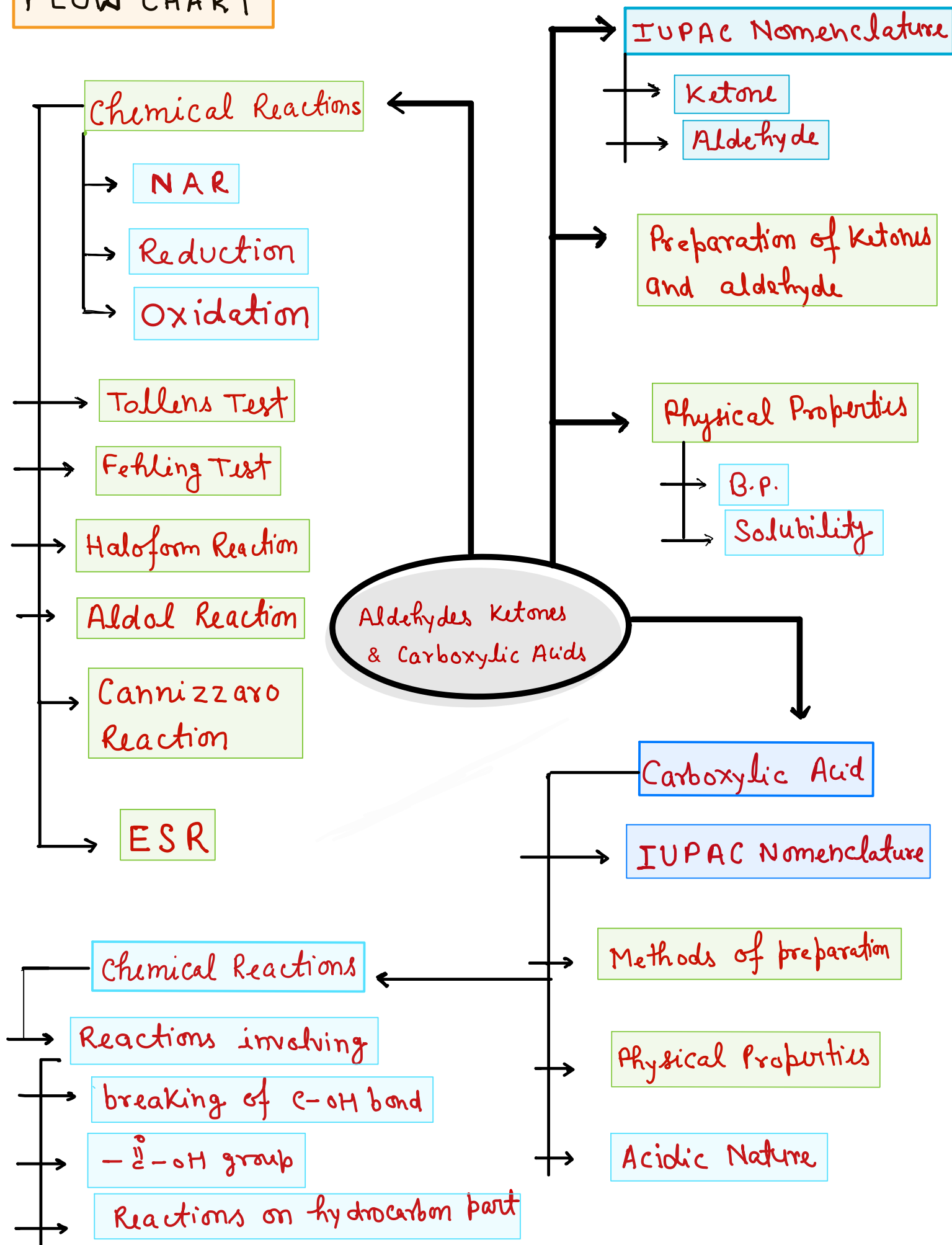
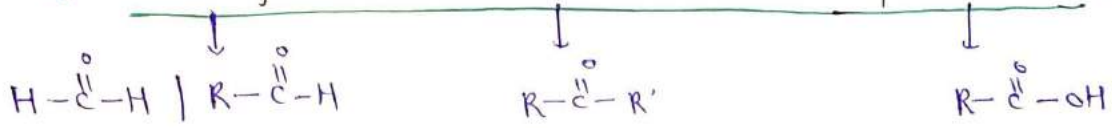


# Aldehydes Ketones And Carboxylic Acids

## FLOW CHART

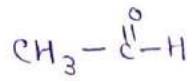


# # Aldehydes, Ketones and Carboxylic Acids #

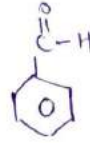


→ Nomenclature of carbonyl group :-

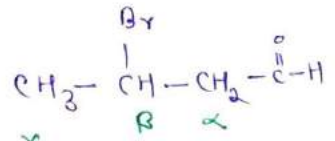
Important common names :-



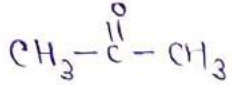
Acetaldehyde



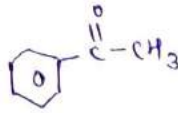
Benzaldehyde



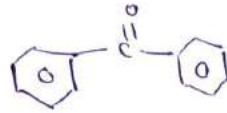
$\gamma$   
B-Bromobutyraldehyde



Acetone



Acetophenone



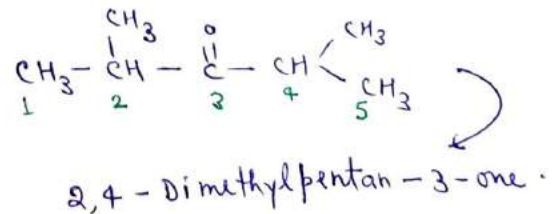
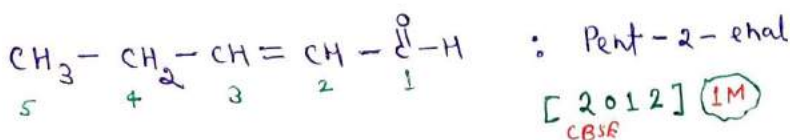
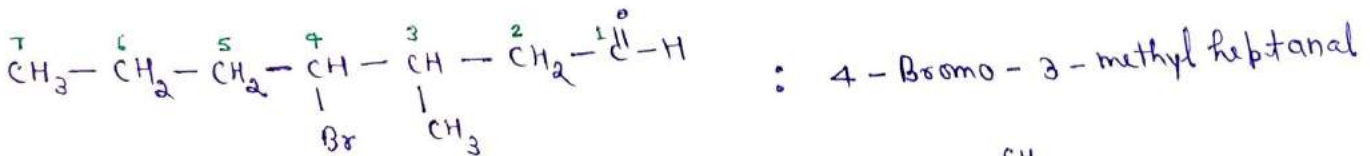
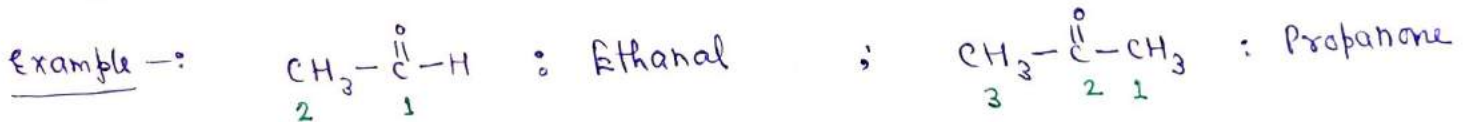
Benzophenone

