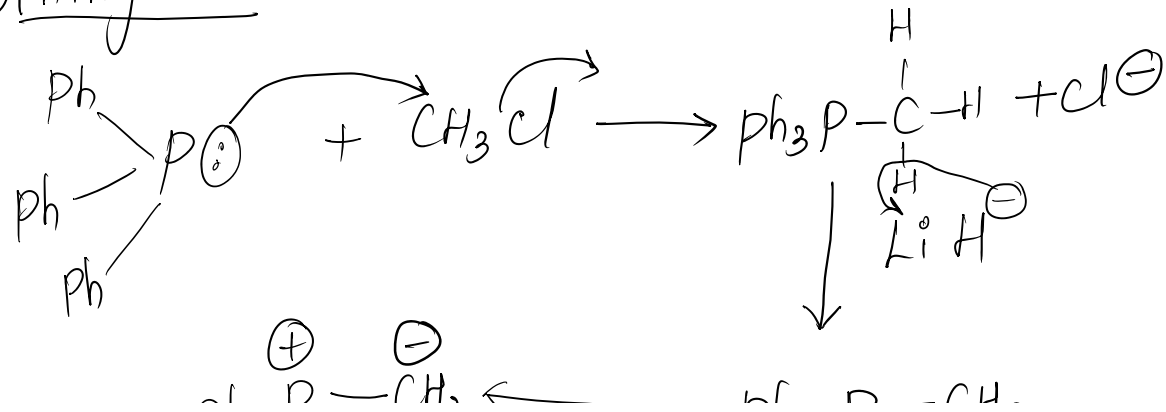


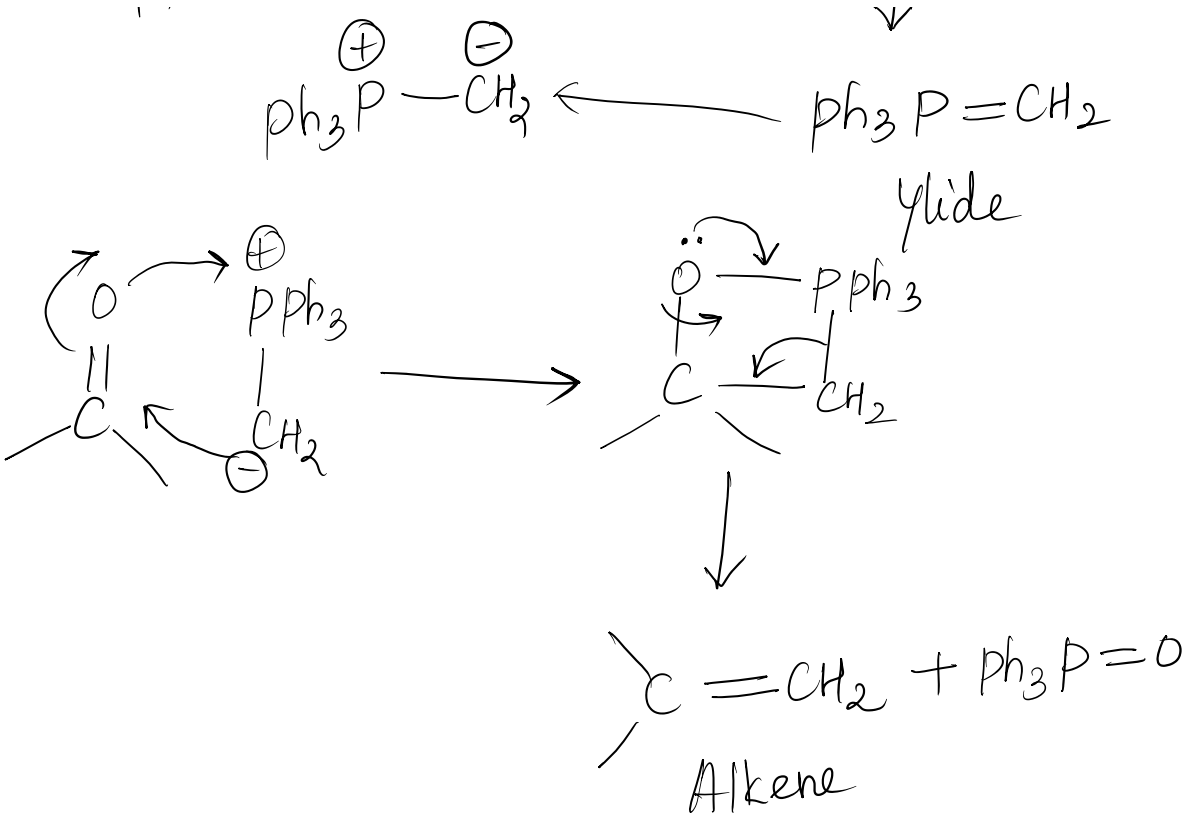


Knoevenagel rxn:

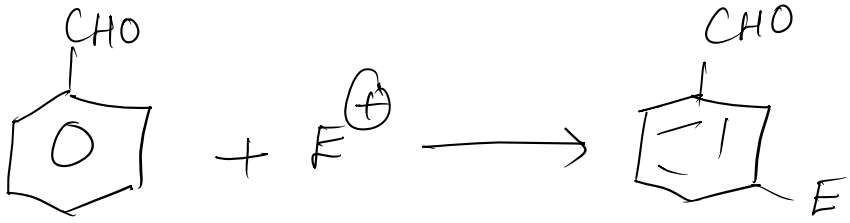


Wittig Rxn:





Electrophilic Substitution.



It won't undergo F.C rxn.

Carboxylic acid (R-COOH)

Naming ⇒ 'oic acid'

Preparation:

(1) Oxidation:

$$R-CH_2OH \xrightarrow{KMnO_4} R-COOH$$

$KMnO_4 / K_2Cr_2O_7 / Conc.\ H_2SO_4 / CrO_3$

(2) Unsat. alcohols:

