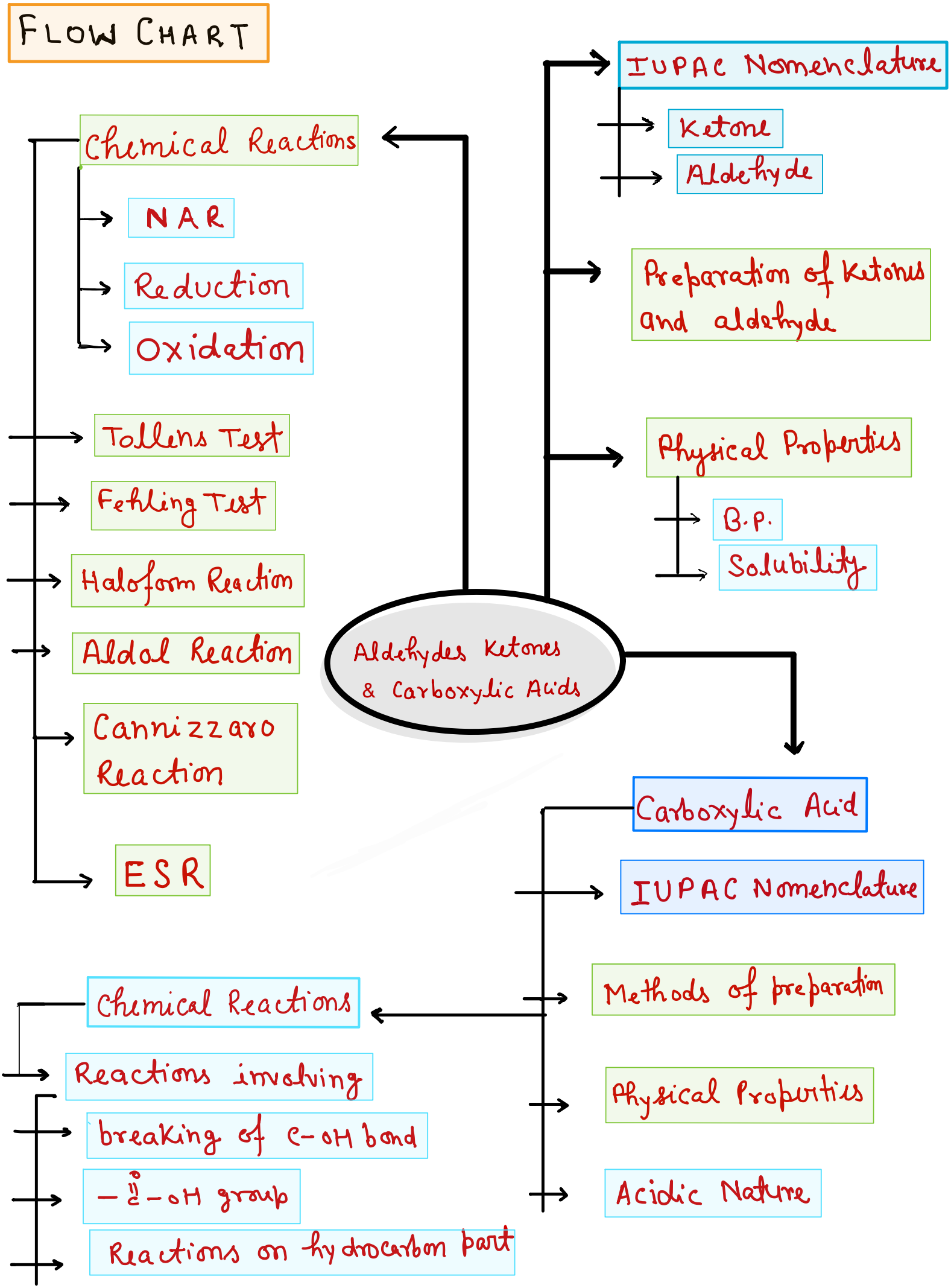
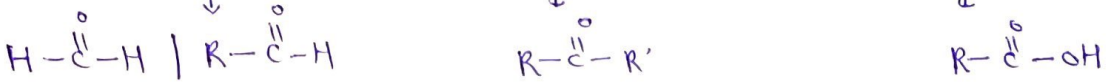
FLOW CHART

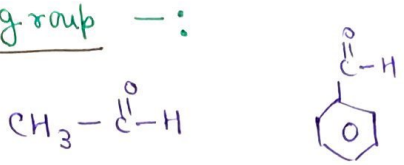

Aldehydes Ketones & Carboxylic Acids
IUPAC Nomenclature
Ketone
Aldehyde
Preparation of Ketones and aldehyde
Physical Properties
B.P.
Solubility
Chemical Reactions
NAR
Reduction
Oxidation
Tollens Test
Fehling Test
Haloform Reaction
Aldol Reaction
Cannizzaro Reaction
ESR
Carboxylic Acid
IUPAC Nomenclature
Methods of preparation
Physical Properties
Acidic Nature
Chemical Reactions
Reactions involving
breaking of C-OH bond
-C(=O)-OH group
Reactions on hydrocarbon part

Aldehydes, Ketones and Carboxylic Acids

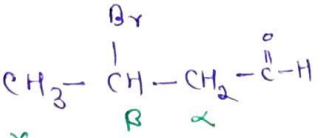


→ Nomenclature of carbonyl group —:

Important common names —:

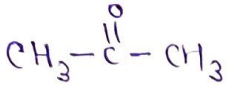


Acetaldehyde Benzaldehyde

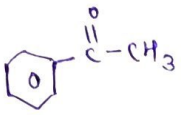


γ β α

β-Bromobutyraldehyde



Acetone



Acetophenone

Benzophenone

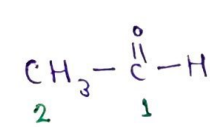
IUPAC Name

→ For aliphatic aldehydes / ketones : Alkane - e + al / one → Alkanal
→ Alkanone

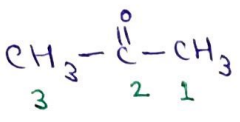
→ In case of aldehydes —: The longest carbon chain is numbered starting from the carbon of aldehyde group.

→ In case of ketones —: Numbering begins from the end nearer to carbonyl group

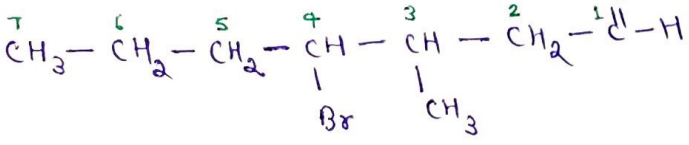
Example —:



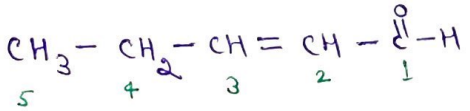
: Ethanal ;



: Propanone

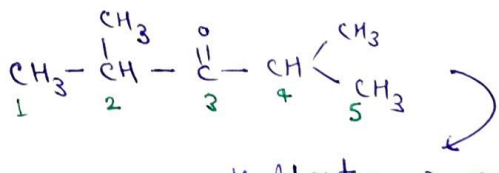


: 4 - Bromo - 3 - methyl heptanal



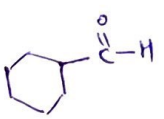
: Pent - 2 - enal

[2012] (1M) CBSE

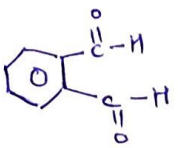


2,4 - Dimethylpentan - 3 - one.

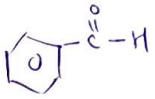
→ When aldehyde group is attached to cyclic ring, then special suffix is used —: [Carbaldehyde]



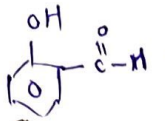
: Cyclohexanecarbaldehyde ;



→ Benzene - 1,2 - di carbaldehyde

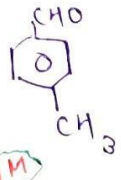


: Benzenecarbaldehyde [Benzaldehyde]

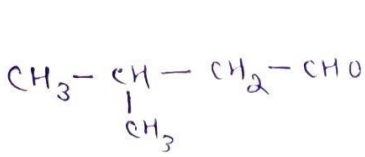


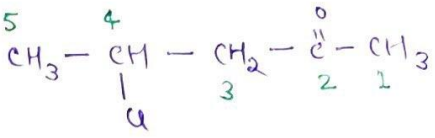
→ 2-Hydroxy benzene carbaldehyde

[2014]

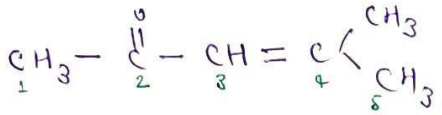
→  4-Methylbenzenecarbaldehyde / (p-Methylbenzenecarbaldehyde)
or
4-Methylbenzaldehyde

[Delhi 2013 / 2014] 1M

→ 3-Methylbutanal 

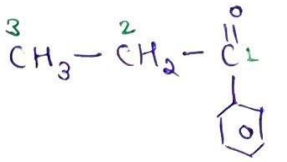
→ 
4-Chloropentan-2-one

Delhi 2013 | 2011 1M

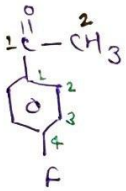
→  : 4-Methylpent-3-en-2-one [2008 | 2011] 1M

[Delhi 2011C] 1M

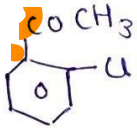
→ Benzene as substituent —: Phenyl

 : 1-Phenylpropan-1-one

[Delhi 2011 | 2010]

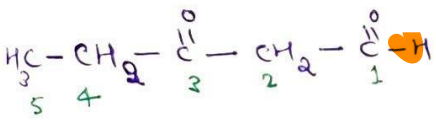
 —: 4-Fluorophenylethanone

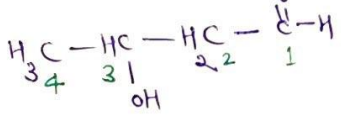
[Delhi 2010] 1M

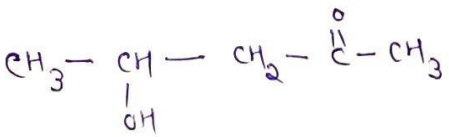
 —: 2-Chlorophenyl ethanone

1M [CBSE 2010]

→ Senior functional group makes 2° suffix and junior makes 2° prefix (substituent)

 : 3-Oxopentanal [Seniority : $-\overset{O}{\overset{\|}{C}}-H > -\overset{O}{\overset{\|}{C}}-$]

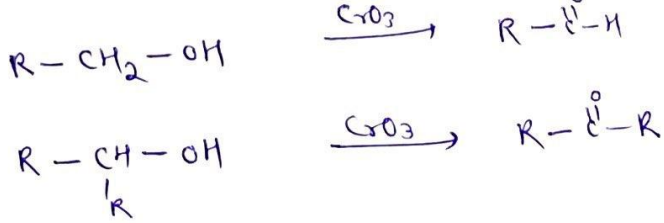
 : 3-Hydroxybutanal [Seniority : $-\overset{O}{\overset{\|}{C}}-H > -OH$]

 : 4-Hydroxypentan-2-one [Seniority : Ketone > Alcohol]

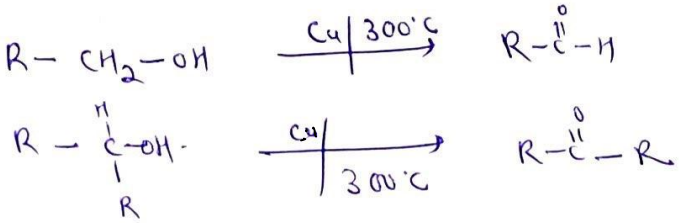
1M [CBSE 2014]

Preparation of aldehydes and ketones

1. Oxidation of alcohols —:



2. Dehydrogenation of alcohols —:



3.) Ozonolysis of alkene :—

$$R-CH=CH-R \xrightarrow[\text{② } Zn/H_2O]{\text{① } O_3} 2\ R-\overset{O}{\overset{\|}{C}}-H$$

$$R-\underset{R}{\overset{|}{C}}=C\begin{matrix}R\\ \diagup\\ \diagdown\\ R\end{matrix} \xrightarrow[2)\ Zn/H_2O]{1)\ O_3} 2\ R-\overset{O}{\overset{\|}{C}}-R$$