## IUPAC Name

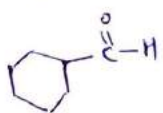
→ For aliphatic aldehydes / ketones : Alkane - e + al/one → Alkanal  
→ Alkanone

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

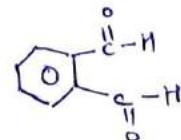
→ In case of ketones :- Numbering begins from the end nearer to carbonyl group



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



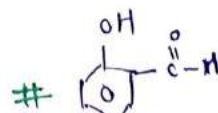
: Cyclohexanecarbaldehyde ; #



→ Benzene-1,2-di-carbaldehyde

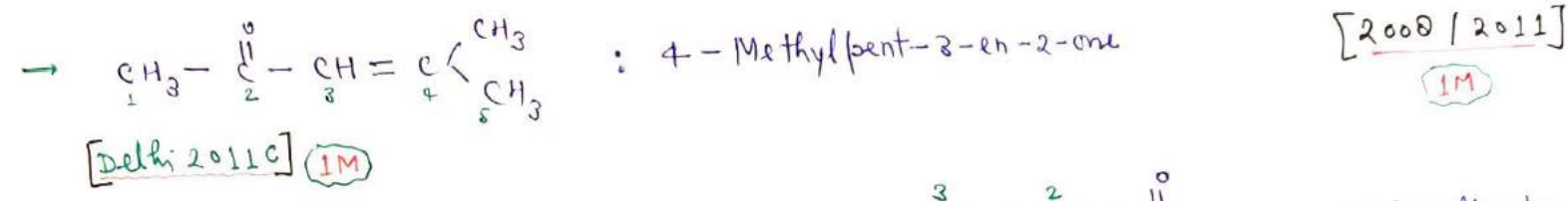
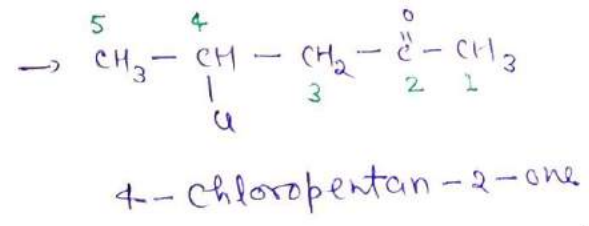
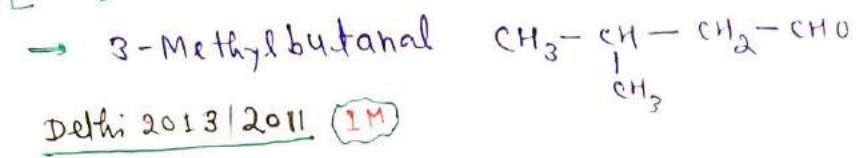
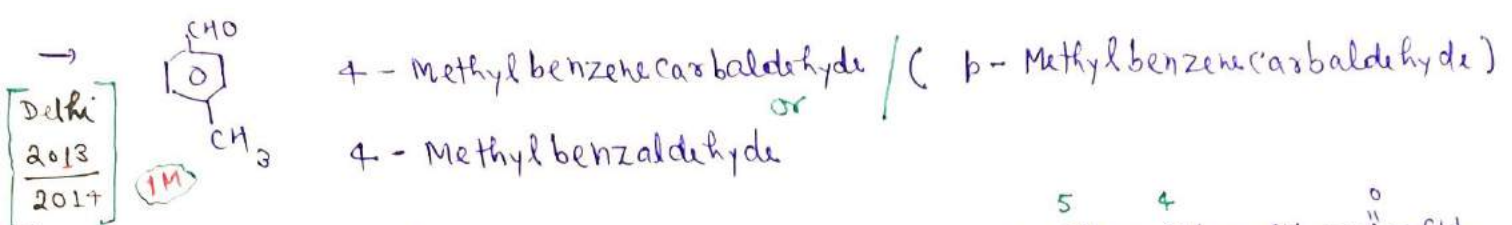


: Benzene Carbaldehyde [Benzaldehyde]

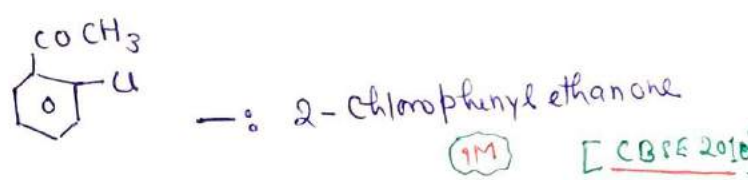
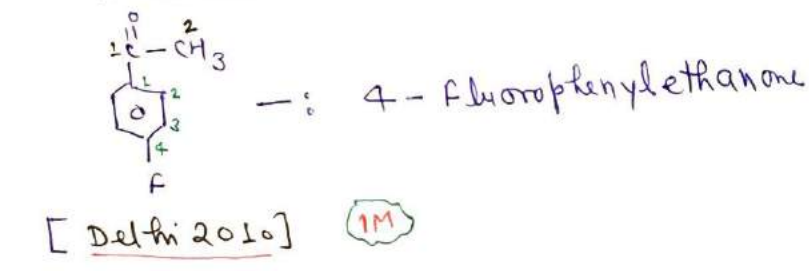
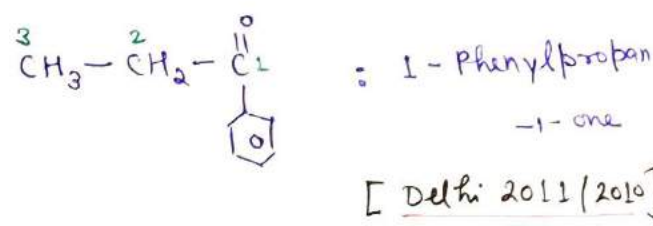


[2014]

