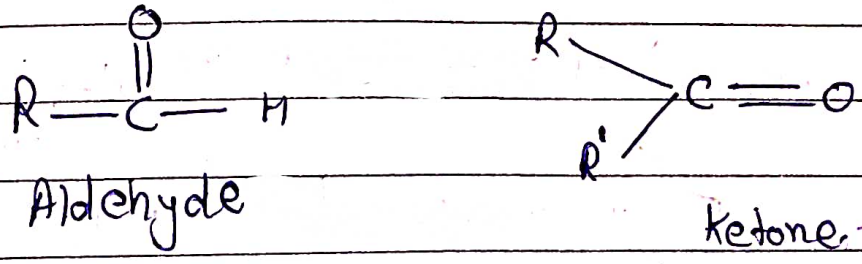
ALDEHYDE, KETONE & CARBOXYLIC ACID



Aldehyde

Ketone.

⇒ Preparation of Aldehyde

(1) By oxidation of primary Alcohol:-

$$CH_3CH_2OH \xrightarrow[KMnO_4]{K_2Cr_2O_7} CH_3CHO$$

ethanol

$$CH_3CH=CHCH_2OH \xrightarrow{PCC} CH_3CH=CHCHO$$

(2) By dehydrogenation of primary Alcohol:-

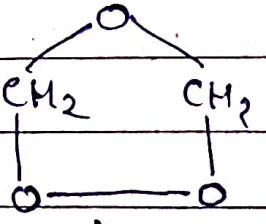
$$CH_3CH_2OH \xrightarrow[557\ K]{Cu} CH_3CHO + H_2\uparrow$$

$$CH_3CH=CHCH_2OH \xrightarrow[557\ K]{Cu} CH_3CH=CHCHO$$

(3) From hydrocarbon:-

(a) By Ozonolysis:-

$$CH_2=CH_2 + O_3 \longrightarrow$$



$$\xrightarrow{Zn/H_2O_2} 2HCHO.$$

$$CH_3-CH=CH_2 + O_3 \xrightarrow{Zn/H_2O_2} CH_3CHO + HCHO$$

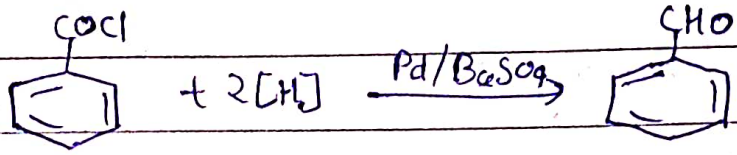
(b) By hydration of alkyne.

$$CH\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} CH_2=CH(OH) \xrightarrow{\text{Tautomerism}} CH_3CHO$$

or $CH_3-\overset{O}{\overset{\|}{C}}-H$

(4) From Acetyl chloride (Rosenmund Reduction)

$$CH_3COCl + 2[H] \xrightarrow{Pd/BaSO_4} CH_3CHO + HCl$$



Benzaldehyde.

(5) From nitriles (Stephen reaction)

$$CH_3CN + 2[H] \xrightarrow{SnCl_2/HCl} CH_3-CH=NH \xrightarrow{H_2O} CH_3CHO + NH_3 \uparrow$$

ethanol

$$CH_3CH_2CH=CHCH_2CN + 2[H] \xrightarrow[(ii)\ H_2O]{(i)\ AlH(i\text{-}Bu)_2} CH_3CH_2CH=CHCH_2CHO$$

Hexan-3-enal

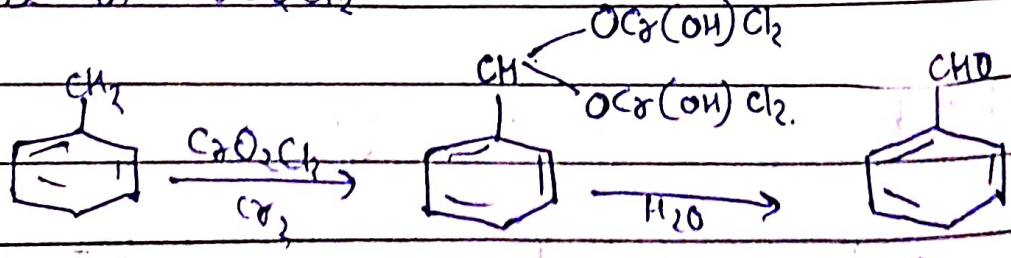
(6) From ether ester

$$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL-H} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H + C_2H_5OH$$

⇒ Preparation of Benzaldehyde :-

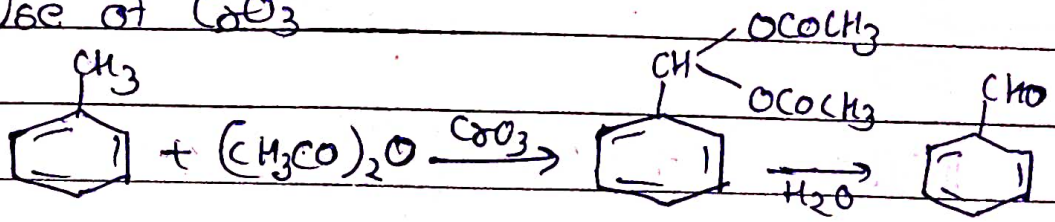
(1) By oxidation of toluene (Ethanol Rxn)