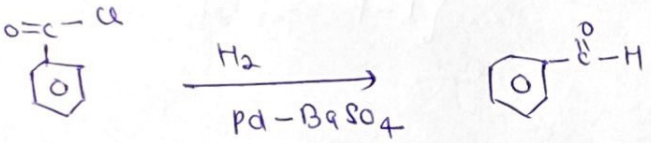
4.) Hydration of alkyne :—

$$CH\equiv CH \xrightarrow[H_2SO_4(aq.)]{HgSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2SO_4]{HgSO_4} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

Preparation of Aldehydes

→ (i) Rosenmund reduction of acid chloride :—



(ii) Stephen's Reduction :—

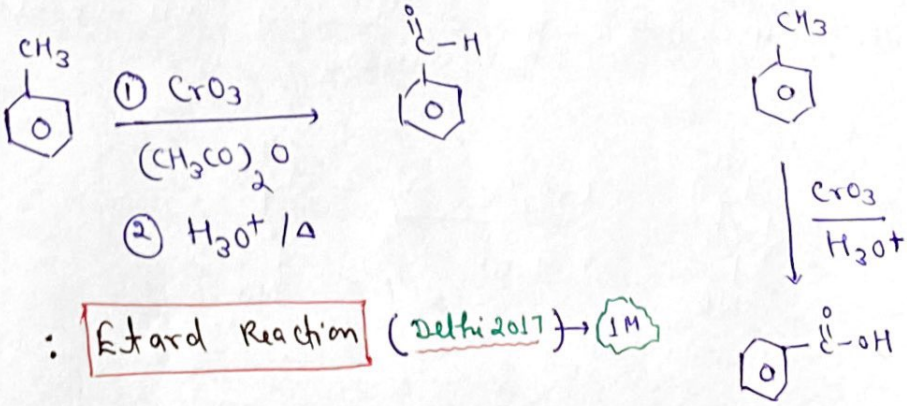
$$R-C\equiv N \xrightarrow{SnCl_2+HCl} R-CH=NH \xrightarrow{H_3O^+} R-\overset{O}{\overset{\|}{C}}-H$$

→ (iii) By DIBAL-H —:

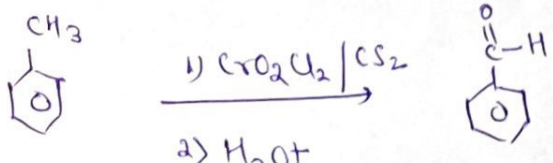
a.) $R-C\equiv N \xrightarrow[2)\ H_2O]{1)\ AlH(iBu)_2} R-\overset{O}{\overset{\|}{C}}-H$

b.) $C_2H_5-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[ii)\ H_2O]{i)\ AlH(iBu)_2} C_2H_5-\overset{O}{\overset{\|}{C}}-H$

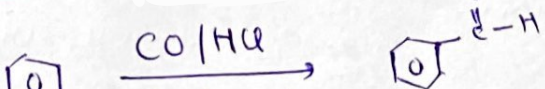
iv] From Hydrocarbon —:



→ Toluene $\xrightarrow[2)\ H_3O^+]{1)\ CrO_2Cl_2/CS_2}$ Benzaldehyde : Etard Reaction (Delhi 2017) → (1M)

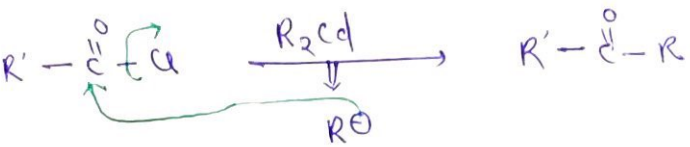


Gattermann – Koch Reaction —:



Preparation of Ketones

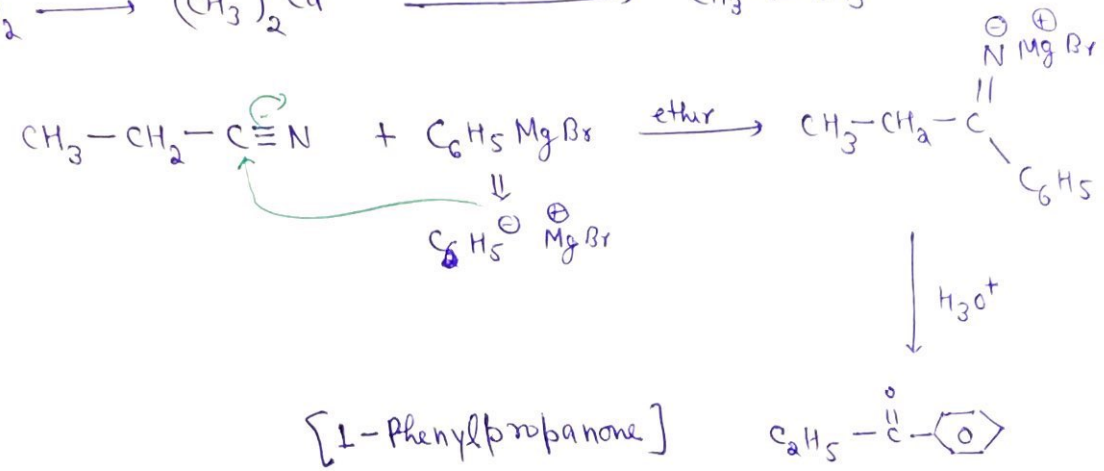
→ (i) **From acyl chlorides** –:



→ $2\,RMgBr + CdCl_2 \longrightarrow R_2Cd + 2\,Mg(Br)Cl$

→ $CH_3MgBr + CdCl_2 \longrightarrow (CH_3)_2Cd \xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-Cl} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

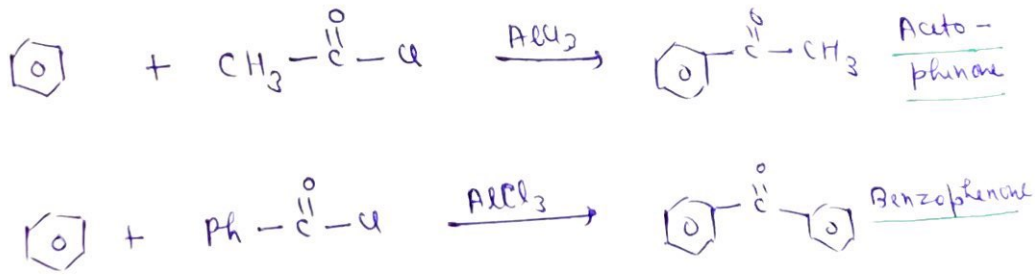
(ii) **From Nitrile** –:



[1-Phenylpropanone] $C_2H_5-\overset{O}{\overset{\|}{C}}-C_6H_5$

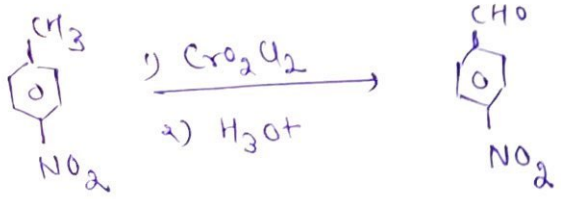
(iii) From Benzene :–

Friedel-Crafts Acylation reaction



1M [Delhi 2012]

$CH_3-C\equiv C-H \xrightarrow[H_2SO_4]{Hg^{2+}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ → [Delhi 2012]



Physical properties

→ **Boiling Point** –: The boiling points of aldehydes and ketones are higher than hydrocarbons and ether of comparable molecular mass. It is due to dipole dipole interaction.

B.P. : $CH_3-CH_2-CH_2-\overset{O^{-\delta}}{\overset{\|}{C}}-H^{+\delta}$ > $CH_3-CH_2-CH_2-CH_2-CH_3$

> $CH_3-CH_2-O-CH_2-CH_3$

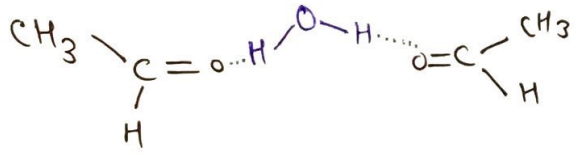
→ Boiling points of aldehydes and ketones are lower than those of alcohol of similar molecular masses due to absence of hydrogen bonding.

B.P. : $CH_3-CH_2-CH_2-CH_2-OH$ > $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$

(Hydrogen Bonding) (Dipole - Dipole interaction)

Solubility → solubility of aldehydes and ketones decreases ⟹ size of alkyl group ↑es.

→ Methanal | Ethanal | propanone are miscible with water because they form hydrogen bond with water.



Chemical Reactions

Nucleophilic Addition Reaction :—

Reaction :— $R-\overset{\overset{O}{\|}}{\overset{\delta+}{C}}-H$ + $Nu^{\ominus}$ → $R-\overset{O^{\ominus}}{\underset{Nu}{\overset{|}{\underset{|}{C}}}}-H$ $\xrightarrow{H^+}$ $R-\overset{OH}{\underset{Nu}{\overset{|}{\underset{|}{C}}}}-H$

Aldehyde : Planar

Tetrahedral intermidiate

Addition Product

Reactivity :→ Aldehydes > Ketones

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

Electrophilicity decreases means that partial +ve charge decreases.

As size of alkyl group ↑es, approach of Nucleophile to carbonyl carbon ↓es.

→ Reactivity order : $H-\overset{\overset{O}{\|}}{C}-H$ > $CH_3-\overset{\overset{O}{\|}}{C}-H$ > Acetone

: Acetaldehyde > Acetone > Methyl t-butyl ketone

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

1M [CBSE 2012]

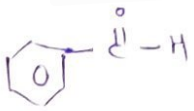
→ $\bigcirc\!\!-\overset{\overset{O}{\|}}{C}-CH_3$ < $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

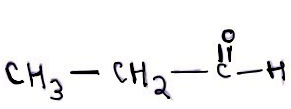
^

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

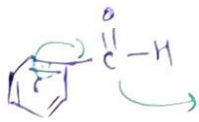
[1M] ←[Delhi 2015]

→ Reactivity for NAR :-





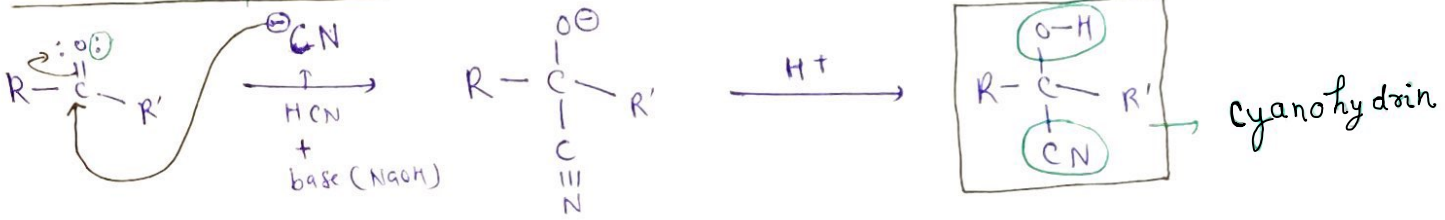
Because polarity of carbonyl group is reduced in benzaldehyde due to resonance.