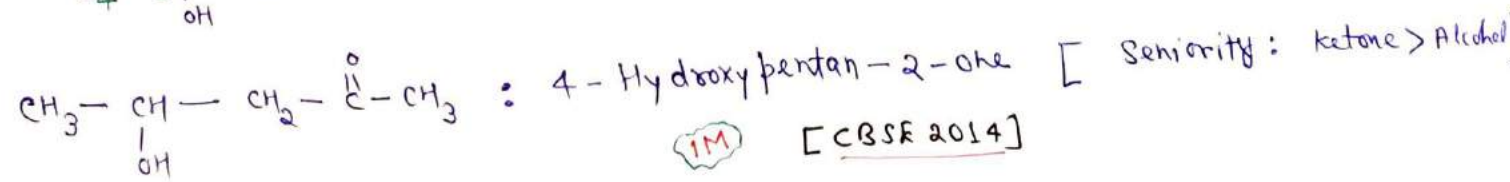
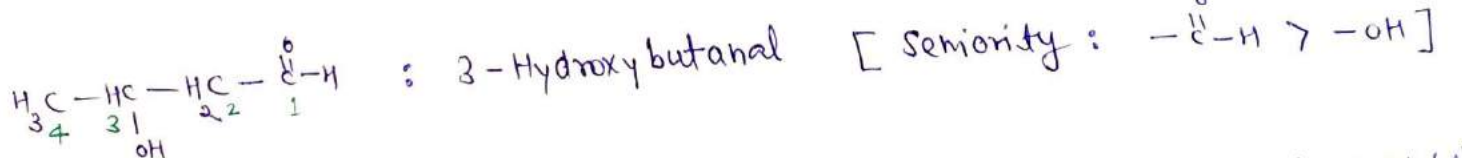
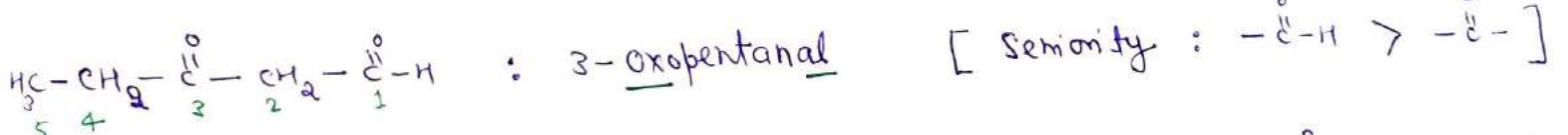
→ 2-Hydroxybenzene carbaldehyde



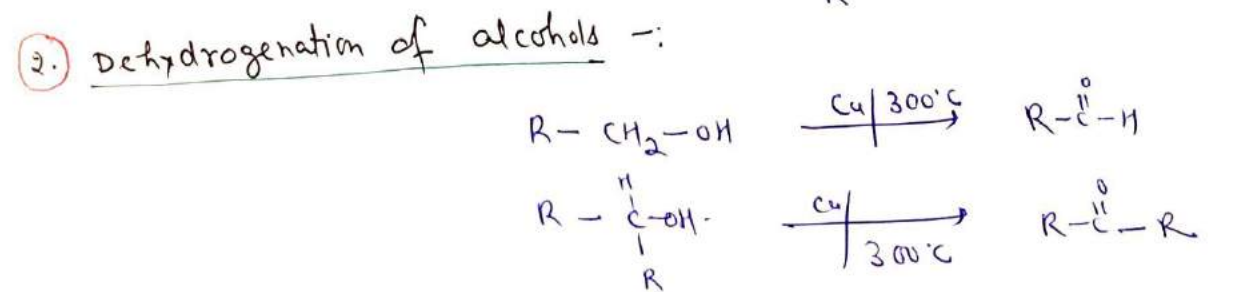
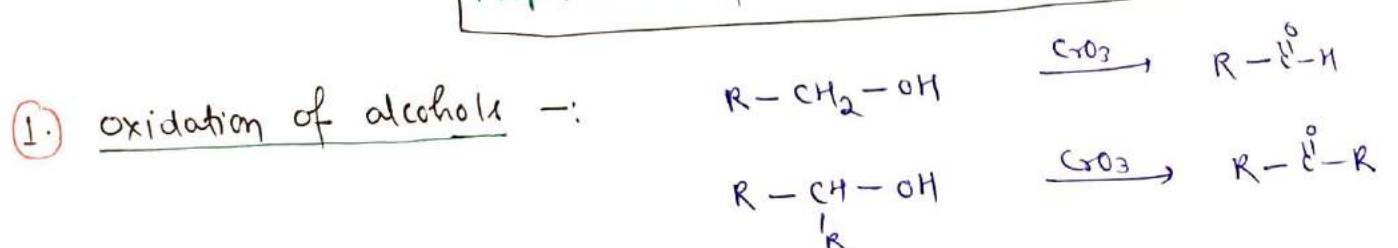
→ Benzene as substituent —: Phenyl



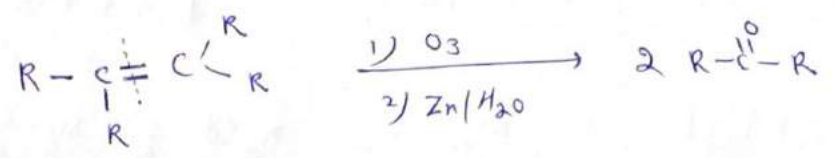
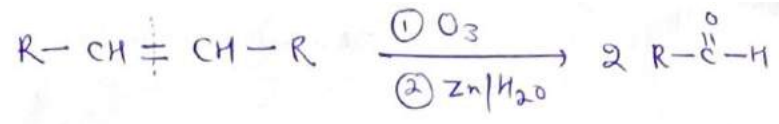
→ Senior functional group makes 2° suffix and junior makes 2° prefix (substituent)



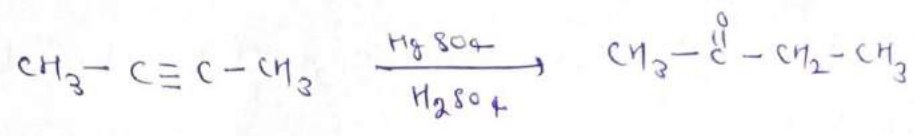
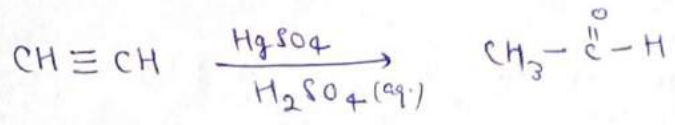
Preparation of aldehydes and ketones