(a) Use of CrO_2Cl_2

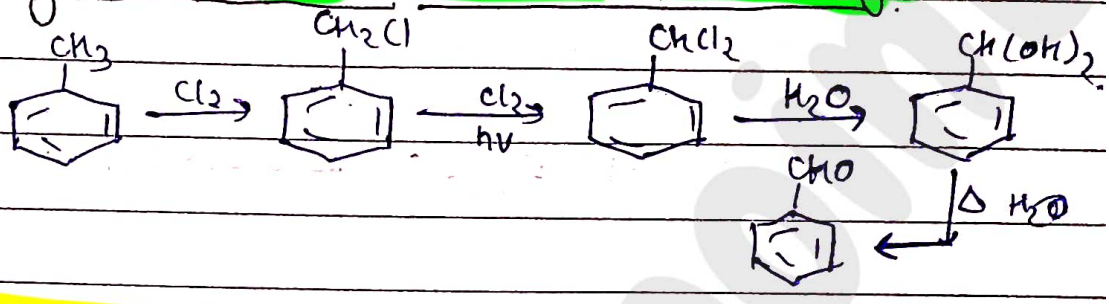


Benzaldehyde

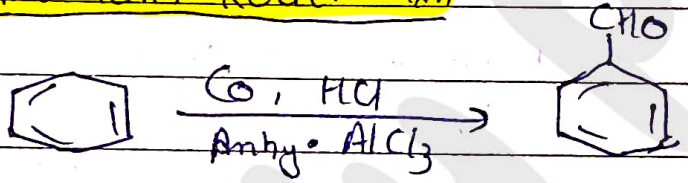
(b) Use of CrO_3



(2) By Side chain chlorination of Methyl

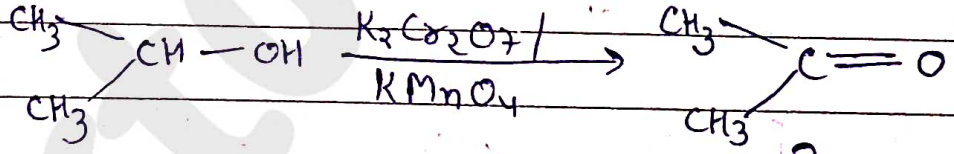


(3) Gattermann koach Rxn



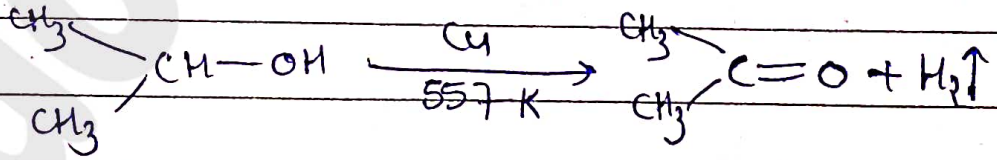
⇒ Preparation of Ketone

(1) By oxidation of Secondary Alcohol



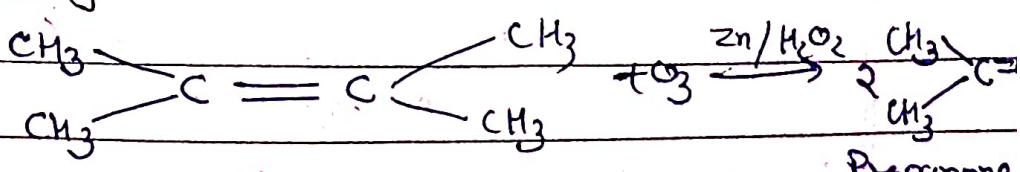
Propanone

(2) By dehydrogenation of Secondary Alcohol



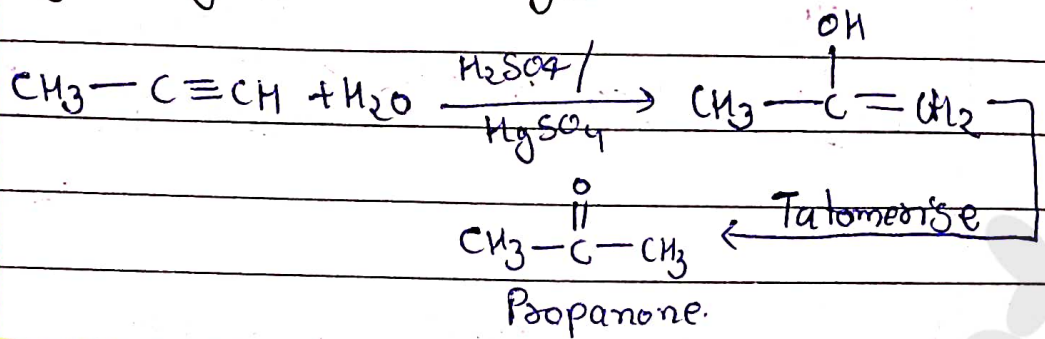
(3) From Hydrocarbon

(a) Ozonolysis

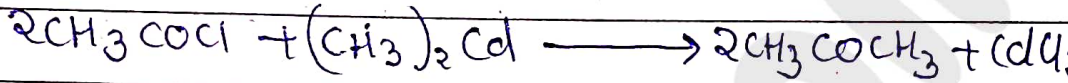


Propanone

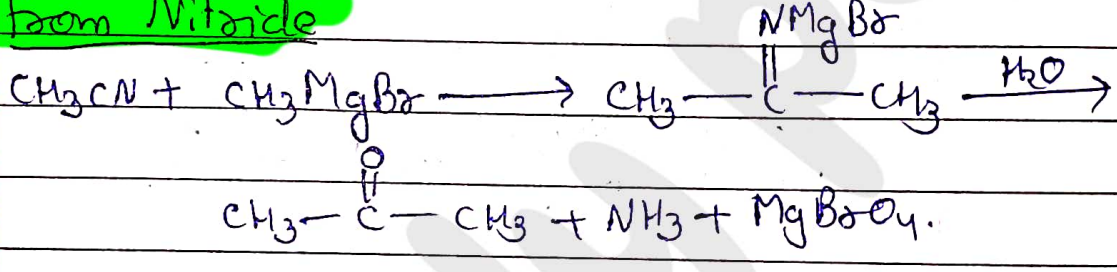
(b) By Dehydration of Alkyne:-



(4) From Acyl Chloride

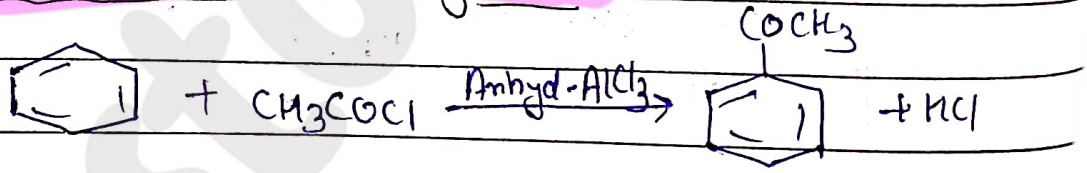


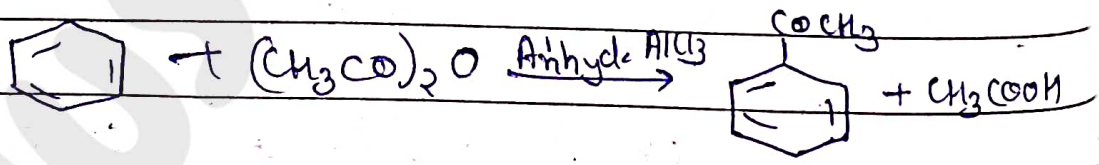
(5) From Nitride



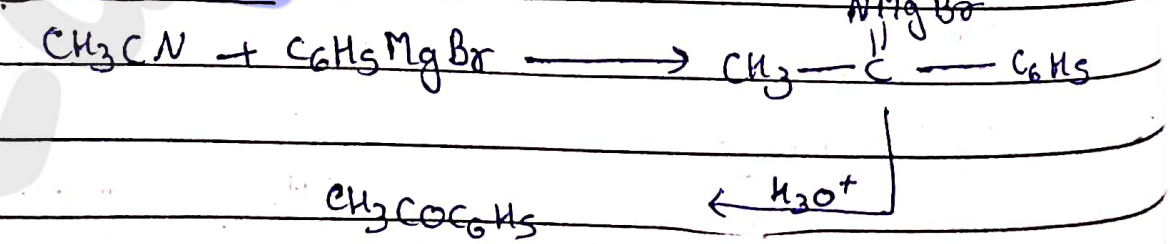
⟹ Preparation of Aromatic Ketone

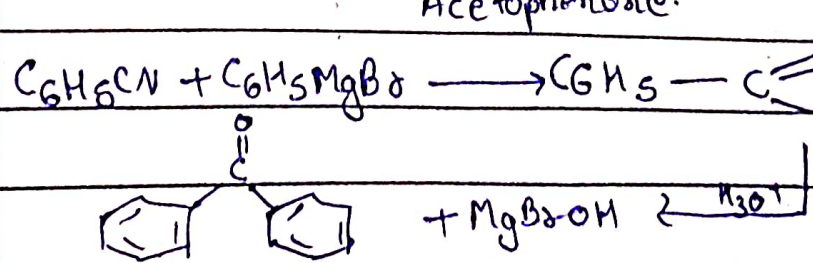