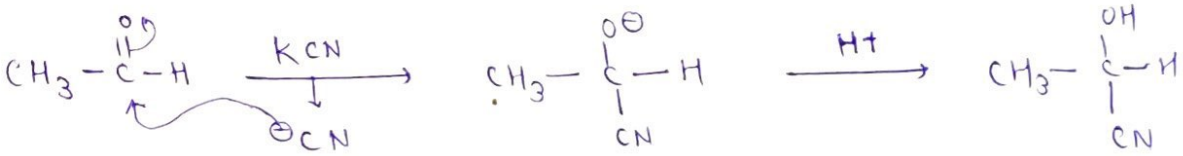
Partial ⊕ve charge ↓ less

Electrophilicity ↓ less

⇒ Addition of HCN :-



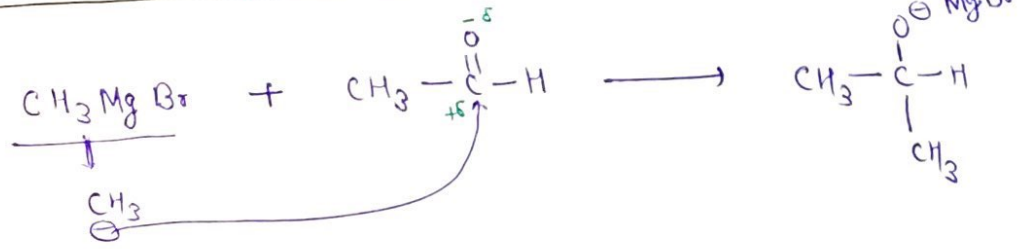
→



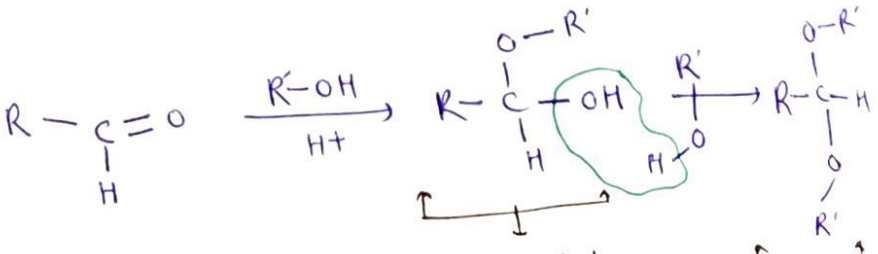
⇒ Addition of sodium hydrogen sulphite :- [$NaHSO_3$]

Crystalline ← [Addition Product]

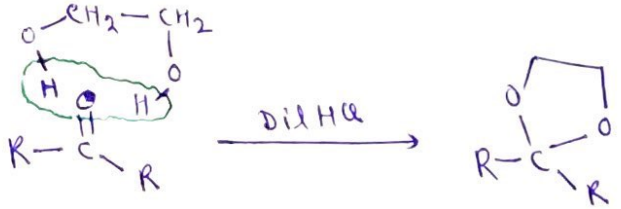
⇒ Addition of Grignard Reagent :-



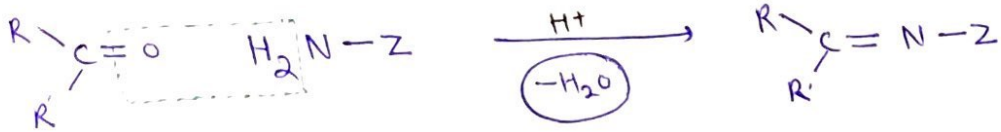
⇒ Addition of alcohols :-

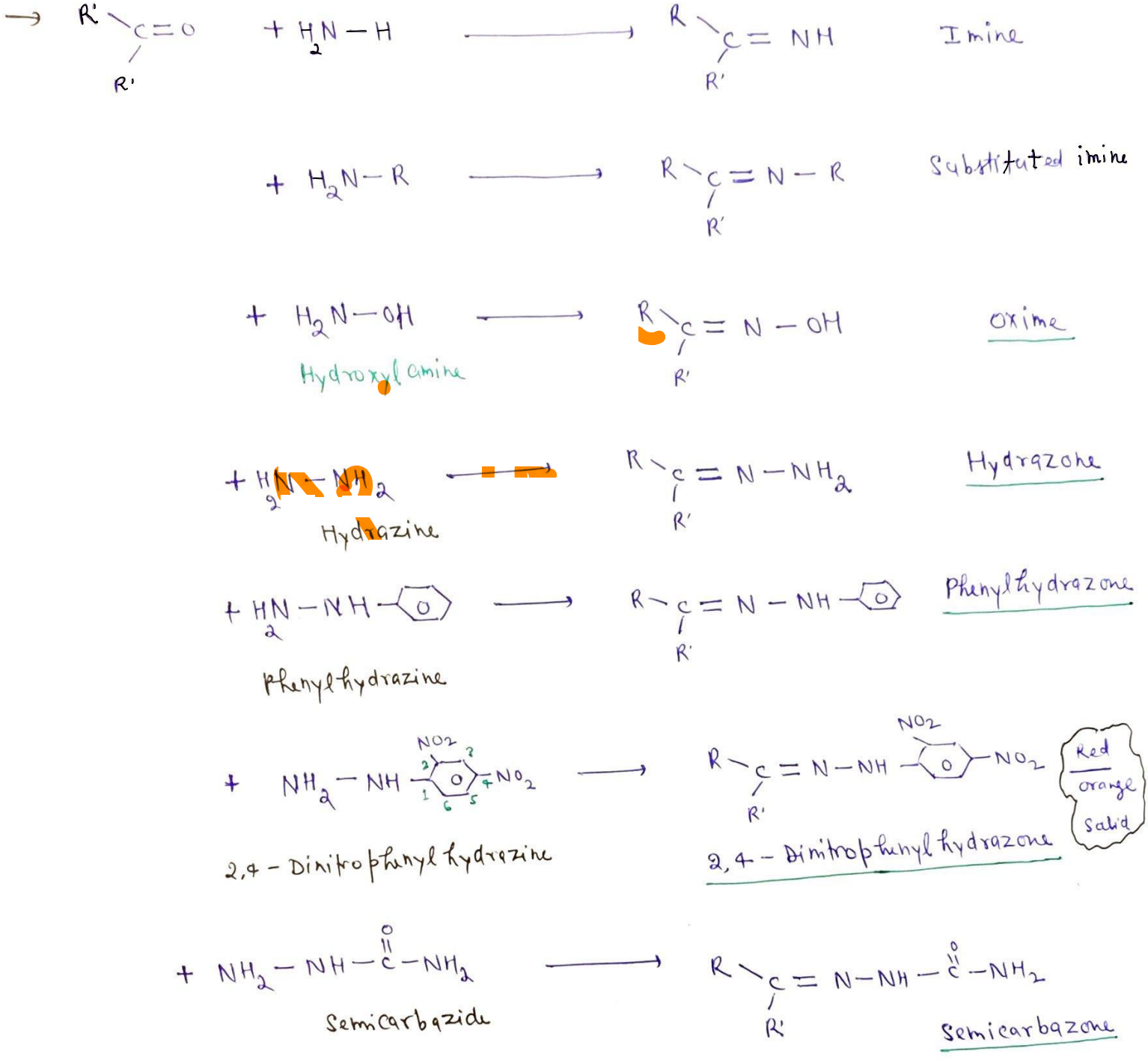


→



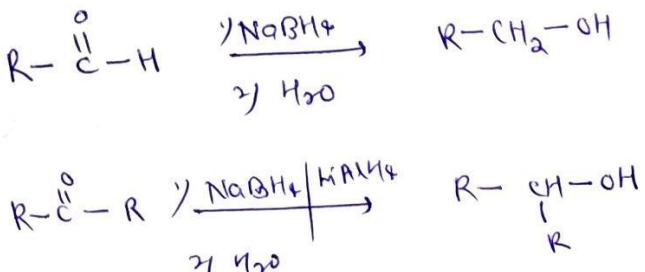
⇒ Addition of Ammonia and its derivatives :-





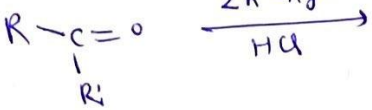
Reduction :—

(i) → **Reduction to alcohols** —:



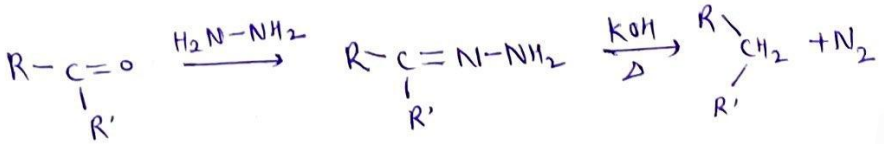
(ii) → **Reduction to hydrocarbons** —:

a.) **Clemmensen Reduction** :—



[Delhi 2017] → [1M]

b.) **Wolff - Kishner Reduction** :—



[Delhi 2016 / 2017 / 2019] → [1M]

Oxidation :- Aldehyde $[R-\overset{O}{\overset{\|}{C}}-H]$ $\xrightarrow{\text{oxidising agent}}$ $R-\overset{O}{\overset{\|}{C}}-OH$

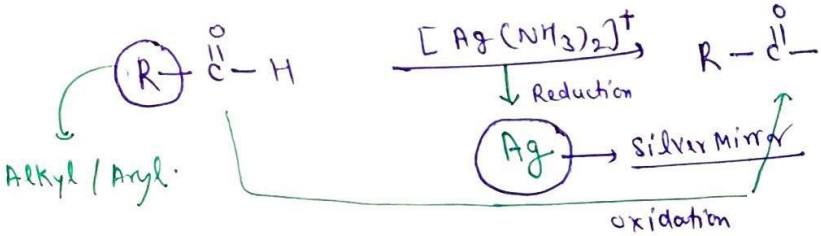
$\rightarrow HNO_3 \mid KMnO_4 \mid K_2Cr_2O_7$

$R-\overset{O}{\overset{\|}{C}}-R$ $\rightarrow$ Tollen's Reagent

$\not\rightarrow$ T·R·/F·R $\rightarrow$ Fehling Reagent

$R-\overset{O}{\overset{\|}{C}}-OH$

$\rightarrow$ **Tollen's Test –:** Tollen's Reagent $\rightarrow$ $NH_4OH + AgNO_3 \longrightarrow [Ag(NH_3)_2]^+$

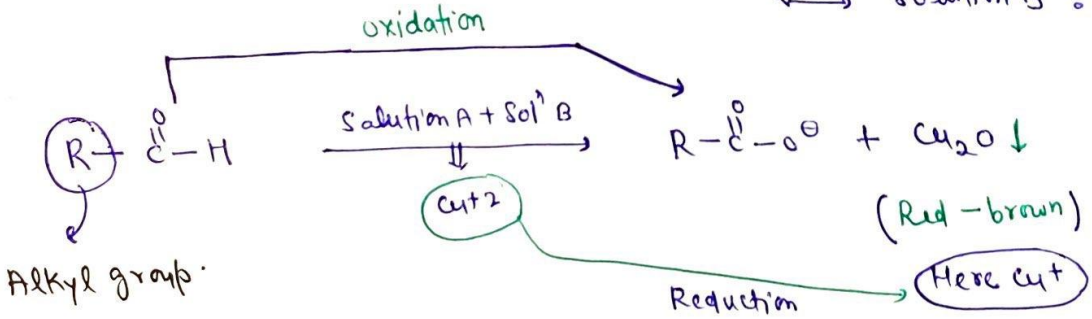


: [Delhi 2010] → 1M

$\rightarrow$ Above reaction is not possible with Ketone. By using above reagent aldehyde and ketone can be identified.

Fehling's Test –: Two parts → Solution A : $CuSO_4$ (aq.)

→ Solution B : Sodium Potassium Tartarate (Rochelle Salt)



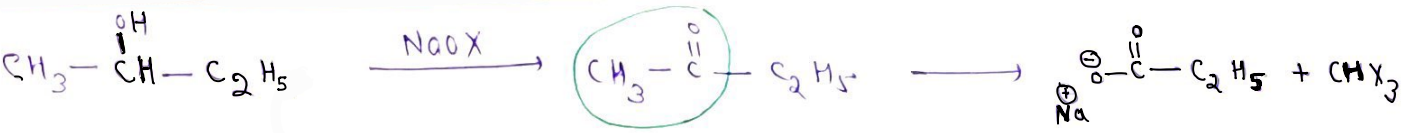
$\rightarrow$ $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[Cu^+]{Cu^{+2}} CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

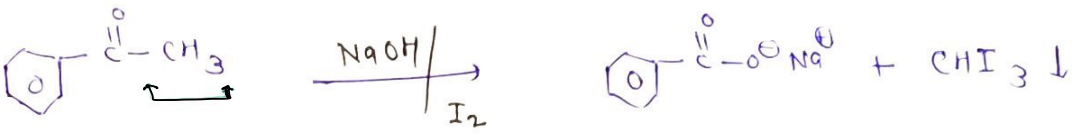
$\rightarrow$ **Haloform Reaction :-** (oxidation of methyl ketone) Reagent –: $\dfrac{NaOH + X_2}{NaOX}$ (Cl | Br | I)

$\rightarrow$ $CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5 \xrightarrow{NaOI} Na^{\oplus}\,O^{\ominus}-\overset{O}{\overset{\|}{C}}-C_2H_5 + CHI_3 \downarrow$ (Yellow ppt)