$$HC\equiv C-CH=CH-CH_2OH \xrightarrow[Acetone]{CrO_3, H_2SO_4} HC\equiv C-CH=CH-COOH$$

$$\text{>C=O} \xrightarrow{(O)} CH_3COOH + HCOOH.$$

Haloform

$$R-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{X_2/OH^-} R-COO^{\ominus} + CHX_3$$

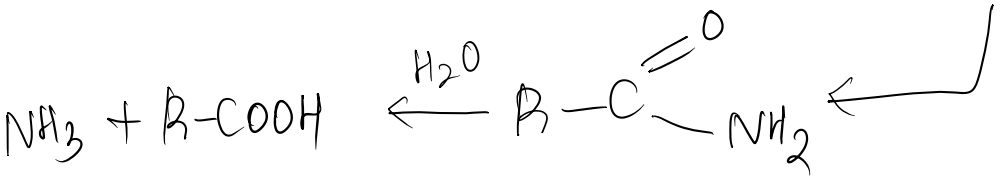
Haloform.

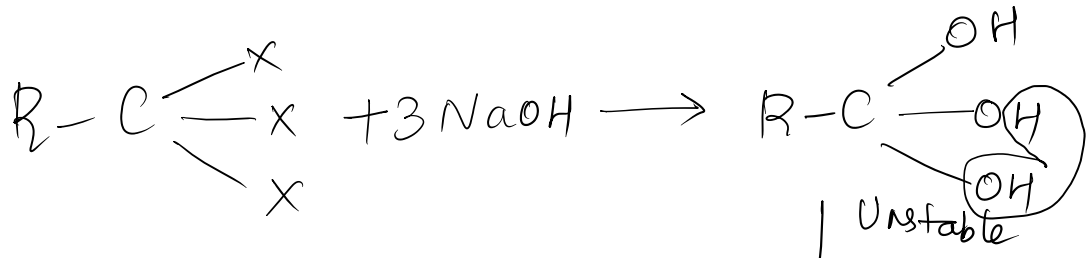
Alkyl cyanides:

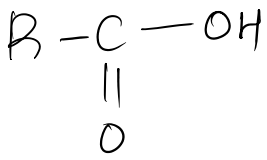
$$R-C\equiv N + H_2O \xrightarrow{H^+/OH^-} \left[R-C(OH)=NH\right]$$