(1) From Friedel Craft Acylation





(2) From Nitride





⇒ Physical properties:-

① Boiling point:-

$CH_3CH_2CH_2CH_3 < CH_3CH_2CH_2CHO < CH_3CH_2COCH_3$
$< CH_3CH_2CH_2CH_2OH$

Aldehyde & Ketone have higher B.P. as Compared to hydrocarbon due to polar nature of Carbonyl group & also have strong dipole-dipole interaction.

Alcohol have higher B.P. as Compared to isomeric aldehyde & Ketone due to Capability of formation of intermolecular H-Bond.

② Solubility:-

Both Aldehyde & Ketone (lower molecule) are Soluble in water due to formation of intermolecular H-Bonding with water molecules.

⇒ Chemical property

Reactivity order $HCHO > CH_3CHO > CH_3COCH_3$

① Nucleophilic Addition Reaction

(a) Addition of HCN

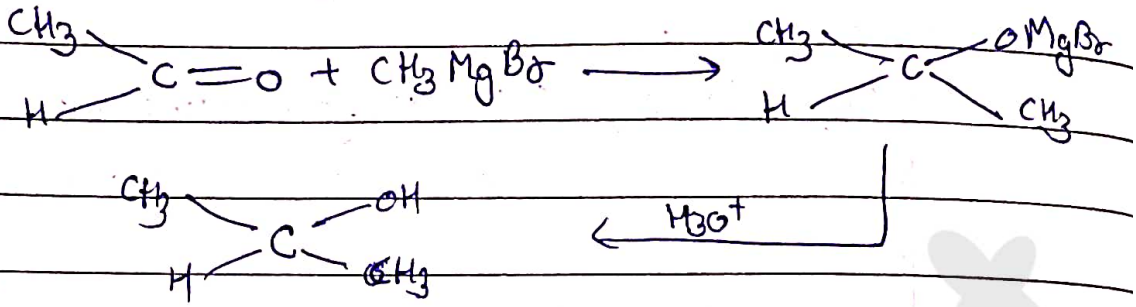
$$>C=O + HCN \longrightarrow >C\begin{matrix}OH\\CN\end{matrix}$$

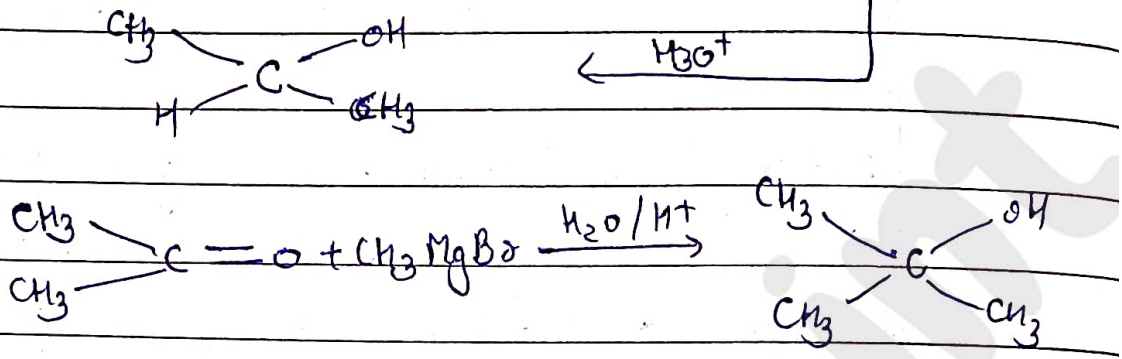
Cyanohydrine.

(b) Addition of Sodium Hydrogen Sulphite.