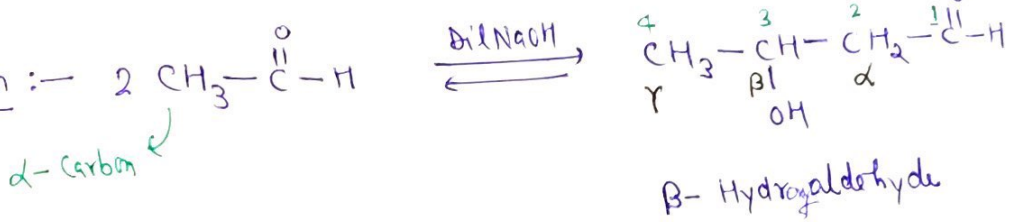
$\rightarrow$ NaOCl $\longrightarrow$ $C_2H_5-\overset{O}{\overset{\|}{C}}-O^{\ominus}\,Na^{\oplus} + CHCl_3$

NaOBr $\longrightarrow$ $C_2H_5-\overset{O}{\overset{\|}{C}}-O^{\ominus}\,Na^{+} + CHBr_3$

→ 

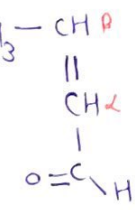
→ 

Aldol Reaction / Aldol Condensation

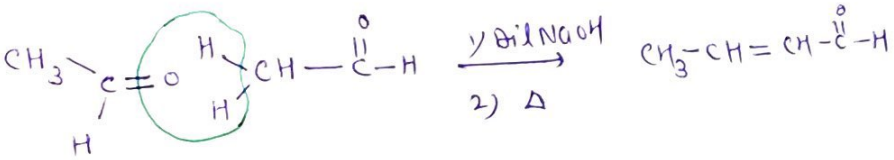
→ Reaction :- 

α-Carbon

β-Hydroxyaldehyde

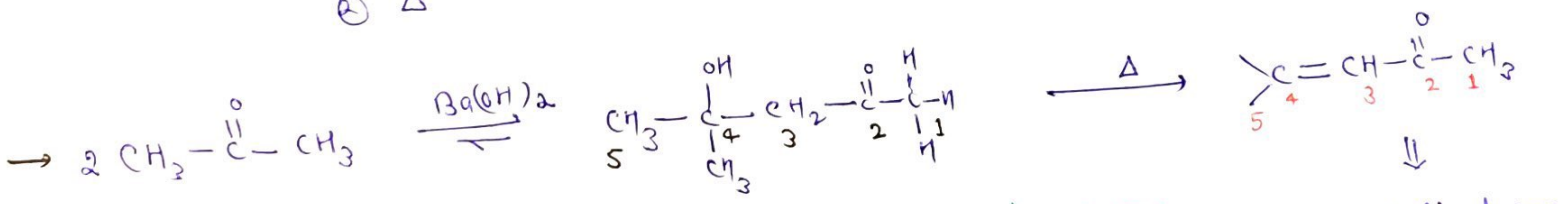


α, β-unsaturated aldehyde.

→ 

→ Aldehyde $\xrightarrow{\text{Dil NaOH}}$ β-Hydroxy aldehyde : Aldol Reaction

Aldehyde $\xrightarrow[\text{② } \Delta]{\text{① Dil NaOH}}$ α-β-unsaturated aldehyde : Aldol Condensation

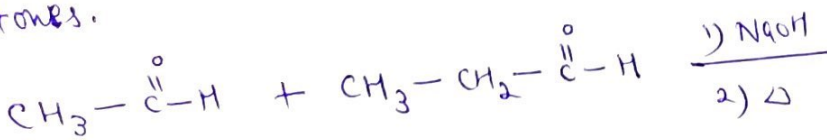
→ 

4-Hydroxy-4-methylpentan-2-one

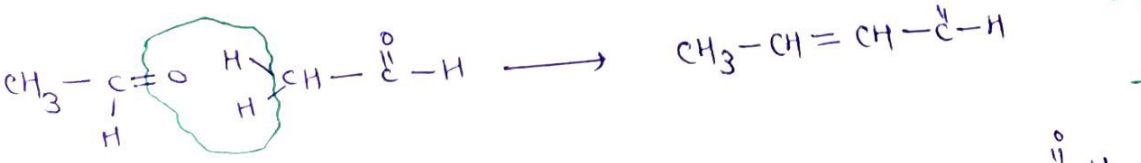
4-Methylpent-3-en-2-one

[Delhi 2012] → [1M]

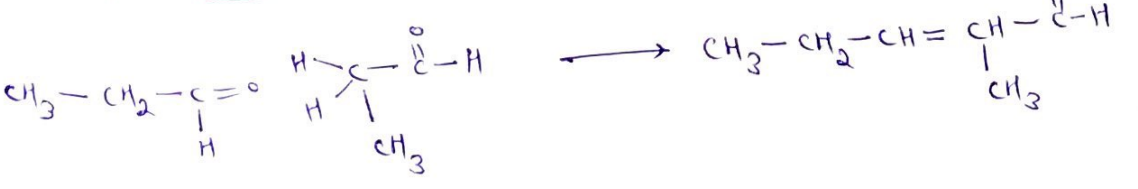
⇒ Cross Aldol Condensation :- Aldol reaction between two different aldehyde or ketones.

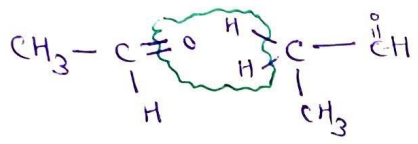
→ 

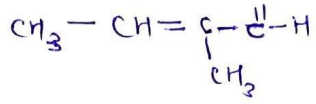
How many products are possible?

a.) 

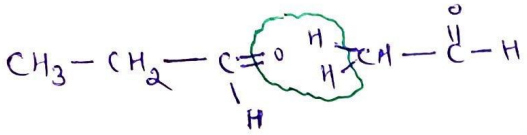
→ Self-Aldol

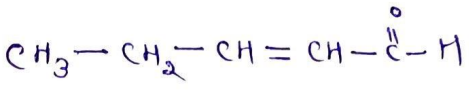
b.) 

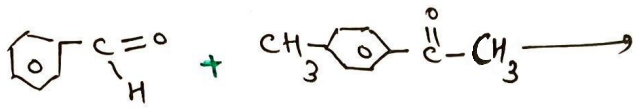
→ 



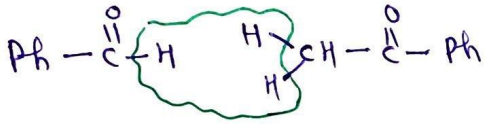
→ Cross aldol Product.

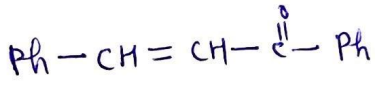
→ 





→ [Delhi 2010] (1M)





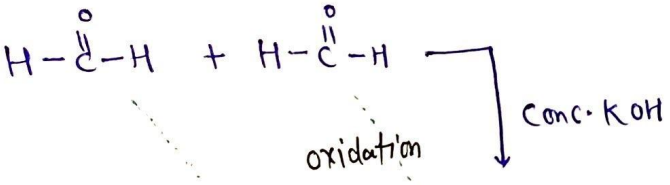
Cannizzaro Reaction

[Delhi 2017 | 2011] → (1M)

→ Con. NaOH | KOH → No. α-Hydrogen → Disproportionation Reaction

Carboxylic acid ← Oxidation ← Aldehyde → Reduction → Alcohol

Carboxylic acid Salt.



Potassium formate

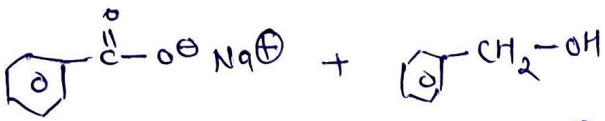
+

Methanol

: [Delhi 2013] → [1 M]

→ [Delhi 2016C]

No α Hydrogen

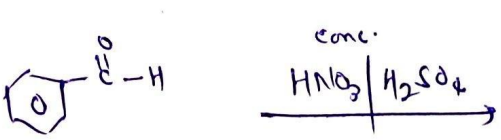


Sodium benzoate.

Benzyl alcohol

Electrophilic Substitution Reaction :-

( : meta-Directing in nature)



[CBSE 2016C | Delhi 2015C] → [1 M] 2013

m-Nitrobenzaldehyde.

Question :- $C_9H_{10}O$ → 2, 4 - DNP Derivative : Presence of Carbonyl grp

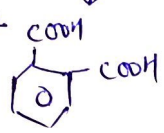
[CBSE 2012]

→ Reduces Tollen's Reagent : Presence of aldehyde

→ gives Cannizaro Reaction : No, α Hydrogen

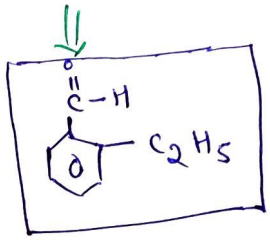
Oxidation

1, 2 + Benzene dicarboxylic



means that substitution at 1, 2 position in reactant.

Then predict the structure.



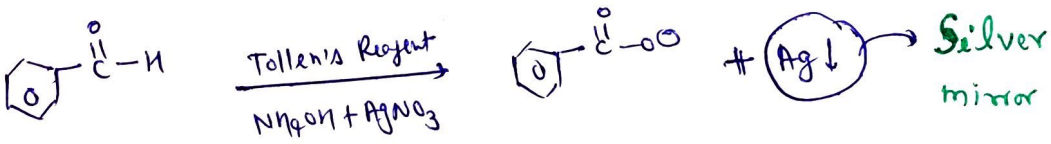
→ Describe a chemical test to distinguish between →

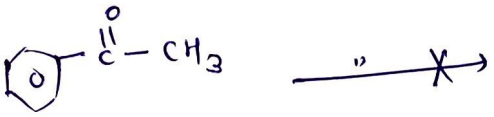
a.) Ethanal and propanal :- $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaOH + I_2} CHI_3\downarrow$ Yellow ppt.

[Delhi 2010] [2M]

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow[+\ I_2]{NaOH}$ No reaction

b.) Benzaldehyde and acetophenone :-

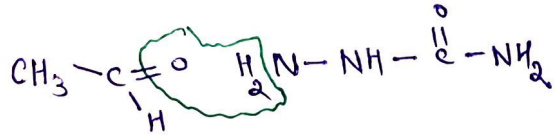




c.) Propan-2-one and pentan-3-one :- $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[+\ I_2]{NaOH} CHI_3\downarrow$ Yellow ppt

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow{\quad} $ No Reaction.

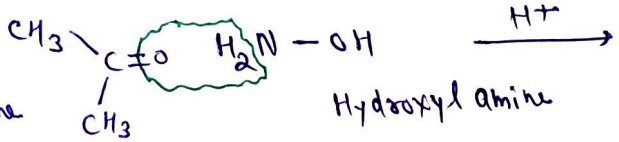
Complete the reactions :-

a.) 

$CH_3-CH=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$

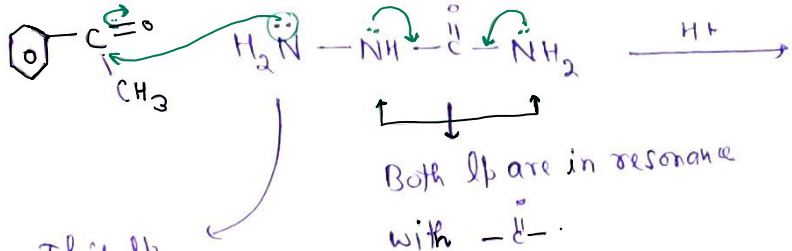
[Semicarbazone of CH_3-CHO]

CBSE [2015] 2M

b.) 

Propanone — Hydroxyl amine — Propanone oxime

→ c.)

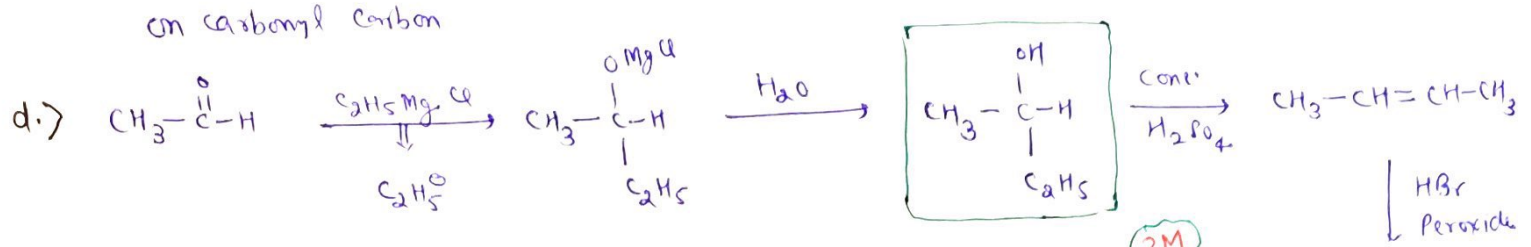


Both lp are in resonance with $-\ddot{C}-$.