Imidol

Imidol

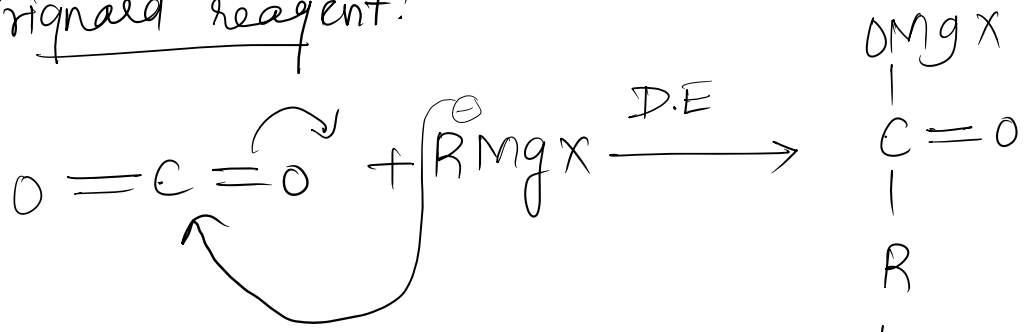


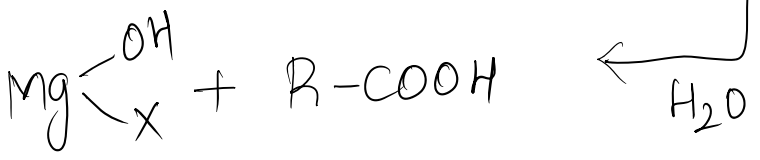




$CHCl_3 + 3NaOH \longrightarrow HCOOH$

Grignard reagent:





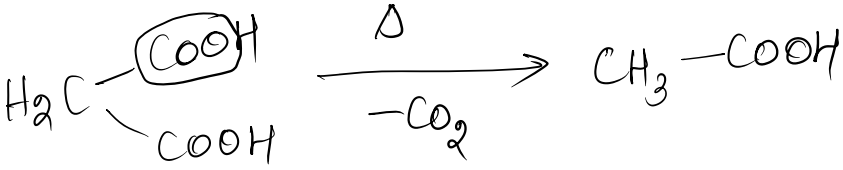
Hydrolysis of ester:

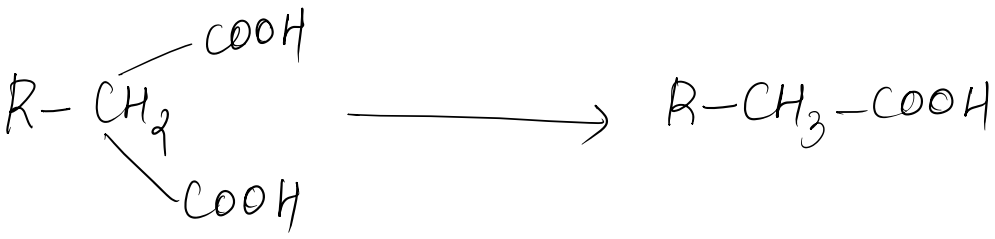
Hydrolysis of ester:

$$RCOOR' + H_2O \longrightarrow R\text{-}COOH + R'OH$$

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

6. Action of heat

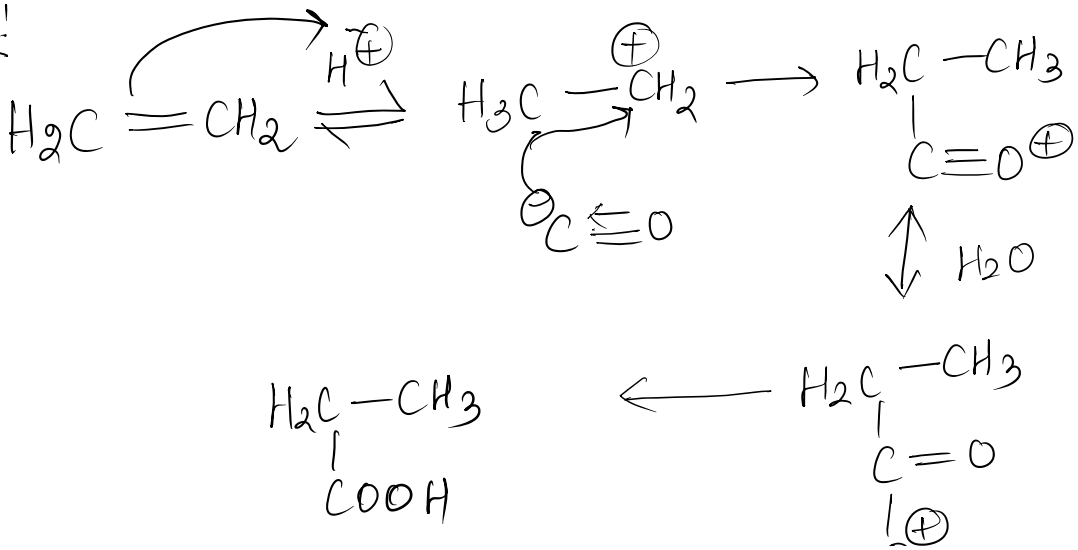


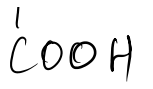


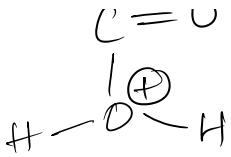
(7) Koch Rxn:

$$H_2\overset{1}{C}=\overset{2}{C}H_2 + \overset{3}{C}O + H_2O \xrightarrow{H_3PO_4} CH_3\text{-}CH_2\text{-}COOH$$

Mech:







$$RCONH_2 + H_2O \longrightarrow RCOOH + NH_3$$

Amide $\xrightarrow{HNO_2}$ $RCOOH + N_2 + H_2O$

$$RCOCl + H_2O \longrightarrow RCOOH + HCl$$

acyl chloride $\xrightarrow{NaOH}$ $RCOO^- Na^+$

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R' + H_2O \longrightarrow R-COOH + R'COOH$$

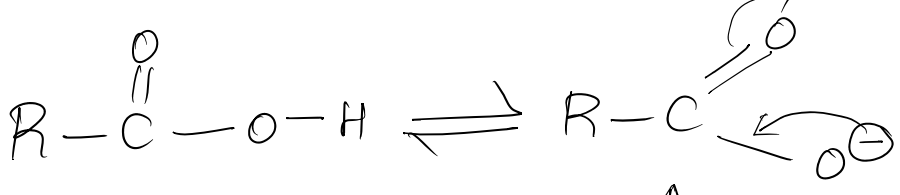
anhydrides

Physical prop

↑ b.pt as size ↑

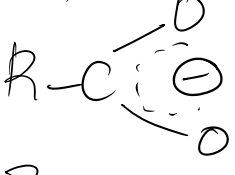
↑ than hydrocarbon.

ka ↑ acidity ↑



EWG ⇒ ↑ acidity

EDG ⇒ ↓ acidity



Resonance Stability

Chemical prop:

1. $RCOOH \rightleftharpoons RCOO^- + H^+$

   - $\xrightarrow{Na} RCOO^- Na^{\oplus}$
   - $\xrightarrow{NH_4OH} RCOO^{\ominus}NH_4^{\oplus}$

2. Carbonates / Bicarbonates.

$$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + CO_2$$

- $\xrightarrow{NaHCO_3} CH_3COONa + CO_2$
- $\xrightarrow{CaCO_3} (CH_3COO)_2Ca + CO_2$

$CO_2 \Rightarrow$ Not Carb. acid
↳ from Carbonate.

$$R-COO^{18}H + NaCO_3 \longrightarrow R-COO^{18}Na + CO_2$$

4) $RCH_2MgBr + RCOOH \xrightarrow{Ether} R'CH_3 + RCOOMgBr$

$$RCOOH + CH_3Li \longrightarrow CH_4 + RCOOLi$$

a) $RCOOH + HOR' \longrightarrow RCOOR'$

Ester

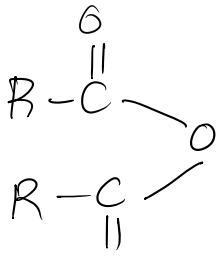
b) $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