3) Ozonolysis of alkene :-

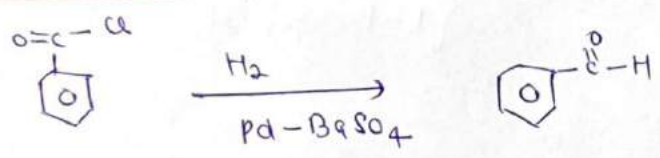


4) Hydration of alkyne :-

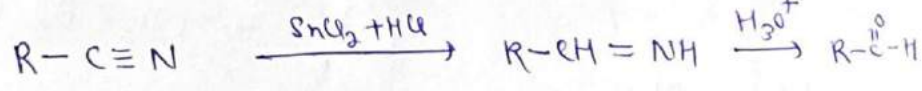


Preparation of Aldehydes

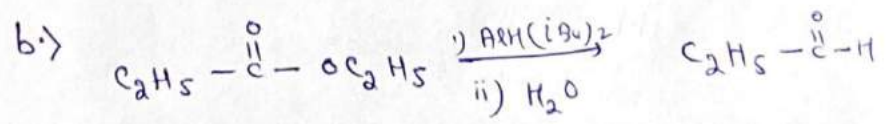
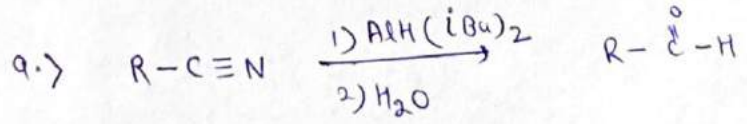
→ (i) Rosenmund reduction of acid chloride :-



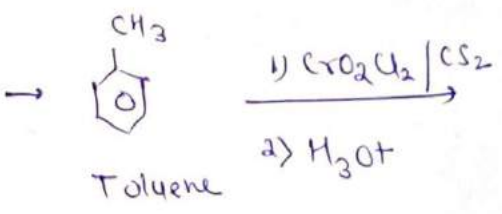
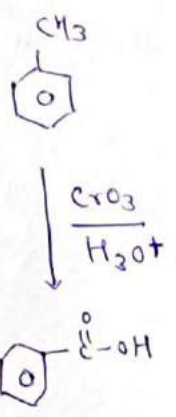
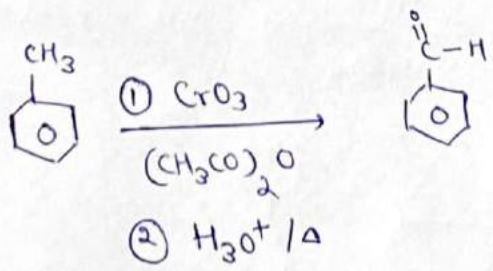
(ii) Stephen's Reduction :-



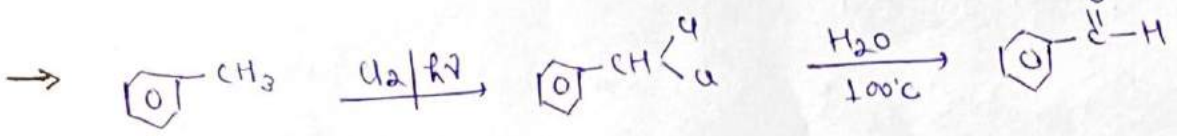
→ (iii) By DIBAL-H :-



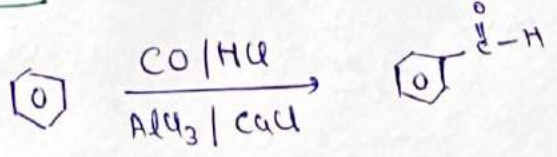
iv] From Hydrocarbon :-



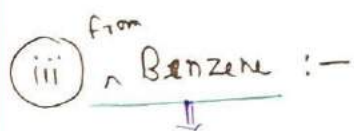
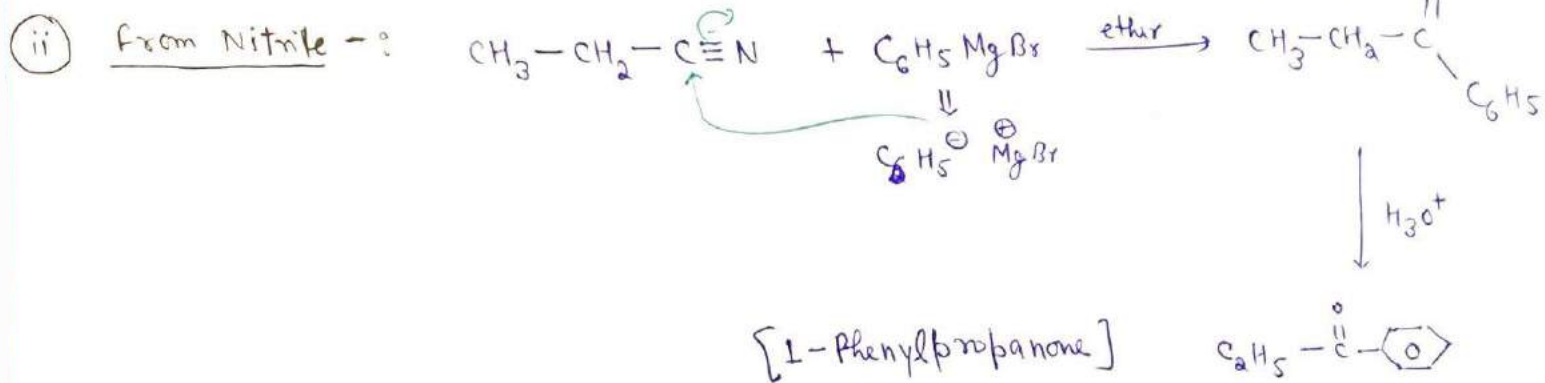
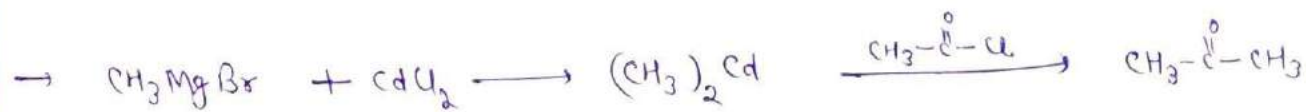
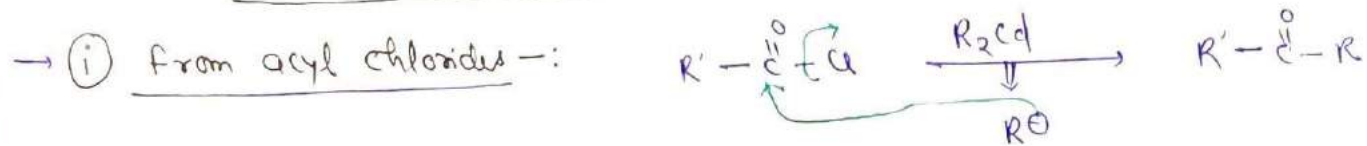
: Etard Reaction (Delta 2017) → 1M



Gattermann - Koch Reaction :-

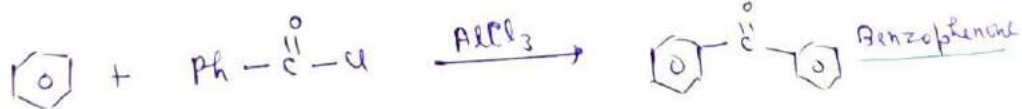
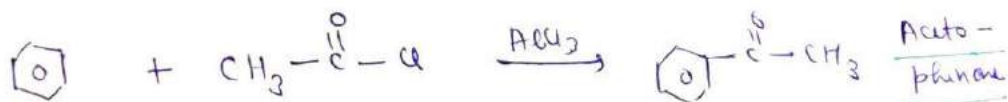