$$>C=O + NaHSO_3 \longrightarrow >C\begin{matrix}OH\\SO_3Na\end{matrix}$$

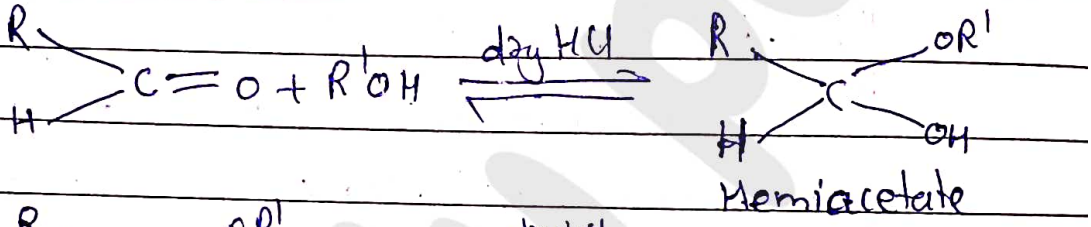
(c) Addition of Grignard Reagent:-



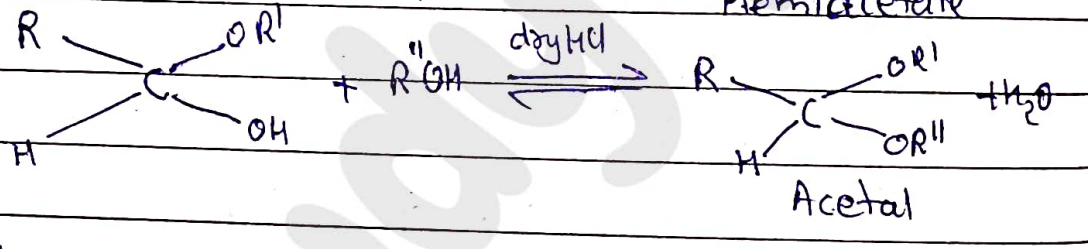


2-Methyl-propane-2-ol

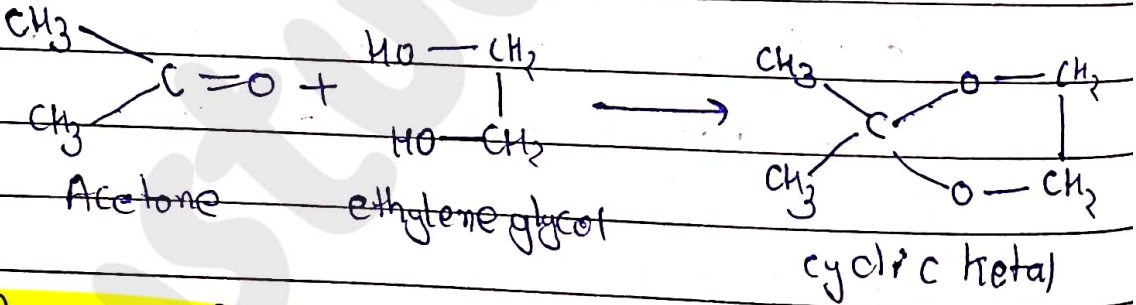
(d) Addition of Alcohol :-



Hemiacetate



Acetal

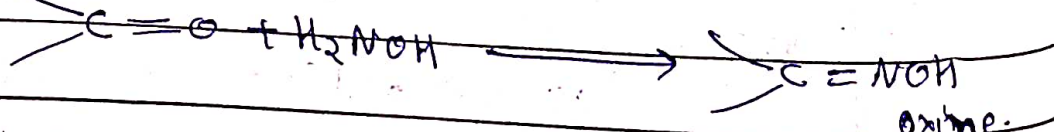


Acetone ethylene glycol cyclic ketal

(2) Reaction of Carbonyl oxygen with other molecules

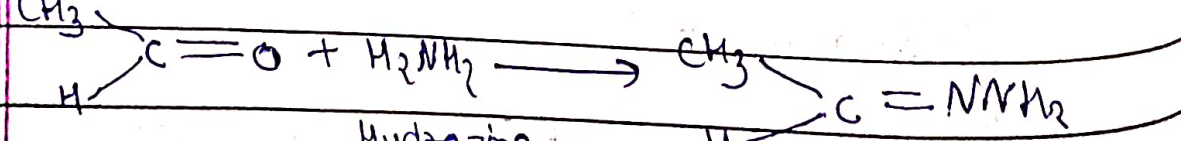
(a) Reacⁿ with Ammonium derivative-

(i) Rxn with hydroxylamine.



oxime.

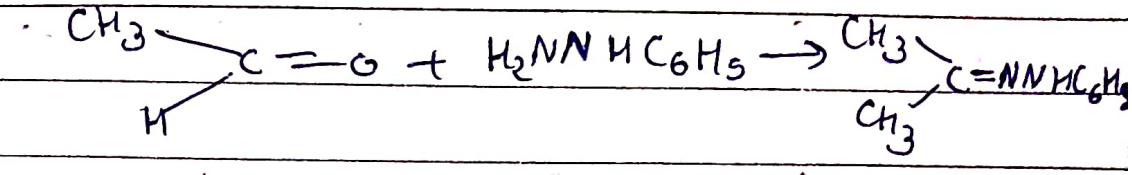
(ii) Reaction with hydroxine:-

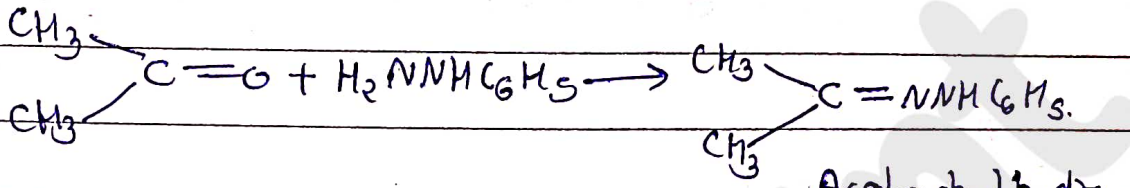


Hydrazine

Acetaldehydrazone.

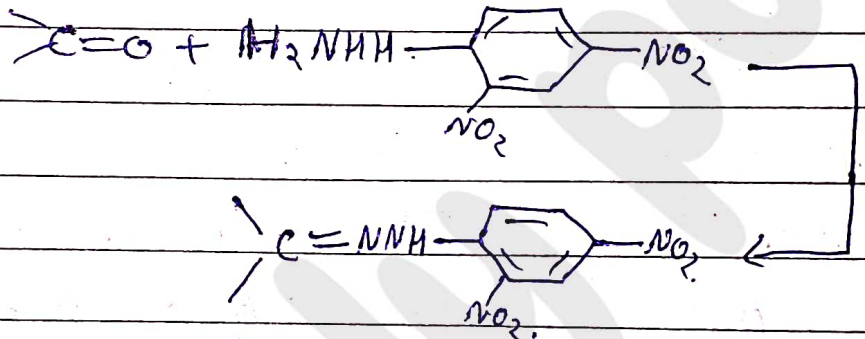
(iii) Reaction with phenyl Hydrazene.





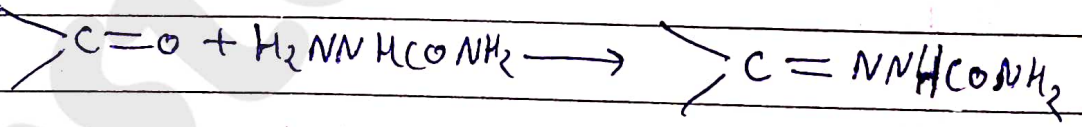
Acetaphyl hydra-zine

(b) Reaction with 2,4-dinitro phenyl Hydrazine.

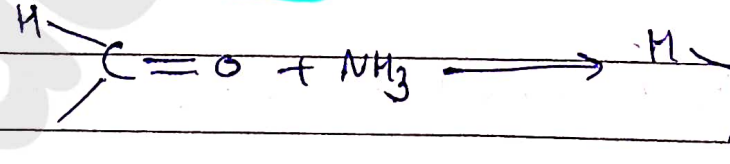


2-4 dinitrophenyl Hydrazine

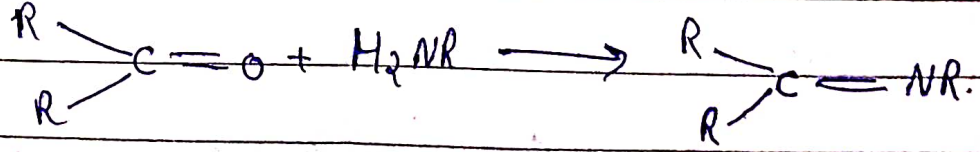
(c) Reaction with Semi Carbazide.