$PCl_3 \longrightarrow CH_3COCl + H_3PO_3$

$SOCl_2 \longrightarrow CH_3COCl + SO_2\uparrow + HCl\uparrow$

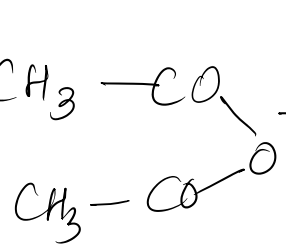
more yield

c) $R-COOH + RCOOH \xrightarrow[(or)\ Conc.H_2SO_4]{P_2O_5, \Delta}$



Anhydride

$CH_3COONa + CH_3COCl \xrightarrow{\Delta}$



$+ NaCl.$

$HCOOH + HCOOH \xrightarrow{160^\circ C} 2CO_2 + H_2O$

$RCOOH + NH_3 \longrightarrow RCOO^-NH_4^+$

$\xrightarrow{\Delta}$ $R-CONH_2$ $\xrightarrow{\Delta, -H_2O}$ $R-CONH_2$

Amide

$R-CONH_2 \xrightarrow[-H_2O]{\Delta} RCN$

Cyanide

Cyanide ... Amide

$$R\text{-}COOH + H_2 \xrightarrow{LiAlH_4} R\,CH_2OH$$

$$H_2C(COOH)_2 \xrightarrow{140\text{-}160^\circ C} CH_3COOH + CO_2$$

Kolbe's Synthesis.

$$RCOONa \rightleftharpoons RCOO^- + Na^{\oplus}$$

Anode: $RCOO^- \longrightarrow R\text{-}R + 2CO_2 + 2e^-$

Cathode: $2Na^{\oplus} + 2e^- \longrightarrow 2Na \xrightarrow{2H_2O} 2NaOH$

$$CH_3COONa + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3\text{-}CH_3$$

$$CH_3COOAg + Br_2 \xrightarrow{CCl_4} CH_3Br + AgBr + CO_2\uparrow$$

Schmidt rxn:

$$RCOOH + N_3H \longrightarrow \underset{\text{Amine}}{RNH_2} + CO_2 + \underset{}{N_2\uparrow}$$

$$RCOOH + \underset{\text{ketene}}{CH_2CO} \longrightarrow \underset{\text{Anhydrides}}{(CH_3CO)_2O}$$

Ketene

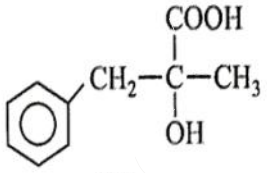
Anhydrides

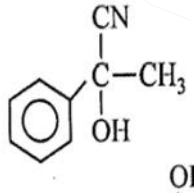
HVZ rxn

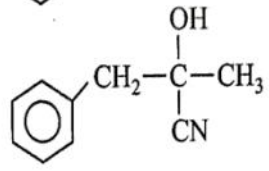
$$CH_3COOH + Cl_2 \xrightarrow[\Delta]{\text{Red P}} \underset{\displaystyle Cl}{\overset{\displaystyle |}{CH_2}}-COOH + HCl.$$

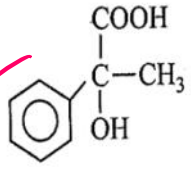
In set of reactions, identify D.

$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{Anhydrous } AlCl_3]{\text{Benzene}} B \xrightarrow{HCN} C \xrightarrow{H_2O} D$$

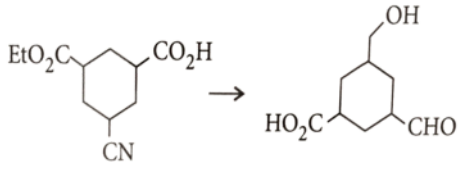
(a) 

(b) 

(c) 

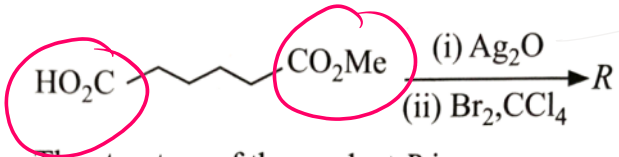
(d) 

The reagent(s) required for the following conversion are

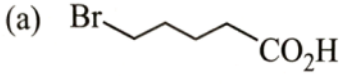


(A) (i) $LiAlH_4$, (ii) H_3O^+
(B) (i) B_2H_6, (ii) DIBAL-H, (iii) H_3O^+
(C) (i) B_2H_6, (ii) $SnCl_2/HCl$, (iii) H_3O^+
(D) $NaBH_4$, (ii) Raney Ni/H_2, (iii) H_3O^+

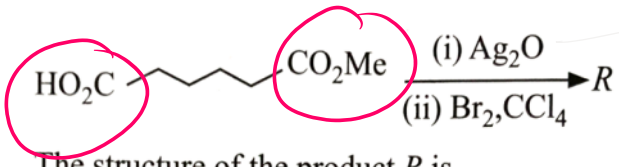
The reaction sequence given below gives product R.