## Preparation of Ketones

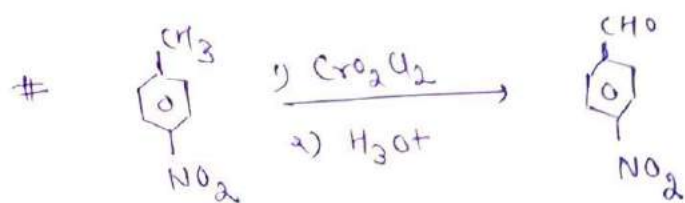
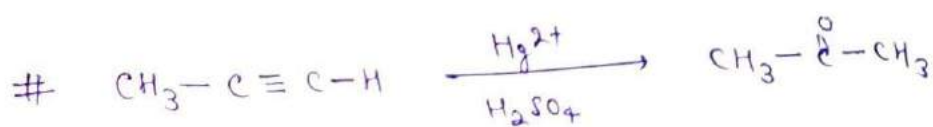


Friedel-Crafts

Acylation reaction



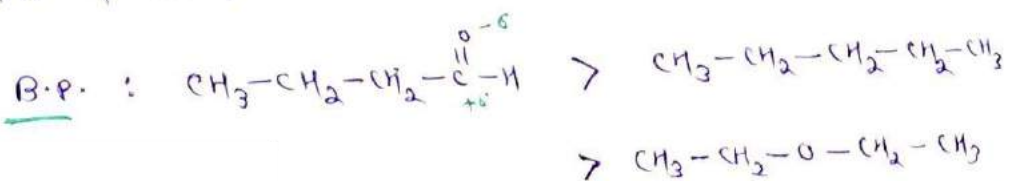
(IM) [Delhi 2012]



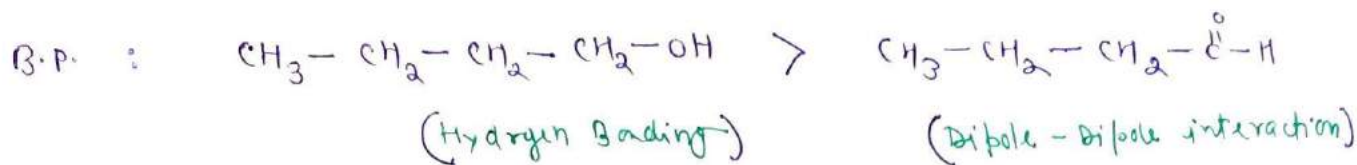
[Delhi 2012]

## 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.

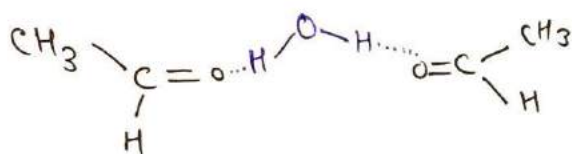


→ Boiling points of aldehydes and ketones are lower than those of alcohol of similar molecular masses due to absence of hydrogen bonding.



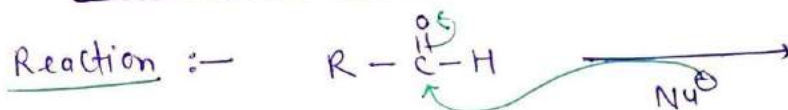
**Solubility** → solubility of aldehydes and ketones decreases ⇒ size of alkyl group ↑.

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

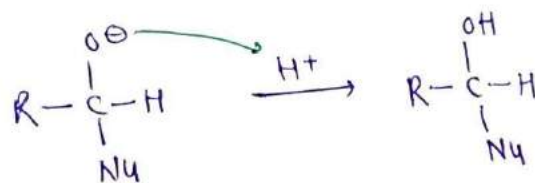


**Chemical Reactions**

Nucleophilic Addition Reaction :-



Aldehyde : Planar



Tetrahedral intermediate

Addition Product

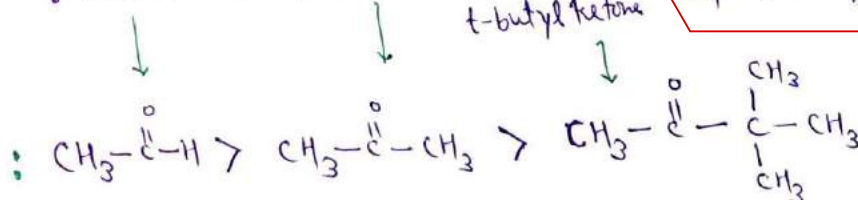
Reactivity : → Aldehydes > Ketones



Electrophilicity decreases means that partial  $\oplus$ ve charge decreases.

→ Reactivity order :  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} > \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} > \text{Acetone}$

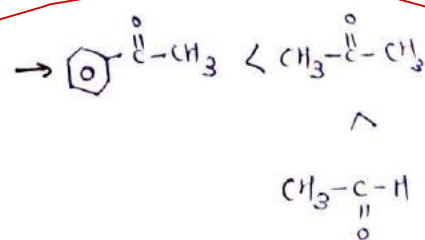
: Acetaldehyde > Acetone > Methyl t-butyl ketone



[1M]

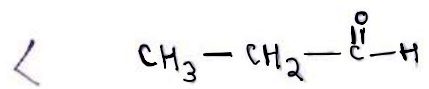
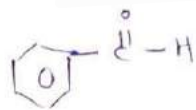
[CBSE 2012]

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

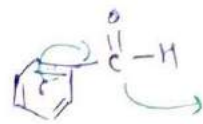


[1M] ← [Delhi 2015]

→ Reactivity for NAR :-

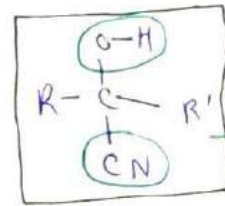
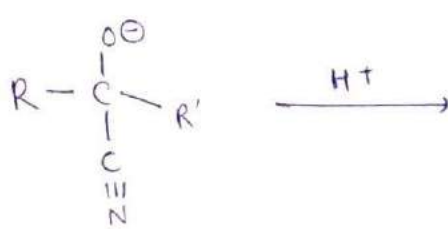
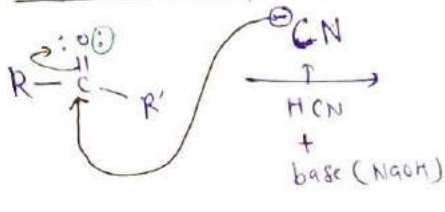


Because polarity of carbonyl group is reduced in benzaldehyde due to resonance.