This lp is free to attack on carbonyl carbon

[Delhi 2012] → 1M

d.)



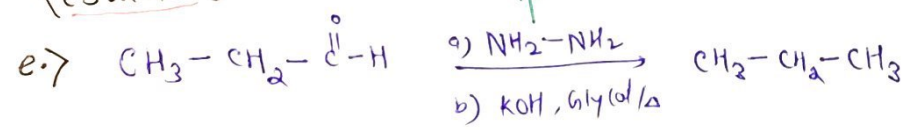
3M

[Delhi 2011C]

[CBSE 2019] → [1M]

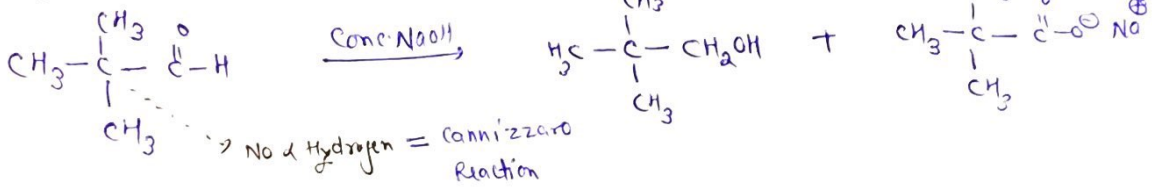
Wolf Kishner Reduction

e.)



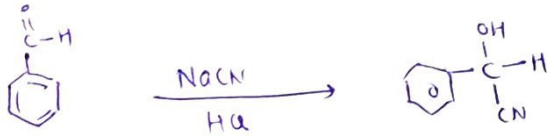
[CBSE 2019] → [1M]

f.)



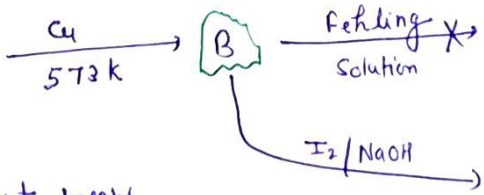
No α Hydrogen = Cannizzaro Reaction

g.)



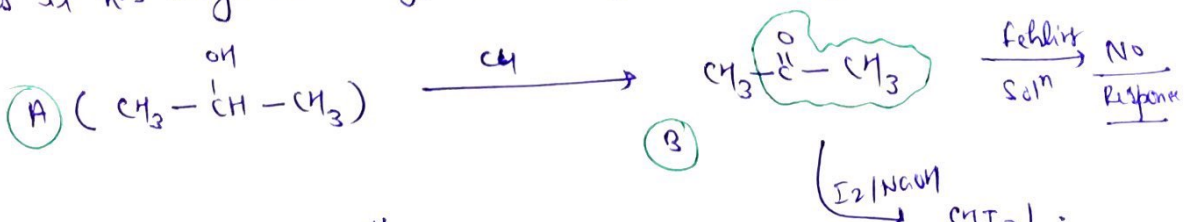
Cyanohydrin : [Delhi 2019] → [1M]

h.) Organic compound (A) [C_3H_6O]

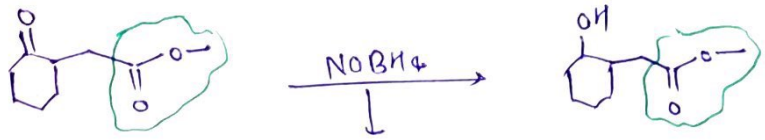


→ B to C conversion is iodoform test, means that B has $-\overset{O}{\overset{\|}{C}}-CH_3$ group and C ⇒ (CHI_3↓).

→ A is alcohol as it has only one oxygen, which is oxidised by Cu.



I.)



It reduces only aldehyde easily.

So, No effect on ester.

Carboxylic Acid → $R-\overset{\overset{O}{\|}}{C}-OH$

Nomenclature :- Alkane − e + oic acid = Alkanoic acid

→ In numbering the carbon chain, the carboxylic carbon is numbered one.

$H-\overset{\overset{O}{\|}}{\underset{1}{C}}-OH$: Methanoic acid [Formic acid] ; $\underset{2}{CH_3}-\overset{\overset{O}{\|}}{\underset{1}{C}}-OH$: Ethanoic Acid [Acetic Acid]

$\begin{matrix}2\,COOH\\ |\\ 1\,COOH\end{matrix}$: Ethanedioic acid [Oxalic Acid]

→ **OMSGAP**

O → Oxalic Acid (n=0) — $\begin{matrix}COOH\\ |\\ COOH\end{matrix}$

M → Malonic Acid (n=1) — $\begin{matrix}COOH\\ |\\ CH_2\\ |\\ COOH\end{matrix}$

S → Succinic Acid (n=2) — $\begin{matrix}COOH\\ |\\ (CH_2)_2\\ |\\ COOH\end{matrix}$

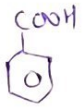
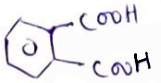
G → Glutaric Acid (n=3)

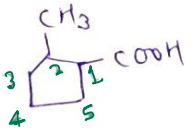
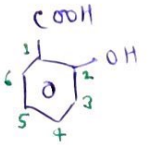
A → Adipic Acid (n=4)

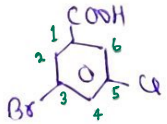
P → Pimelic Acid (n=5)

$\begin{matrix}COOH\\ |\\ (CH_2)_n\\ |\\ COOH\end{matrix}$

→ If $-\overset{\overset{O}{\|}}{C}-OH$ group is present on ring then suffix : carboxylic acid

 : Benzenecarboxylic acid ;  : (Phthalic acid) Benzene-1,2-dicarboxylic acid

 : 2-Methylcyclohexane-1-carboxylic acid ;  : 2-Hydroxybenzoic acid or 2-Hydroxybenzenecarboxylic acid. [Delhi 2014] 1M

 : 3-Bromo-5-chlorobenzoic acid [CBSE 2011C] 1M

→ $\underset{4}{CH_3}-\underset{\underset{OH}{13}}{CH}-\underset{2}{CH_2}-\overset{\overset{O}{\|}}{\underset{1}{C}}-OH$: 3-Hydroxybutanoic acid [CBSE 2014] 1M

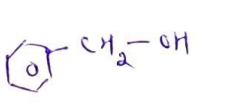
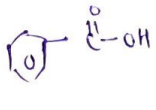
→ $\overset{6}{CH_3}-\overset{5}{C}\equiv\overset{4}{C}-\overset{3}{CH}=\overset{2}{CH}-\overset{\overset{O}{\|}}{\overset{1}{C}}-OH$: Hex-2-en-4-yn-1-oic acid [Delhi 2011C] 1M

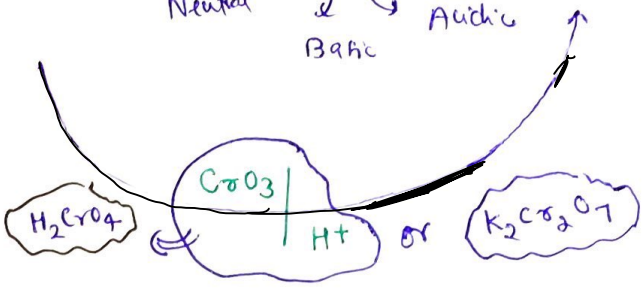
Methods of preparation :-

(i) From 1° Alcohols / Aldehyde :- $R-\overset{O}{\overset{\|}{C}}-H$ / $R-CH_2-OH$ $\xrightarrow{KMnO_4}$ $R-\overset{O}{\overset{\|}{C}}-OH$

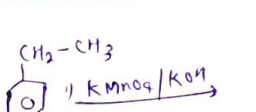
Neutral, Basic, Acidic

→ $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[OH^-]{KMnO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH$

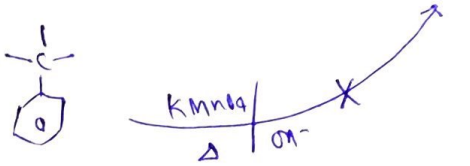
→  $\xrightarrow[H^+]{KMnO_4}$ 



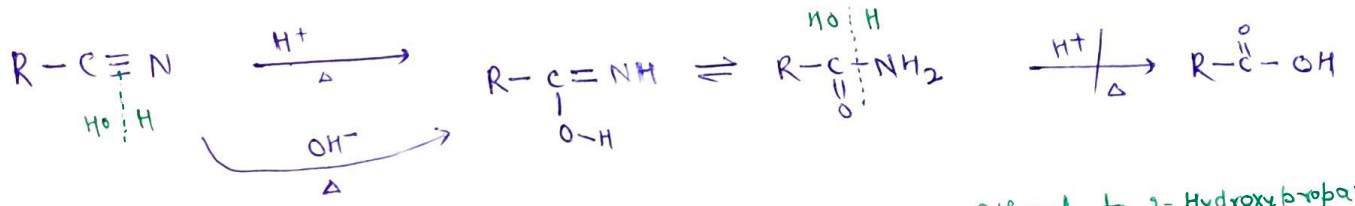
(ii) From Alkylbenzen :-

→  : [Delhi 2019]

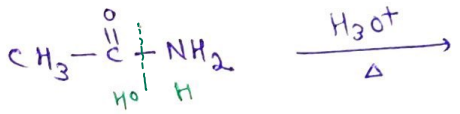
: [Delhi 2015]

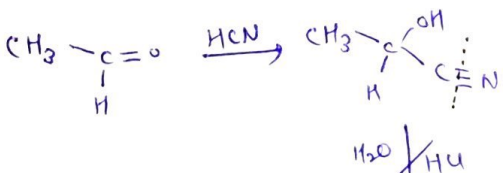


(iii) From nitriles and amides :-

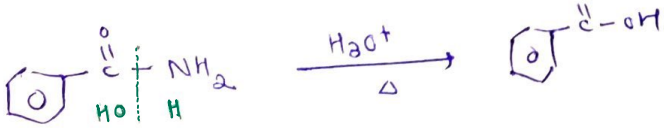


→ Ethanal to 2-Hydroxypropanoic acid

→  Ethanamide

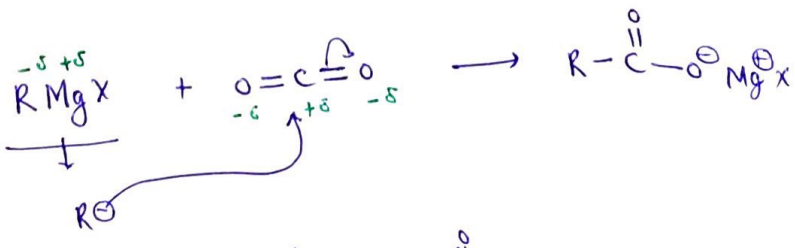


[CBSE 2013]