(d) Reaction with NH_3

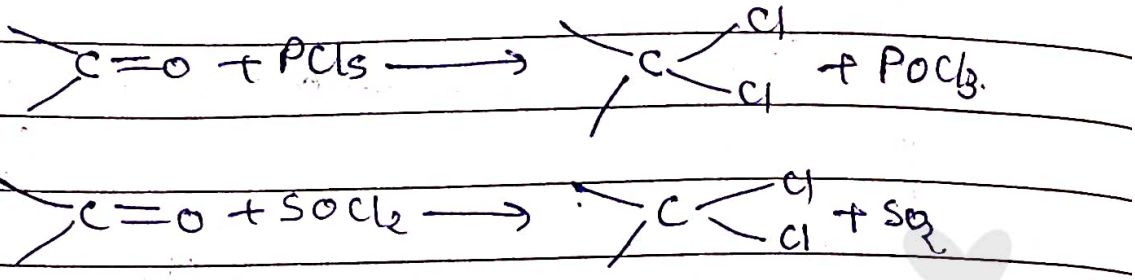


(Caldoimine)



Ketimine.

Reaction with PCl_5 & $SOCl_2$



(3) Oxidation

(a) Oxidation of Aldehyde

$CH_3COOH \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3COOH$.

$CH_3CHO \xrightarrow{PCC} CH_3COOH$

(b) Aldehyde Reduce to following reagent

(i) Tollen's Reagent :- It is a Ammonical $AgNO_3$ Sol^n

$AgNH_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3$.

$AgOH + 2NH_4OH \longrightarrow [Ag(NH_3)_2]^+OH^-$ + tollen's Reagent

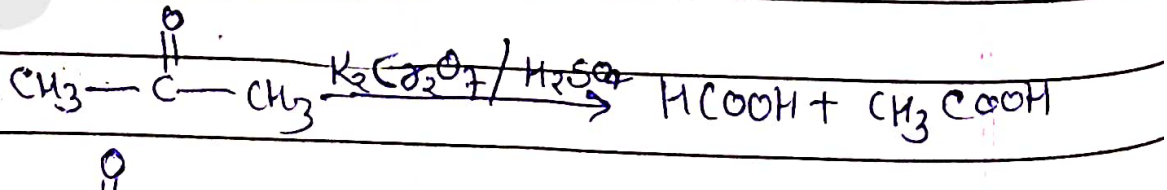
$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3COO^- + 2Ag + 2H_2O + 4NH_3$ (Silver Mirror)

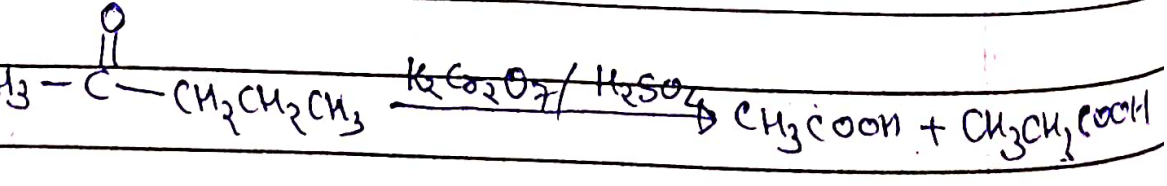
(ii) Felling Solution :-

It is Alkaline $CuSO_4$ Sol^n Containing Sodium Potassium tartarate ($KNaC_4H_4O_6, 4H_2O$).

$HCHO + 2Cu^{2+} + 5OH^- \longrightarrow HCOO^- + Cu_2O + 3H_2O$

(c) Oxidation of Ketone :-

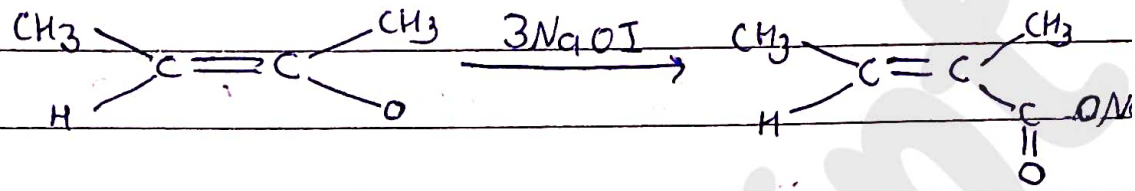




(d) Oxidation of Methyl ethane by Haloform Reaction

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

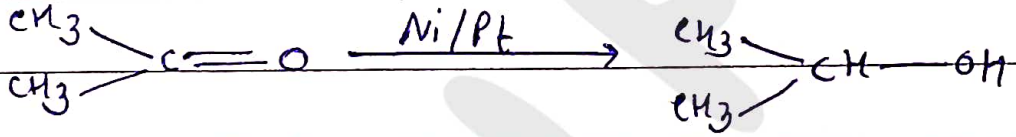
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{2NaOI} CH_3-\underset{\underset{O}{\|}}{C}-ONa + CHI_3 + NaOH$$