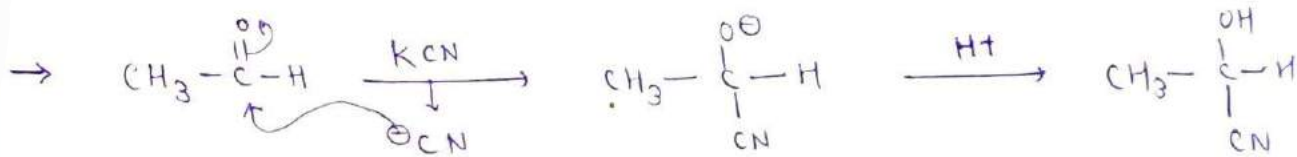


Partial  $\oplus$ ve charge  
↓  
Electrophilicity  $\downarrow$

→ Addition of HCN :-



Cyanohydrin

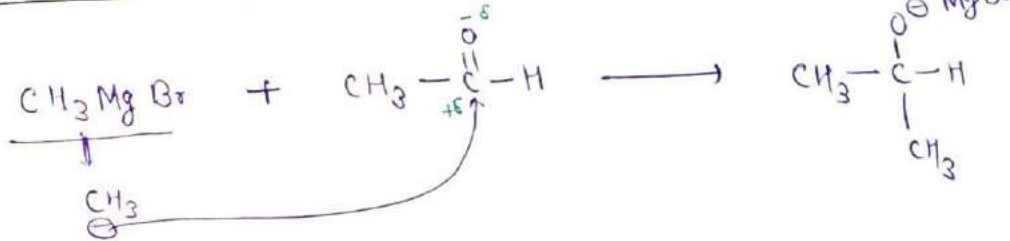


→ Addition of sodium hydrogen sulphite :- [NaHSO<sub>3</sub>]

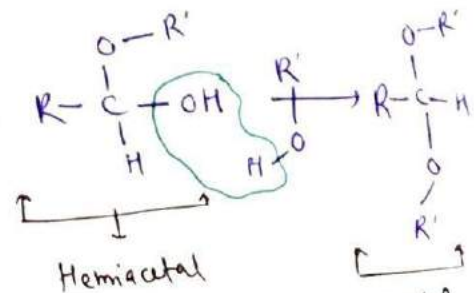
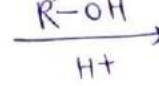
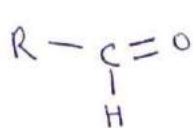


Crystalline ← [Addition Product]

→ Addition of Grignard Reagent :-

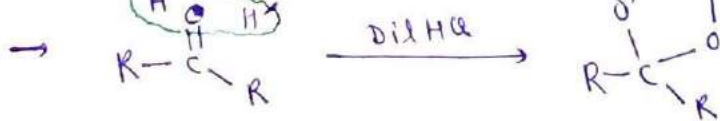


→ Addition of alcohols :-



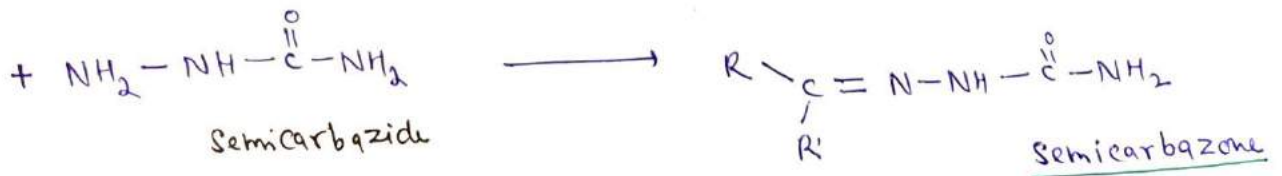
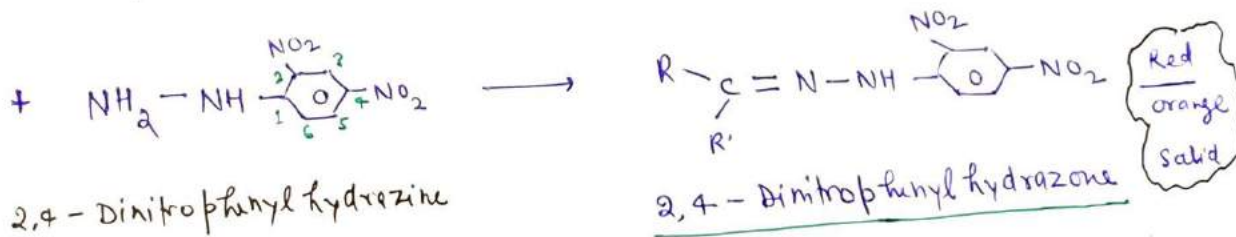
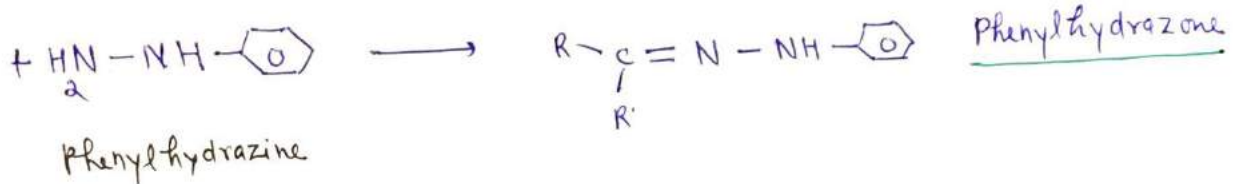
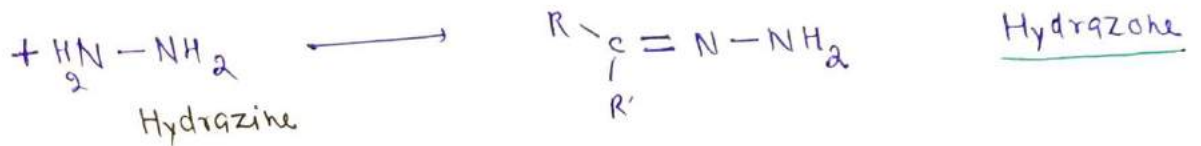
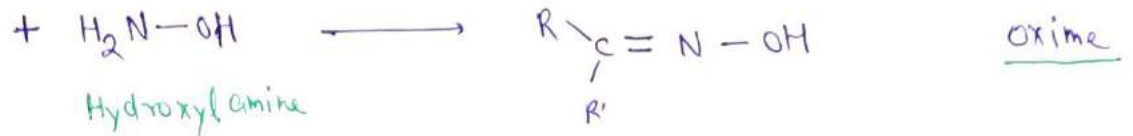
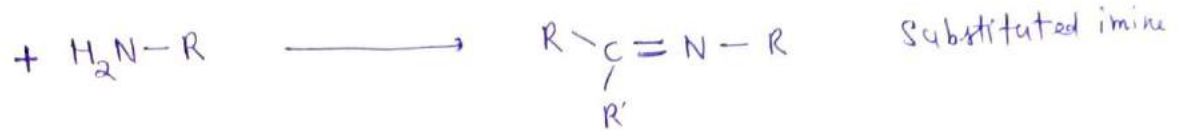
Hemiacetal