→ 

Benzamide

(iv) From Grignard Reagents :-

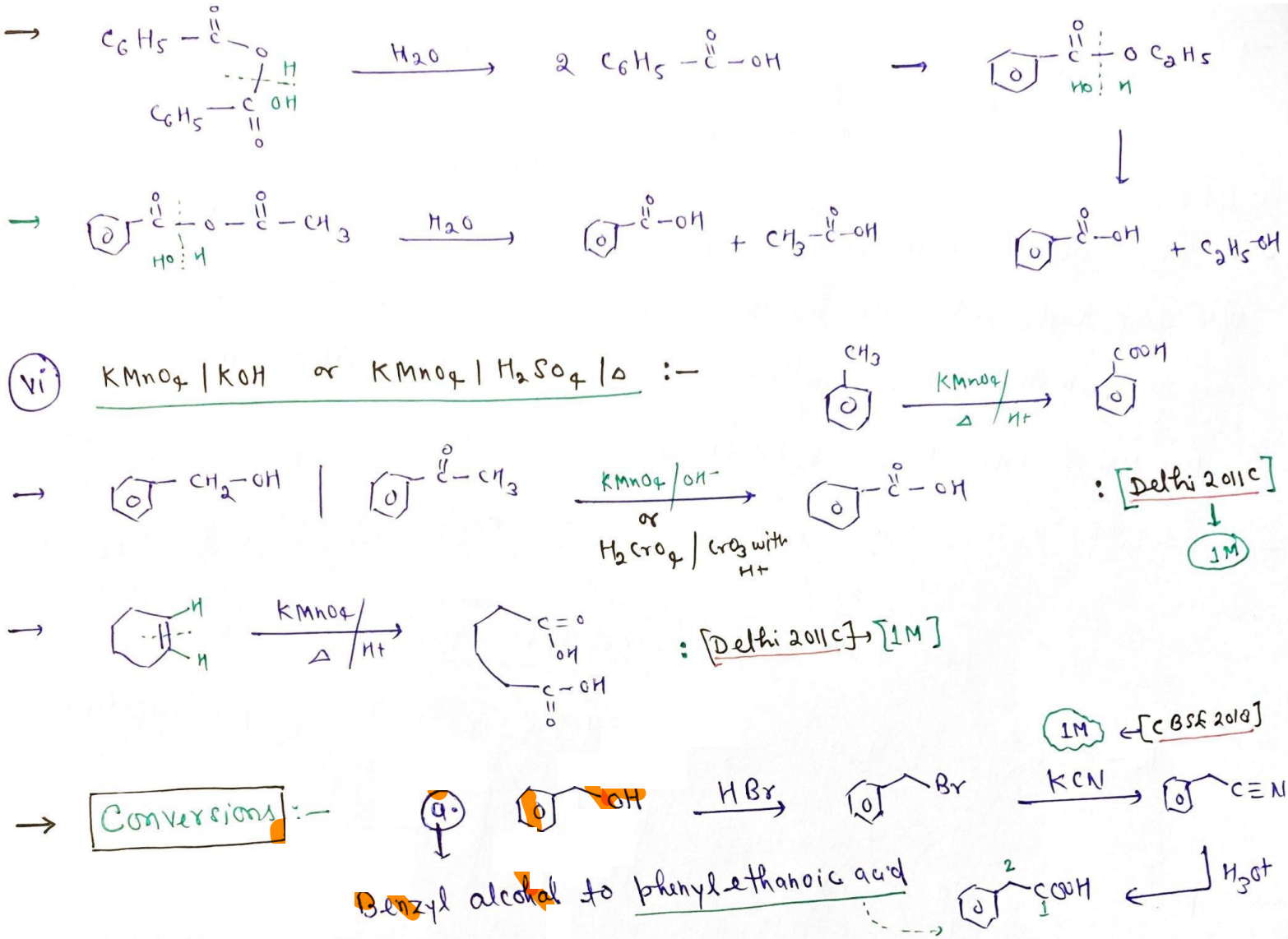


→ $CH_3MgBr + O=C=O \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OMgBr \xrightarrow{H_3O^+} CH_3-\overset{O}{\overset{\|}{C}}-OH$

(v) Acyl Halide : $R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + HCl$

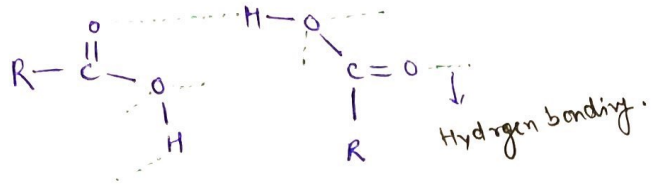
Anhydride : $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \longrightarrow 2\,R-\overset{O}{\overset{\|}{C}}-OH$

Ester : $R-\overset{O}{\overset{\|}{C}}-OR \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + R-OH$

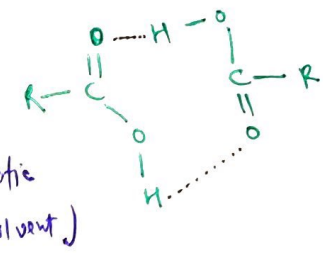


Physical Properties

→ Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable mass. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

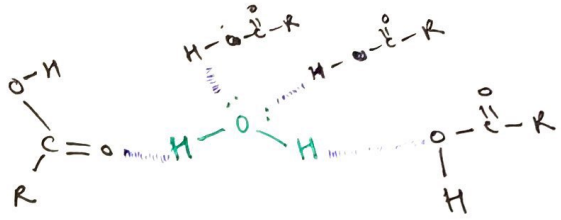
→ 

→ Association of carboxylic acid as dimer (in vapour / aprotic solvent)



Solubility

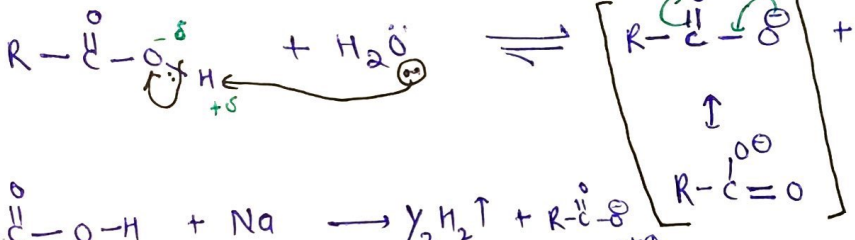
→ Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to formation of hydrogen bonding with water.



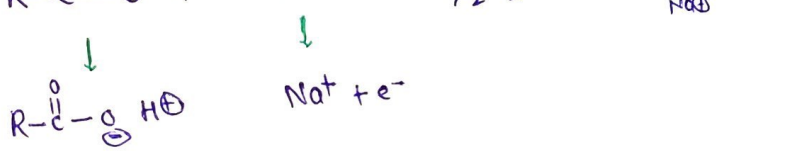
→ As No. of Carbon ↑ ⇒ Solubility ↓

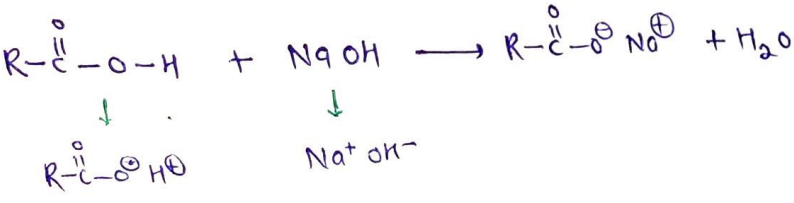
→ Solubility order : $CH_3-CH_2-CH_2-COOH > CH_3(CH_2)_6COOH$

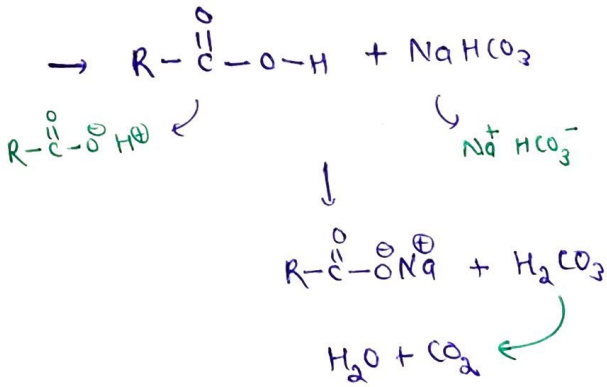
Acidic Nature of Carboxylic Acid

→  : Acidic Nature

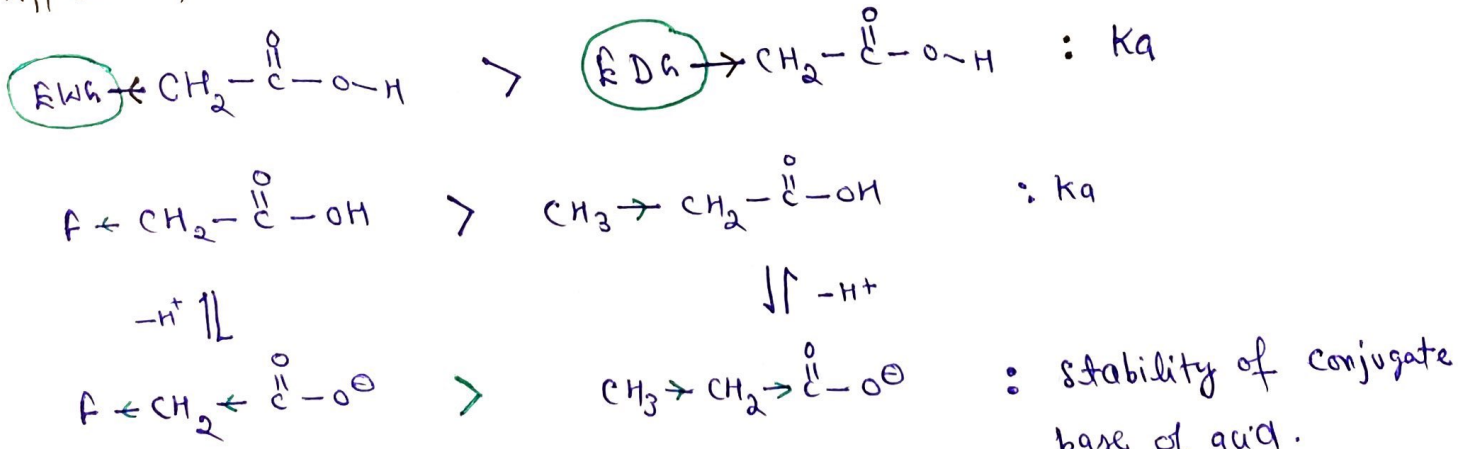
→

→ 

→ 

→ 

→ Effect of substituents on acidity of carboxylic acids :-



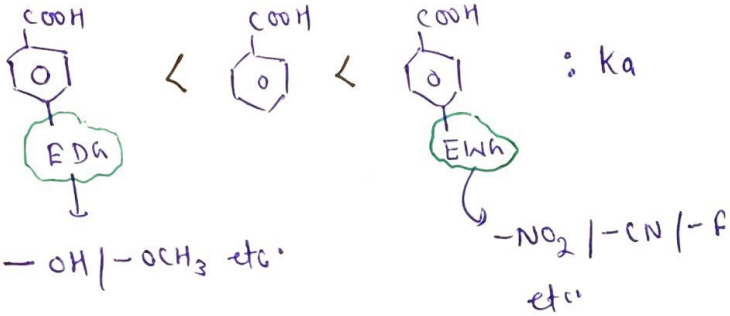
⇒ **Acidity (Ka) ∝ Stability of conjugate base**

→ CF_3-COOH > CCl_3-COOH : Ka (F is more electronegative than Cl.

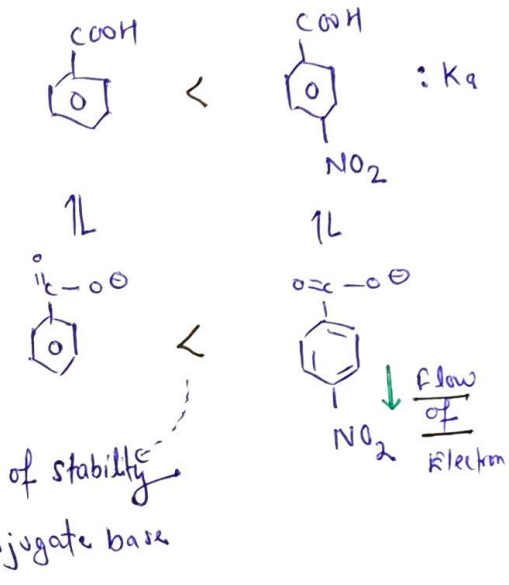
→ $F-CH_2-COOH$ > $Cl-CH_2-COOH$ > $Br-CH_2-COOH$ > $I-CH_2-COOH$: Ka

→ F > B > A : Ka means that, $HCOOH$ > C_6H_5-COOH > CH_3-COOH : Ka

Formic Acid — Benzoic Acid — Acetic Acid

→ 

→ [Delhi 2010] → [IM]



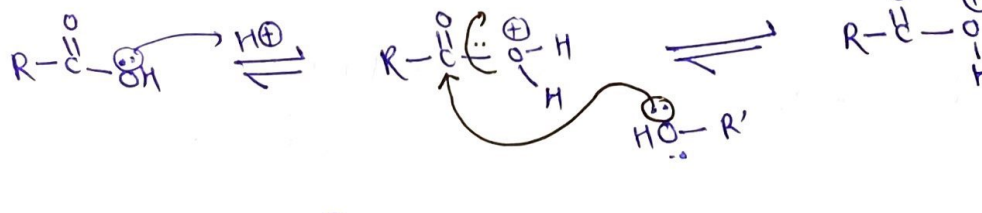
Reactions involving breaking of C–OH bond

① **Formation of anhydride :–** (By using dehydrating agent : Conc. H_2SO_4 / $\xrightarrow{\Delta}$; P_2O_5 / $\xrightarrow{\Delta}$)