(4) Reduction

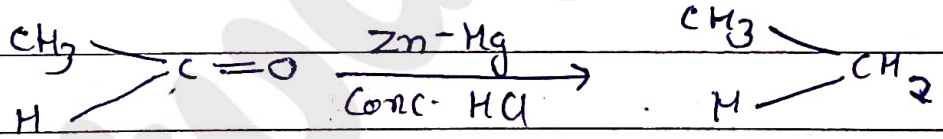
(a) Reduction of Alcohol

$$CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH$$

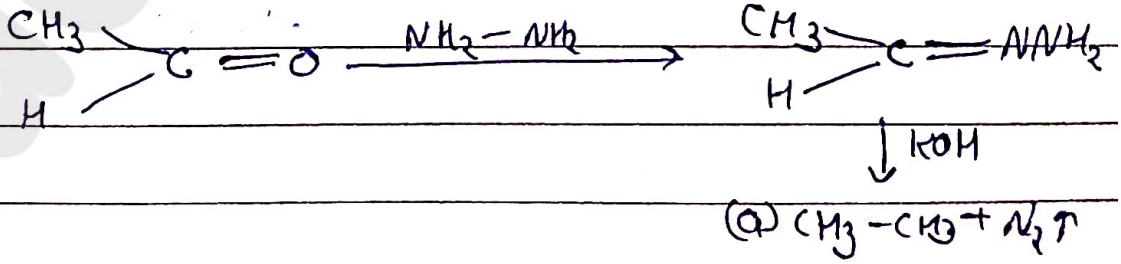


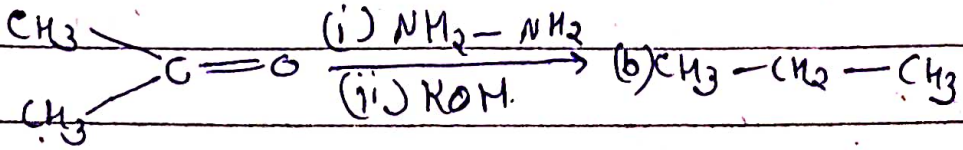
(b) Reduction of hydrocarbon

(i) Clemmenson's reduction



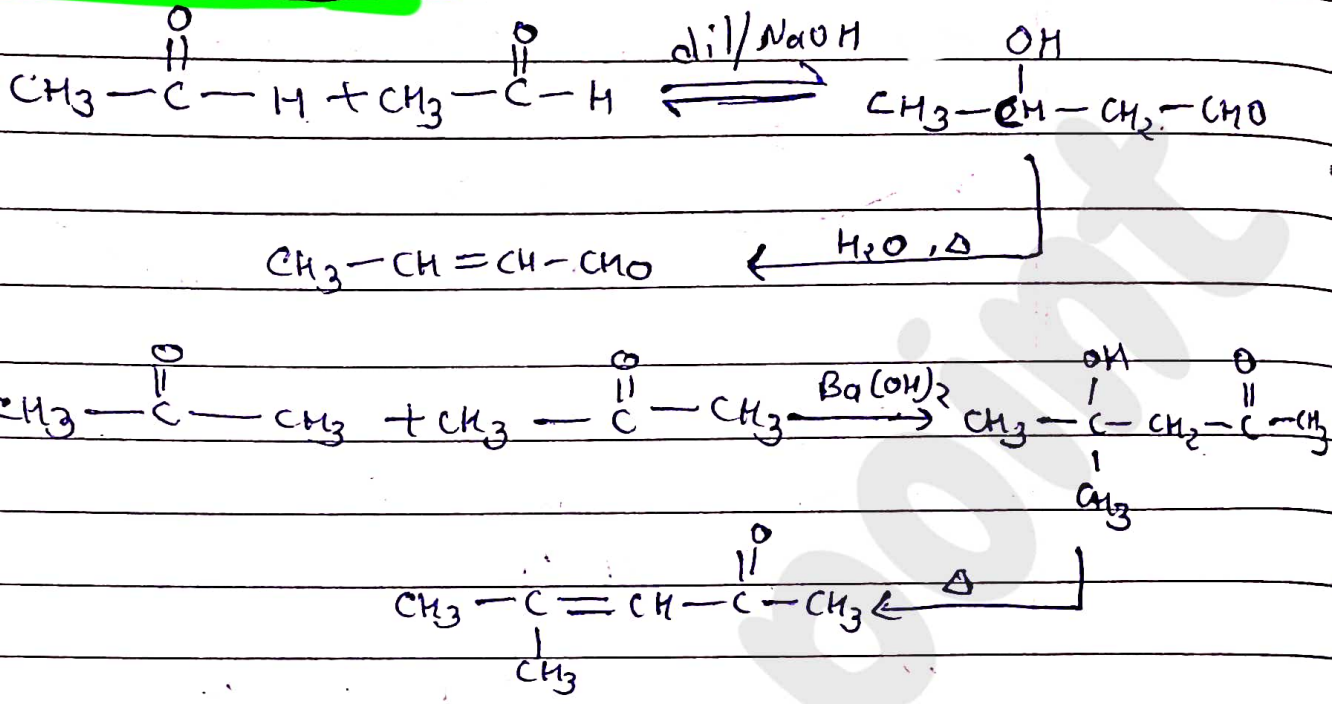
(ii) Wolf kishans Reduction



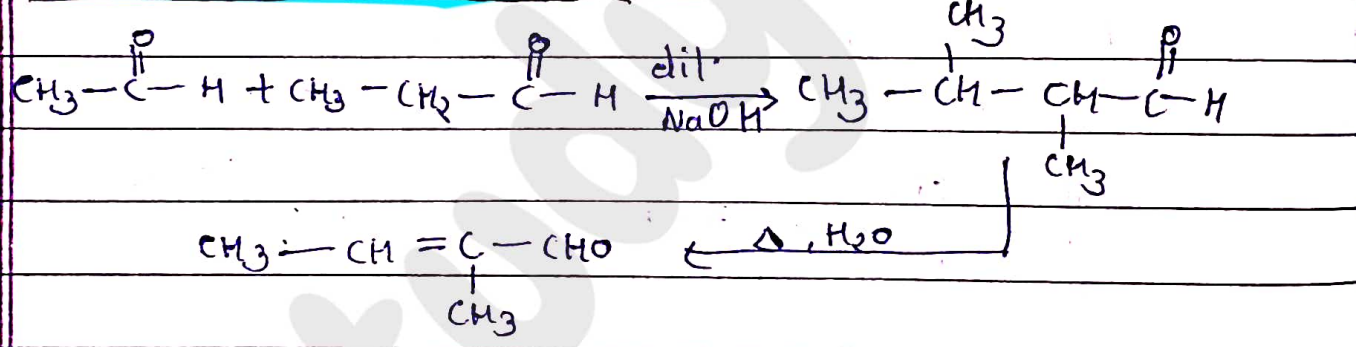


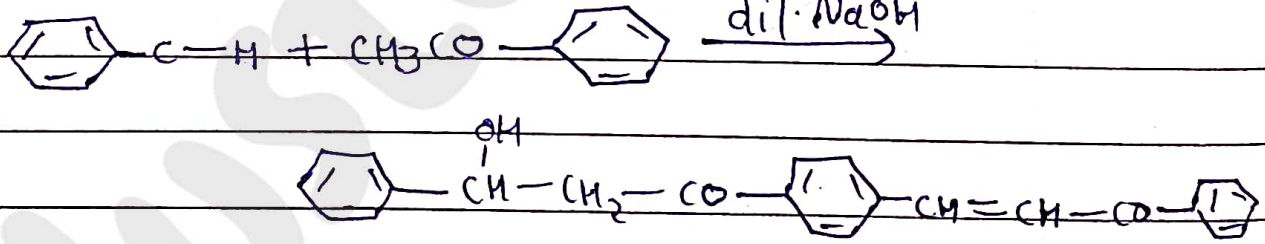
(5) Reduction due to α-Hydrogen

(a) Aldal Condensation



(b) Cross-Aldal Condensation



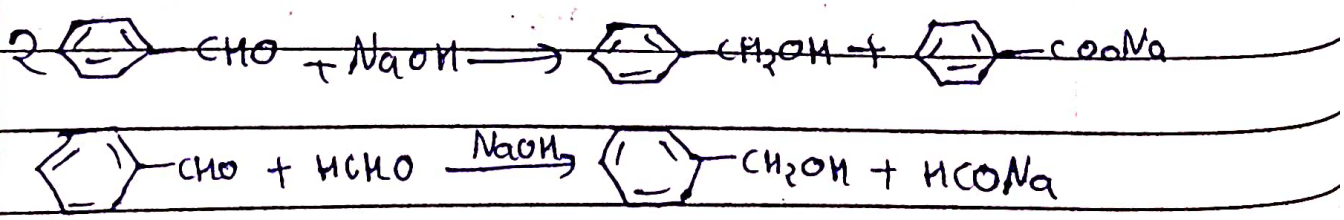


1,3-diphenyl-2-enone.