Acetal

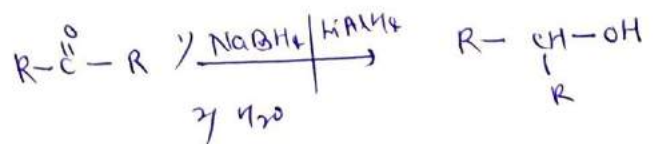
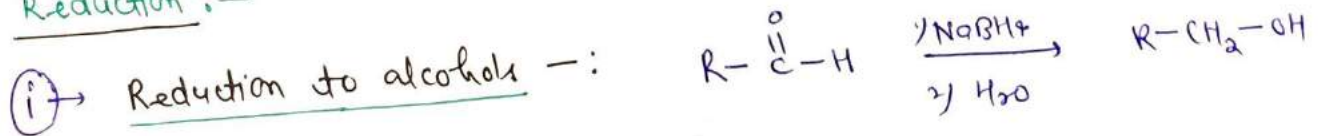


→ Addition of Ammonia and its derivatives :-

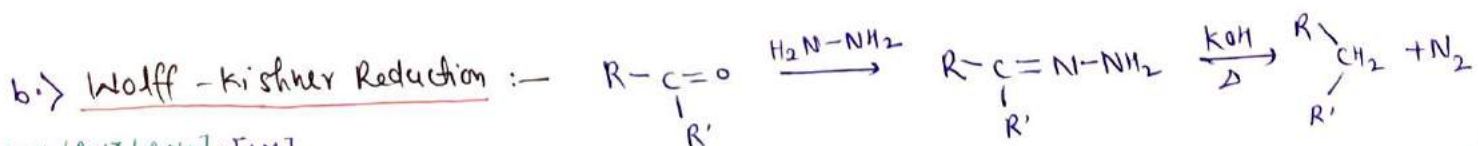
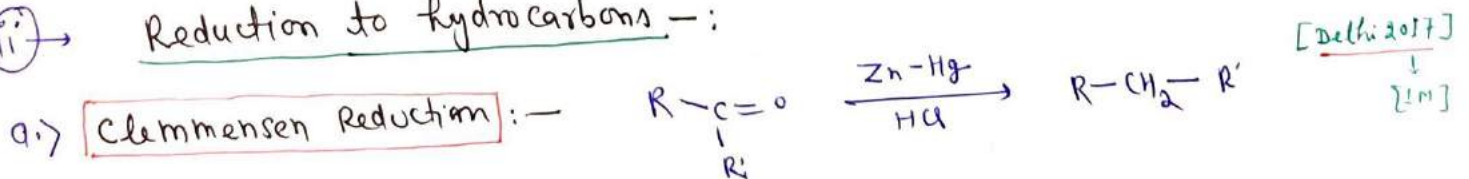




### Reduction :-



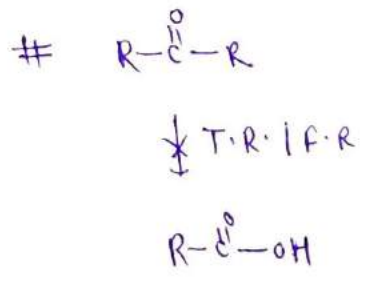
(ii) Reduction to hydrocarbons :-



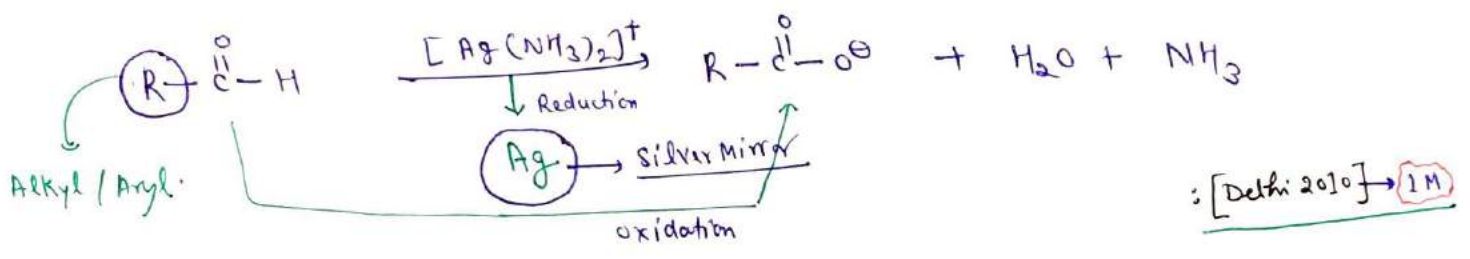
Oxidation :-



- $\rightarrow HNO_3 / KMnO_4 / K_2Cr_2O_7$
- $\rightarrow$  Tollen's Reagent
- $\rightarrow$  Fehling Reagent

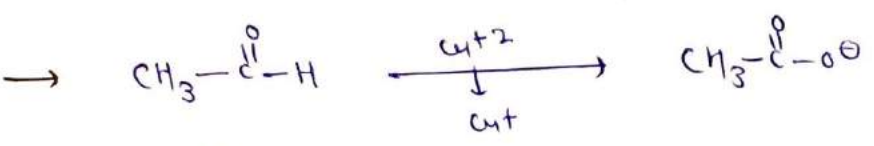
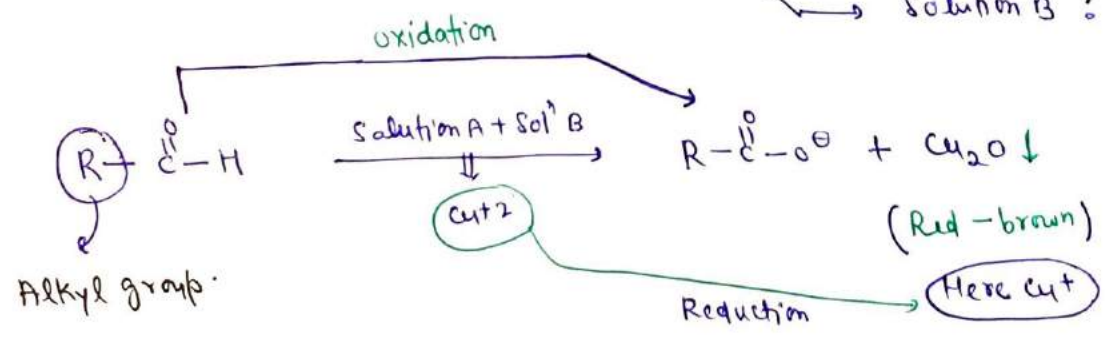


Tollen's Test :- Tollen's Reagent  $\rightarrow NH_4OH + AgNO_3 \rightarrow [Ag(NH_3)_2]^+$