$CH_3-COOH + HO-COCH_3 \xrightarrow[(-H_2O)]{P_2O_5 / \Delta} CH_3-CO-O-CO-CH_3$

② **Esterification :–** $R-COOH + H-O-R' \overset{H^+}{\rightleftharpoons} R-CO-O-R' + H_2O$

Mechanism :–



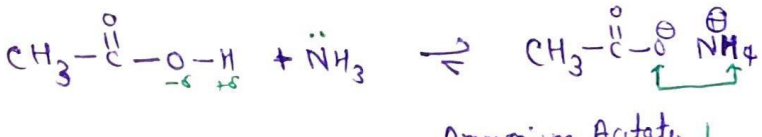
③ $R-COOH \xrightarrow{PCl_5} R-COCl + POCl_3 + HCl$

$3\,R-COOH \xrightarrow{PCl_3} 3\,R-COCl + H_3PO_3$

$R-COOH \xrightarrow{SOCl_2} R-COCl + SO_2\uparrow + HCl\uparrow$

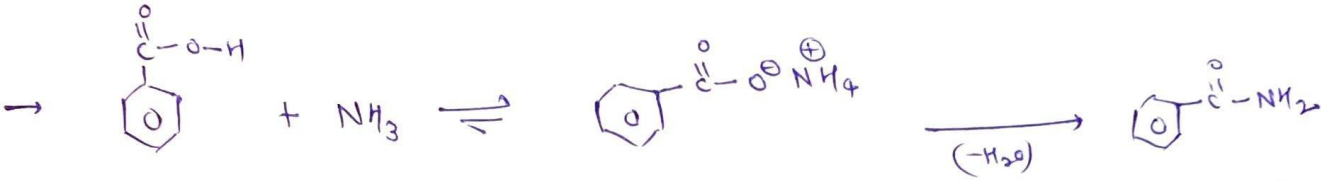
Side products are gases and escape the reaction mixture making pure $R-COCl$.

→ [4] Reaction with ammonia —:



Ammonium Acetate

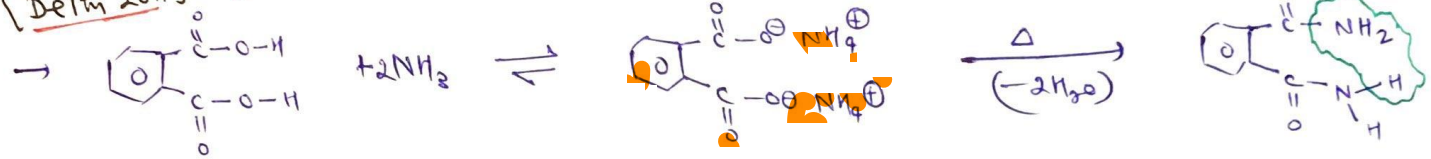
Acetamide



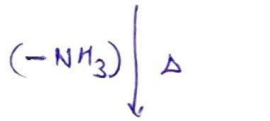
Ammonium Benzoate

Benzamide

[Delhi 2011]: [2.5 M]



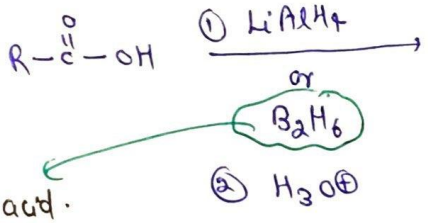
Phthalic Acid



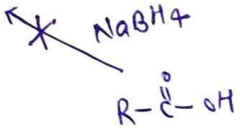
Phthalimide

→ **Reactions involving $-\overset{O}{\overset{\|}{C}}-OH$ group**

1°] Reduction :—



B_2H_6 is best for acid.



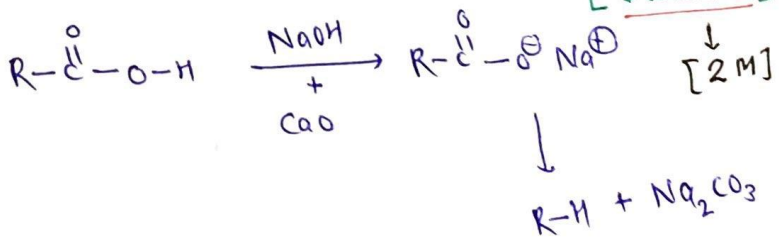
2°] Decarboxylation :— [Removal of CO_2]

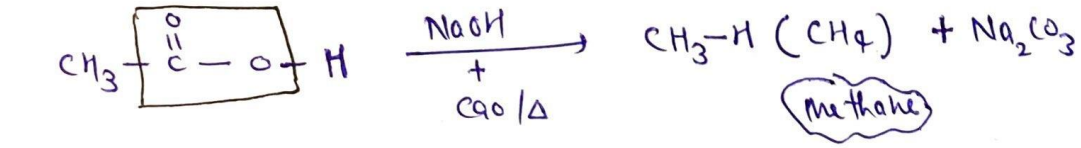
→ [Delhi 2012] → [1M]

[Delhi 2017] → [2 M]

→ Soda - Lime Decarboxylation :

NaOH + CaO : Reagent

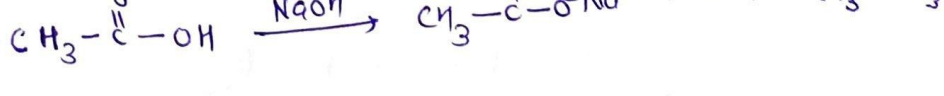


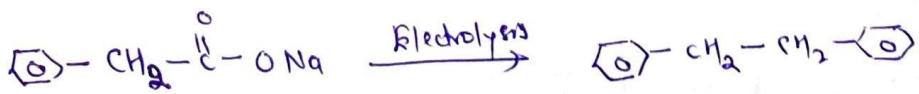


Methane

→ Acid to alkane Conversion

→ Kolbe Electrolysis —:

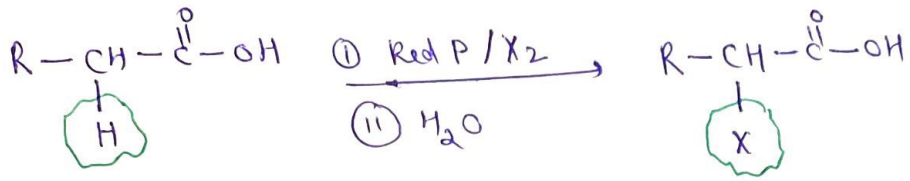




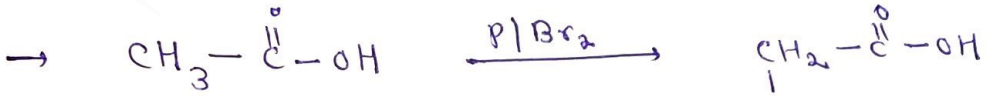
Reaction on hydrocarbon part

[Delhi 2017] - [2M]
(CBSE 2010)

(i) Halogenation :— Hell - Volhard - Zelinsky Reaction (HVZ Reaction)

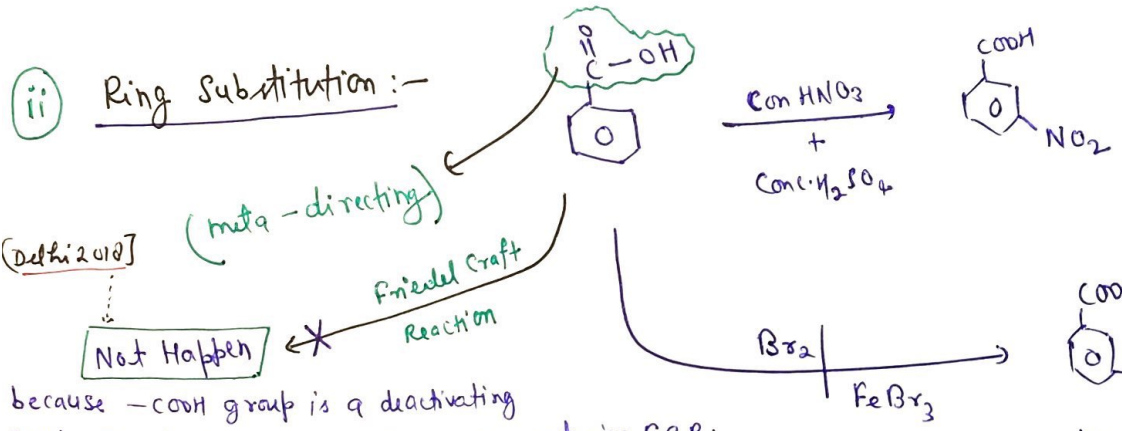


α - Halocarboxylic acid

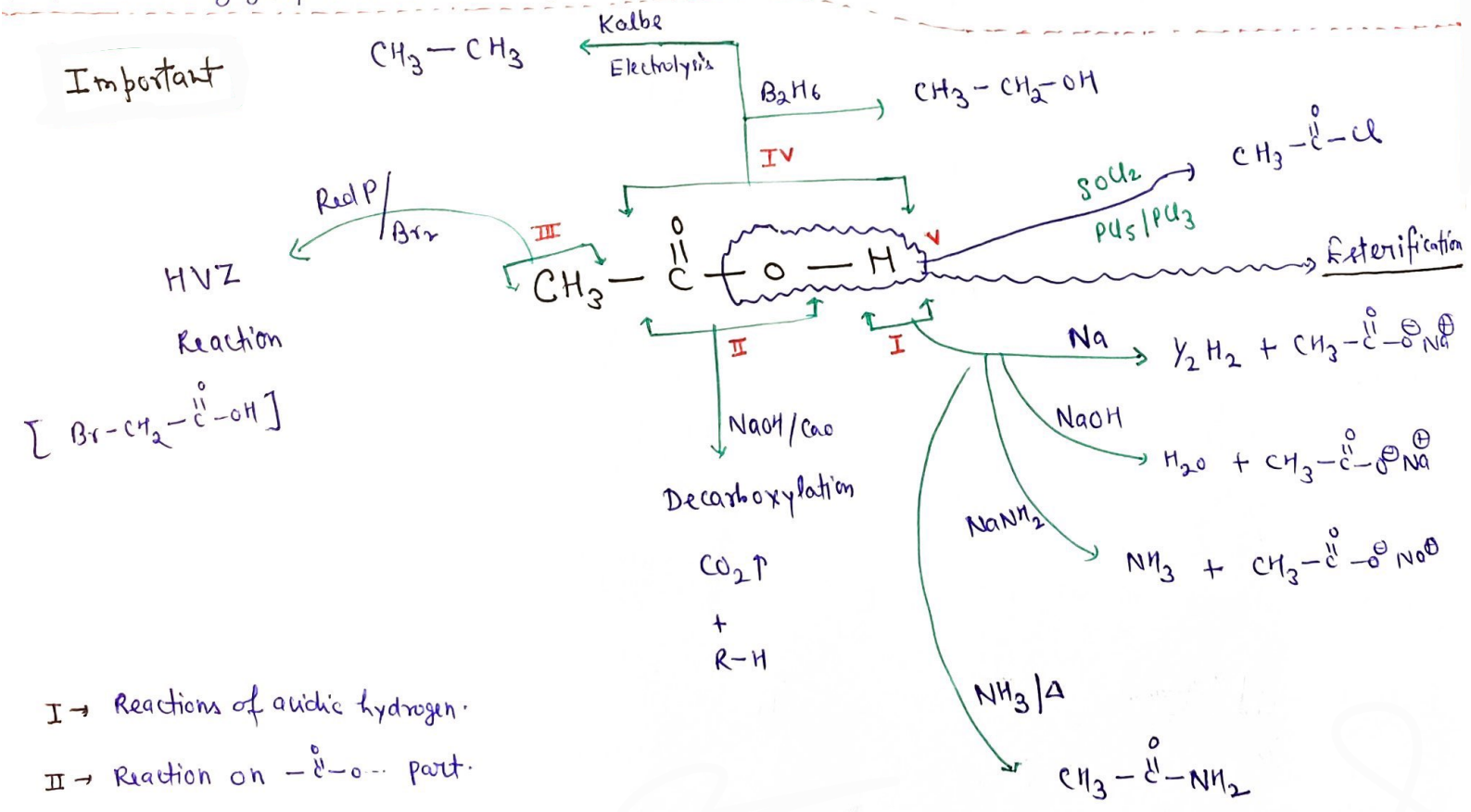


[Delhi 2014] → [1M]
[Delhi 2013C] → [1M]
[CBSE 2016] → [1M]

(ii) Ring Substitution :—



Important



I → Reactions of acidic hydrogen.