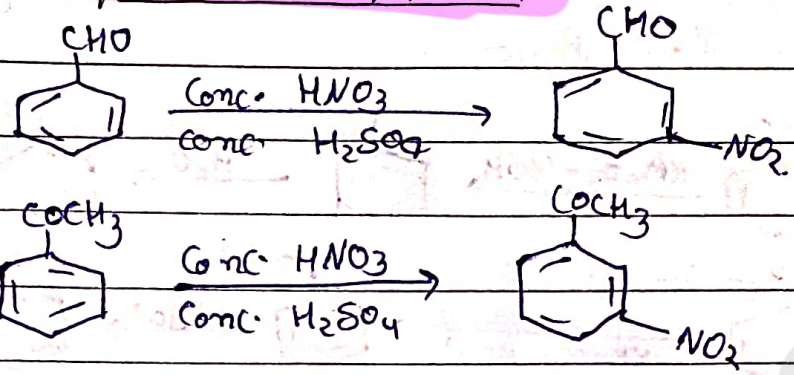
(6) other Reaction

Canizzaro Rxn :-

$$2HCOOH + NaOH \longrightarrow \underset{\text{(Methanol)}}{CH_3OH} + HCOONa$$



⑦ Electrophilic Substitution



Carboxylic Acid:-

⇒ Preparation of Carboxylic Acid:-

① By oxidation of primary Alcohol & Aldehyde.

$$CH_3CH_2OH \xrightarrow{KMnO_4/H_2SO_4} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

$$CH_3CHO \xrightarrow{PCC} CH_3COOH$$

② from Nitrile & Amide

$$CH_3CN \xrightarrow[H_3O^+]{H^+/OH^-} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O]{H^+/OH^-} CH_3COOH + NH_3$$

③ from Grignard Reagent:

$$CH_3MgBr + CO_2 \xrightarrow{dry\ ether} CH_3-\overset{O}{\overset{\|}{C}}-MgBr \xrightarrow{H_2O} CH_3COOH + Mg\begin{matrix}Br\\OH\end{matrix}$$

④ Hydrolysis of acyl chloride & anhydride.

$$CH_3COCl \xrightarrow{H_2O} CH_3COOH + HCl$$

$$\begin{matrix}C_2H_5CO\\CH_3-CO\end{matrix}\!\!>O \xrightarrow{H_2O} C_2H_5COOH + CH_3COOH$$

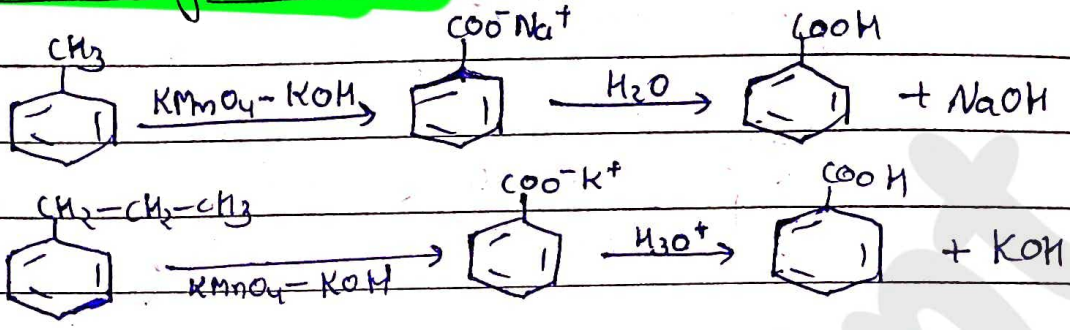
⑤ from Ester

$$CH_3CH_2CH_2COOC_2H_5 \xrightleftharpoons{NaOH} CH_3CH_2CH_2COO^-Na^+ + C_2H_5OH$$

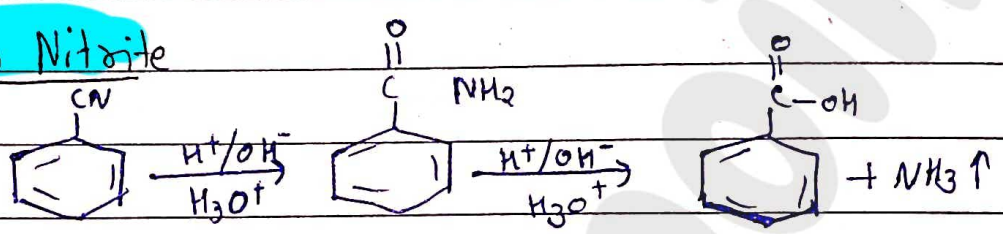
$$CH_3CH_2CH_2COOH + NaOH \xleftarrow{H_3O^+} CH_3CH_2CH_2COO^-Na^+$$

⇒ Preparation of Benzoic Acid:-

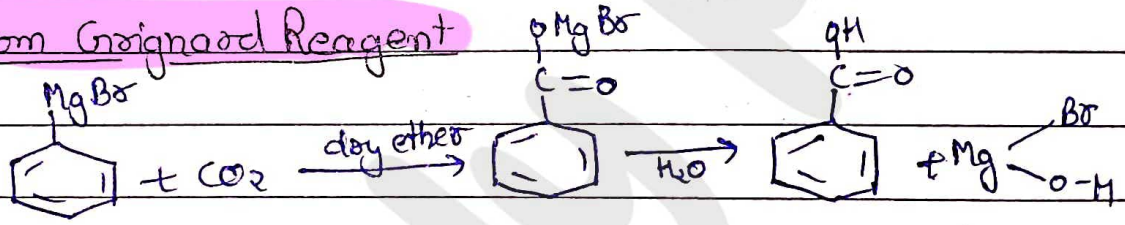
(1) from Alkyl Benzene



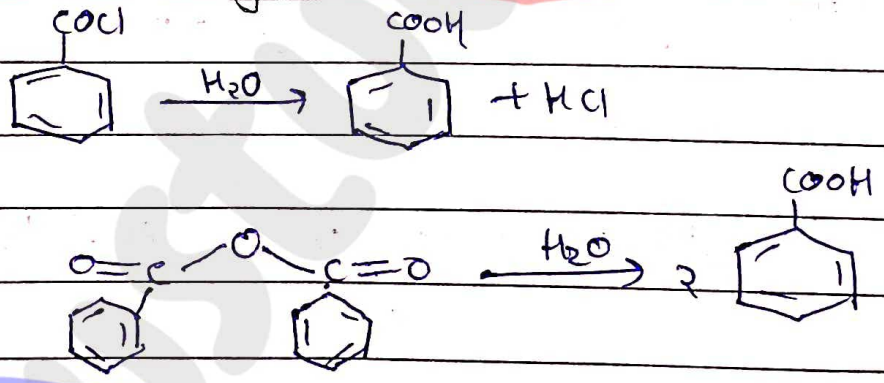
(2) from Nitrile



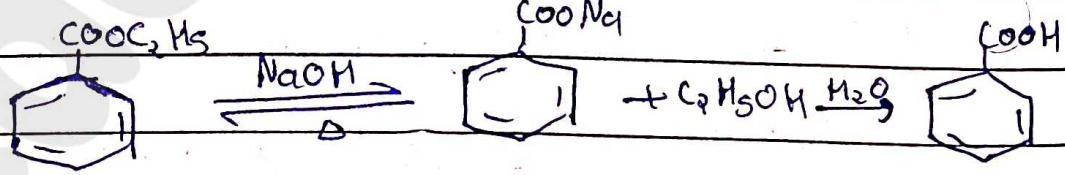
(3) from Grignard Reagent



(4) from Acidanhydride & chloride



(5) from Ester



⇒ Chemical properties

Acidic properties:

$CH_2ICOOH < CH_2BrCOOH < CH_2ClCOOH < CH_2FCOOH$

$CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$

$HCOOH > CH_3COOH > CH_3CH_2COOH$

$CH_2ClCH_2CH_2COOH < CH_3CHClCH_2COOH < CH_3CH_2CHClCOOH$

I Reaction involving cleavage of OH Bond.

(a) Reaction with metal

$$2CH_3COOH + 2Na \longrightarrow 2CH_3COO^-Na^+ + H_2\uparrow$$

$$2CH_3COOH + Zn \longrightarrow (CH_3COO)_2Zn + H_2\uparrow$$

(b) Reaction with Alkali

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

(c) Reaction with bicarbonate

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2$$

II Reaction involving cleavage of C–O bond.

(a) formation of Anhydride.

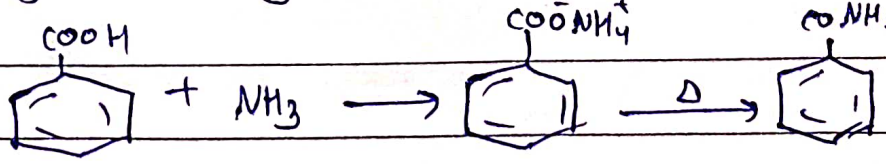
$$2CH_3-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{\Delta,\ P_2O_5} CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

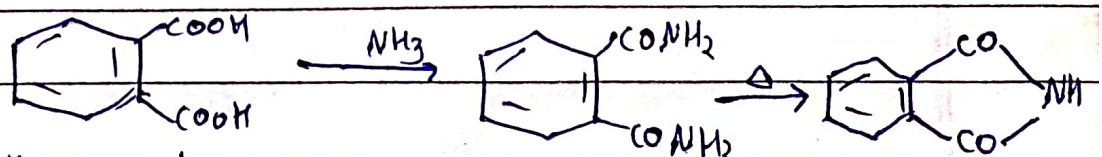
(b) Esterification

$$CH_3COOH + HOC_2H_5 \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

(c) Rxn with Ammonia

$$CH_3COOH + NH_3 \longrightarrow CH_3COO^-NH_4^+ \xrightarrow{\Delta} CH_3CONH_2$$





Phthalic acid — phthalamide — phalimide

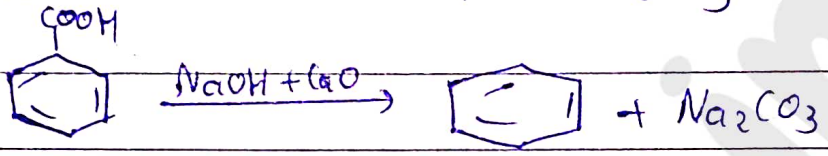
III Rxn involving - COOH group

(a) Reduction

$$CH_3COOH \xrightarrow[(ii)\,H_2O]{(i)\,LiAlH_4 \text{ or } B_2H_6} CH_3CH_2OH$$

(b) Decarboxylation

$$CH_3COOH \xrightarrow{NaOH+CaO} CH_4 + Na_2CO_3$$

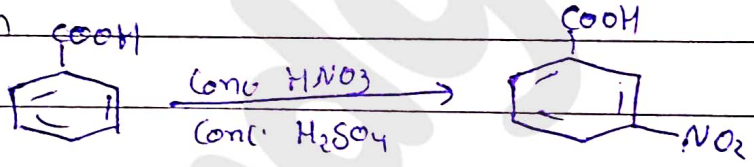


(c) Halogenation [Hell Volhard Zelinsky (HVZ) Rxn.)

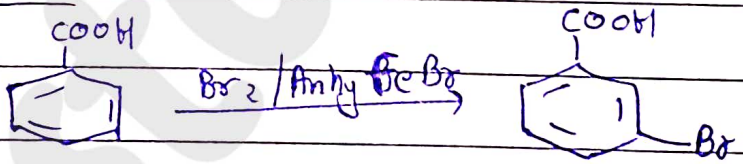
$$CH_3CH_2COOH \xrightarrow[\Delta]{Cl_2,\ Red\ P} CH_3-\underset{Cl}{\underset{|}{C}}HCOOH$$

IV Electrophilic Substitution

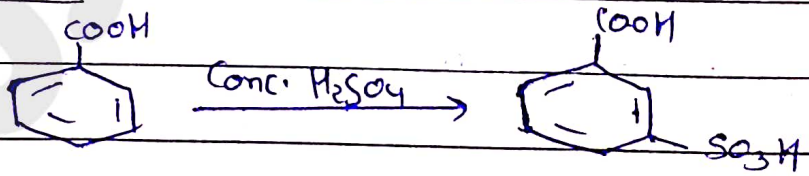
(a) Nitration



(b) Halogenation



(c) Sulphonation



Chemical Test

(1) Aldehyde → 2 Test

(a) Tollen's Test

(b) Fehing's Test

(2) Ketone :- It perform iodoform test.

(3) Carboxylic Test :- (a) Esterification
(b) Iodoform

⇒ Physical Properties

① **Solubility**:- Carboxylic acid (up to 4C atom) is soluble in water due to polar nature of carbonyl group as alkyl alcohol & formation of intermolecular ~~mass~~ H-bonding, solubility ↓ with ↑ the ~~molar~~ molecular mass of compound. Benzoic Acid are soluble in hot water but not to cold water.

② **Boiling Point**:- Carboxylic Acid have higher B.P. due to formation of intermolecular hydrogen bond ~~due~~ B.P. of Carboxylic Acid much higher than Aldehyde, ketone & alcohol due to they form two intermolecular H-Bond with same molecule ∴, it form cyclic dimer

③ **Melting point**:- Aromatic Acid have higher M.P. than Aliphatic acid due to their crystal lattice Structure.