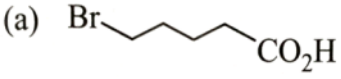
The structure of the product *R* is

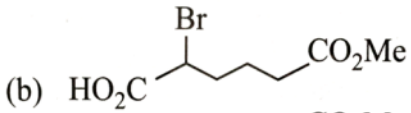
(a) 

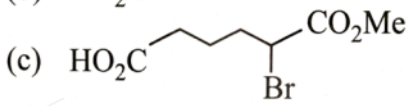
The reaction sequence given below gives product R.

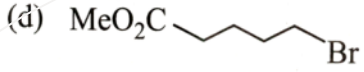


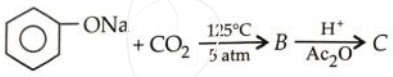
The structure of the product *R* is

(a) 

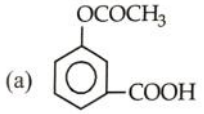
(b) 

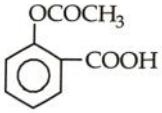
(c) 

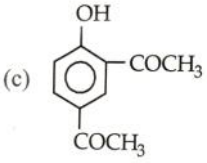
(d) 

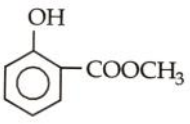


The major product *C* would be

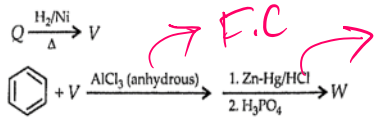
(a) 

(b) 

(c) 

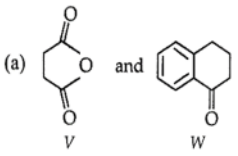
(d) 

In the following reaction sequences V and W are, respectively



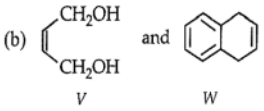
F.C → clemmensen.

CH_2

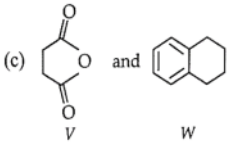
(a)  and

V W

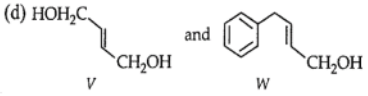
X

(b) 

V W

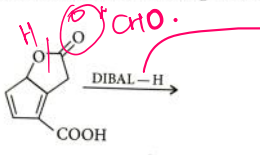
(c) 

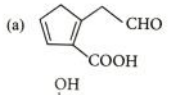
V W

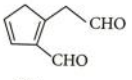
(d) 

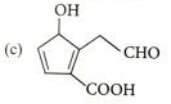
V W

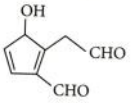
The major product obtained in the following reaction is



(a) 

(b) 

(c) 

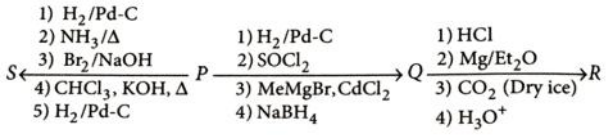
(d) 

✓

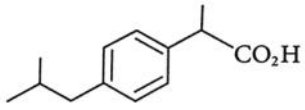
→ cyanide, ester lactone / amide, Carb. acid.

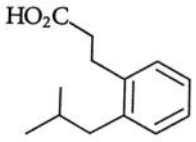
↳ -CHO

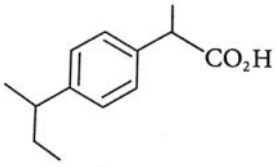
An organic acid P ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes another set of reactions to product S.



The compound R is

(a) 

(b) 

(c) 

(d)