II → Reaction on —C(=O)—O— part.

III → Reaction on hydrocarbon part.

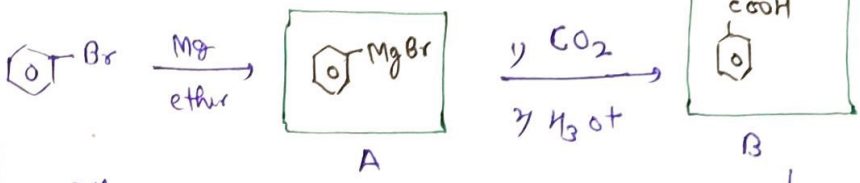
IV → Reaction on —C(=O)—OH.

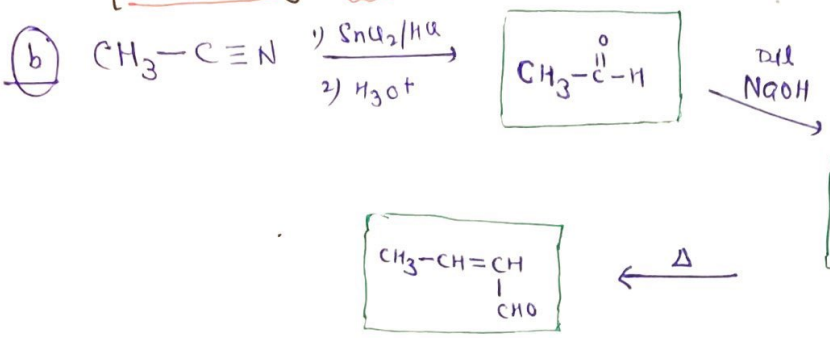
V → Reactions on —OH part.

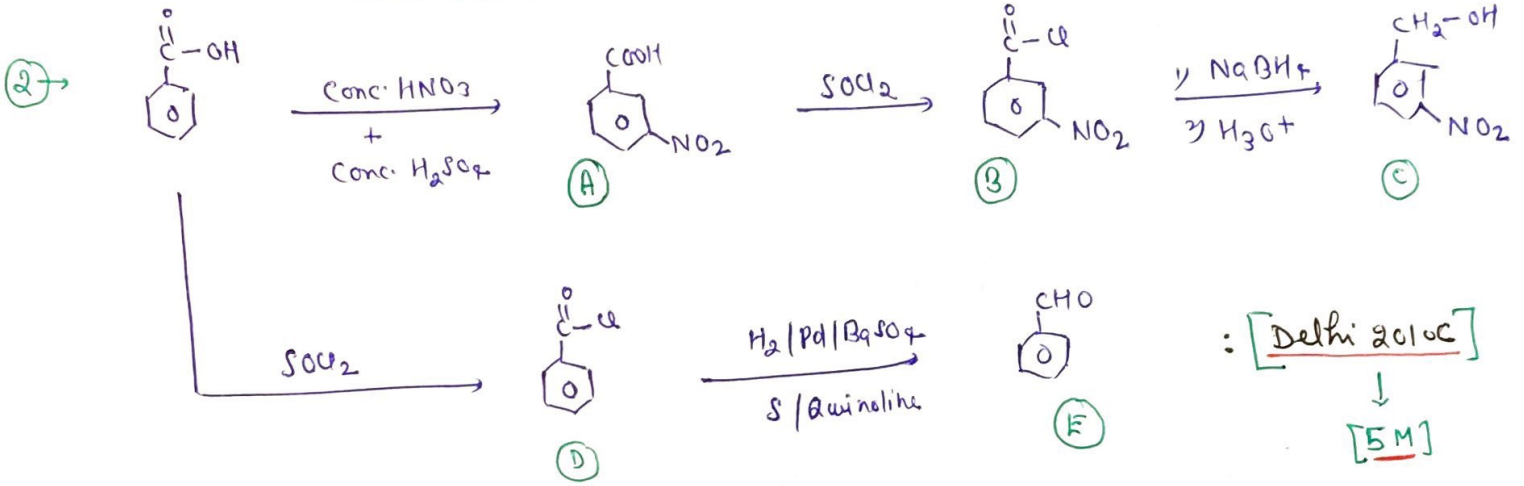
Important Previous Year Questions

(1) Structure of A / B / C :-

[Delhi 2017] → (3M)

(a) 

(b) 

(2) 

: [Delhi 2010C] → [5M]

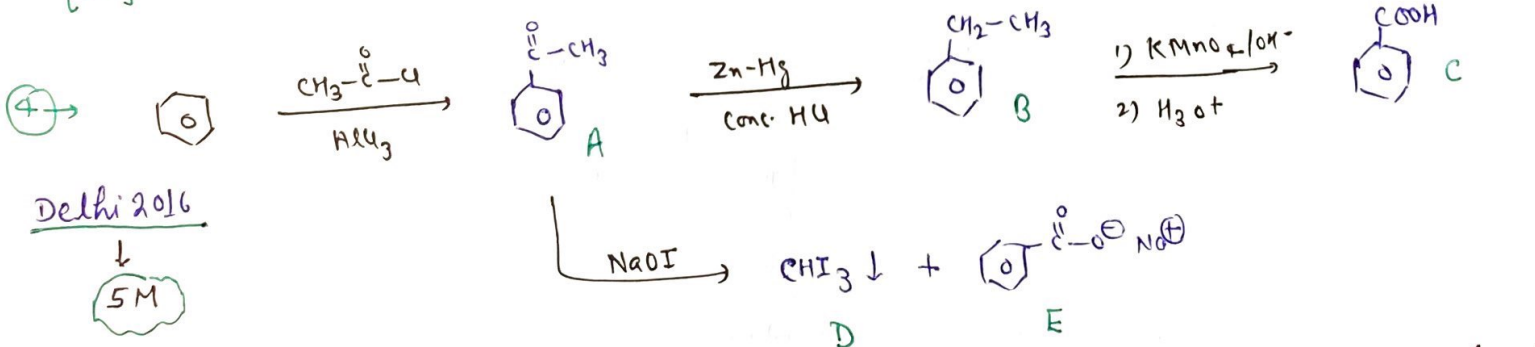
(3) Acidity Order :

[CBSE 2015, Delhi 2013C] → [1M]

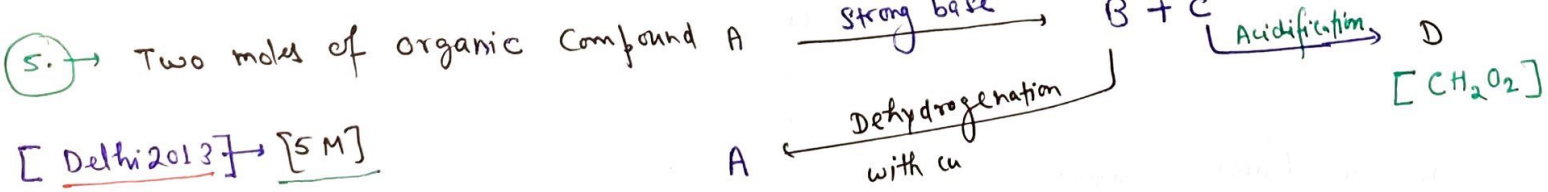
$F-CH_2-COOH > Cl-CH_2-COOH > CH_3-COOH$

$-F$ / $-Cl$ both are $-I$ group

$-CH_3$ $+I$ group.

(4) 

Delhi 2016 → 5M

(5) Two moles of organic compound A 

[Delhi 2013] → [5M]

Answer :- D ⇒ Carboxylic acid → $H-COOH$

B → Alcohol → CH_3-OH → (Cu) → A ($H-CHO$)

C → $H-COO^-$

Then A must be $H-CHO$ as strong base represent cannizzaro.

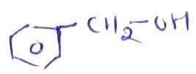
6.] Organic compound A $\xrightarrow{NaOH}$ B + C

[CBSE 2013|2012C] → 3M

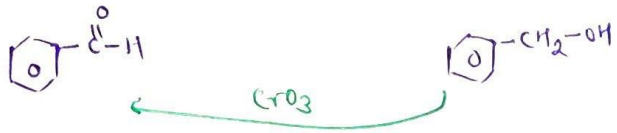
B [C_7H_8O] $\xrightarrow{CrO_3}$ A

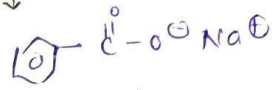
C: Sodium salt of acid $\xrightarrow{Soda\text{-}lime\ /\Delta}$ D (Aromatic Hydrocarbon)

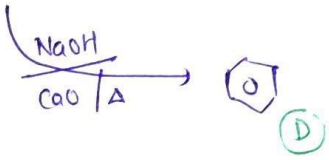
→ Answer

B (C_7H_8O) has only one oxygen : Alcohol : 

(A) Aldehyde $\xrightarrow{NaOH}$ Alcohol (B) + Salt of acid (C)

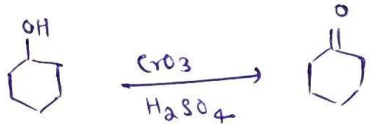




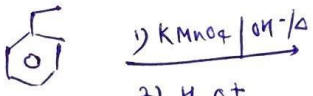


7.] How the following conversions can be brought about?

a.] Cyclohexanol to cyclohexan-1-one



b.] Ethyl benzene to benzoic acid

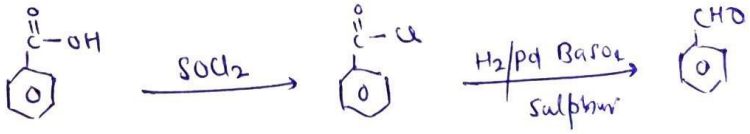


: [Delhi 2017]

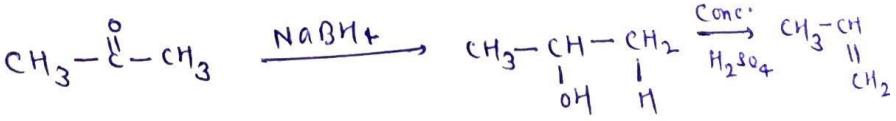
c.] Bromobenzene to benzoic acid

3M → [CBSE 2010 | Delhi 2008]

d.] Benzoic acid to benzaldehyde [2015] → 1M

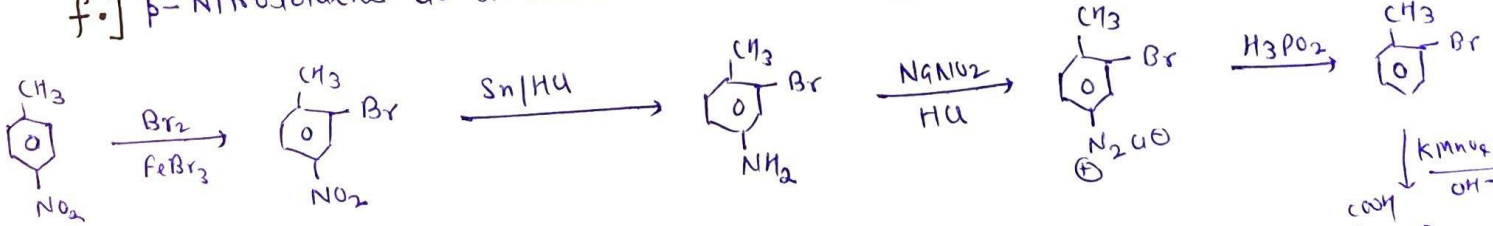


e.] Propanone to propene

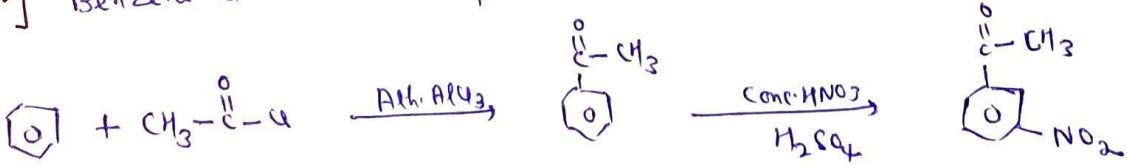


[Delhi 2017] → 2M

f.] p-Nitrotoluene to 2-bromobenzoic acid :- 2019



g.] Benzene to m-nitroacetophenone :— Delhi 2015C → 1M



Benzene.

m-Nitroacetophenone.