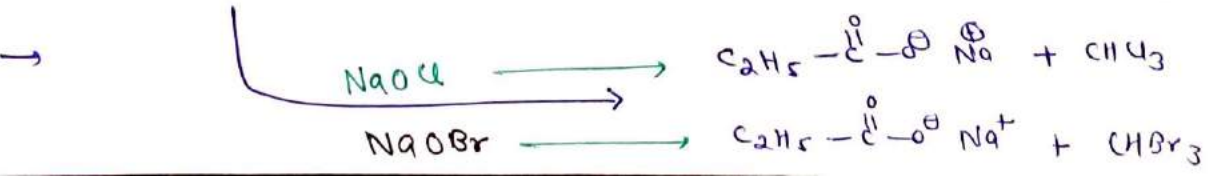
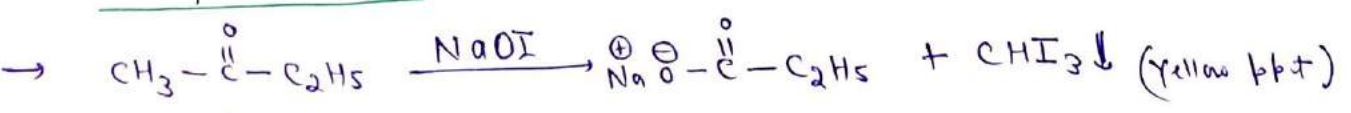


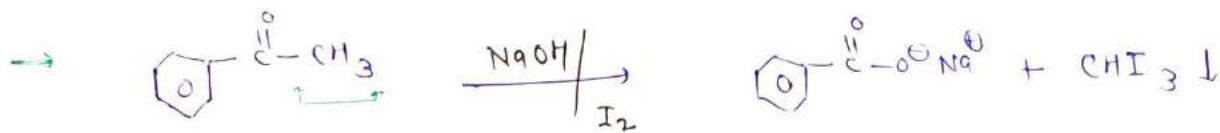
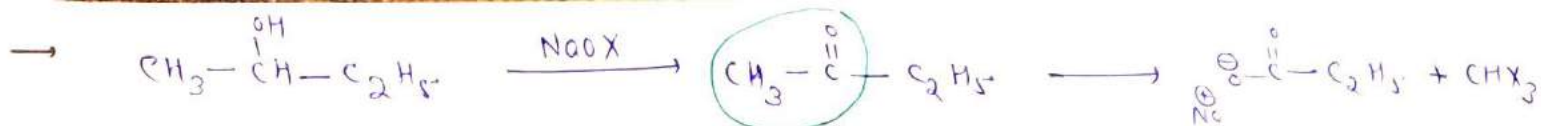
$\rightarrow$  Above reaction is not possible with ketone. By using above reagent aldehyde and ketone can be identified.

Fehling's Test :- Two parts  
 Solution A :  $CuSO_4$  (aq.)  
 Solution B : Sodium Potassium Tartrate (Rochelle salt)

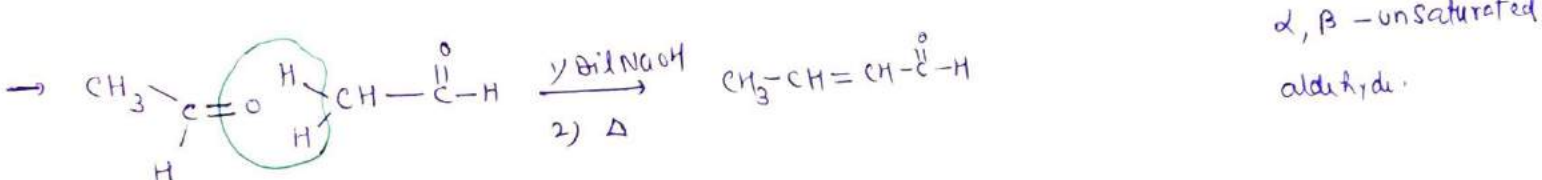
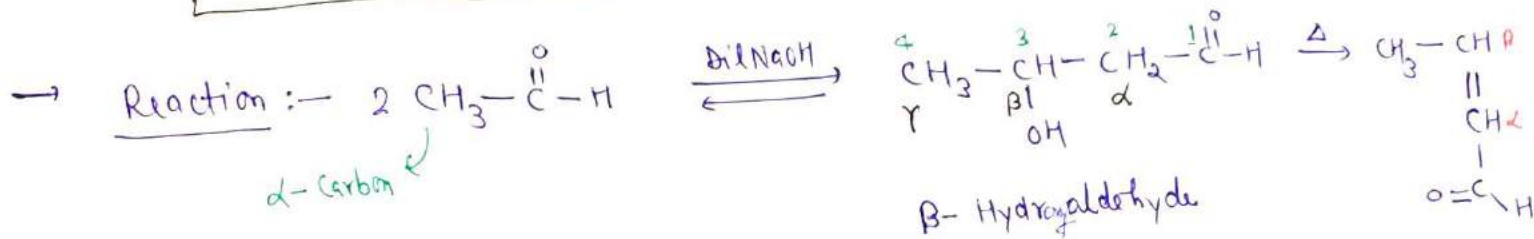


Haloform Reaction :- (oxidation of methyl ketone) Reagent :-  $\frac{NaOH + X_2}{NaOX}$



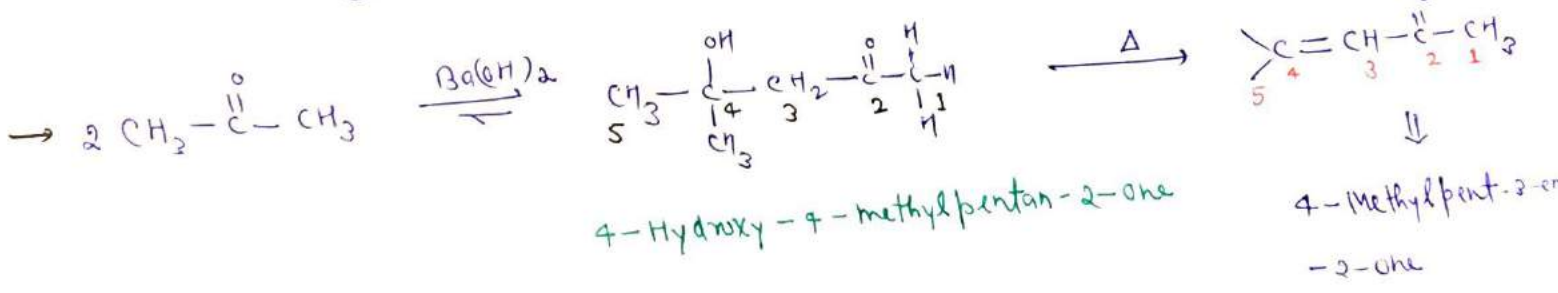


## Aldol Reaction / Aldol Condensation



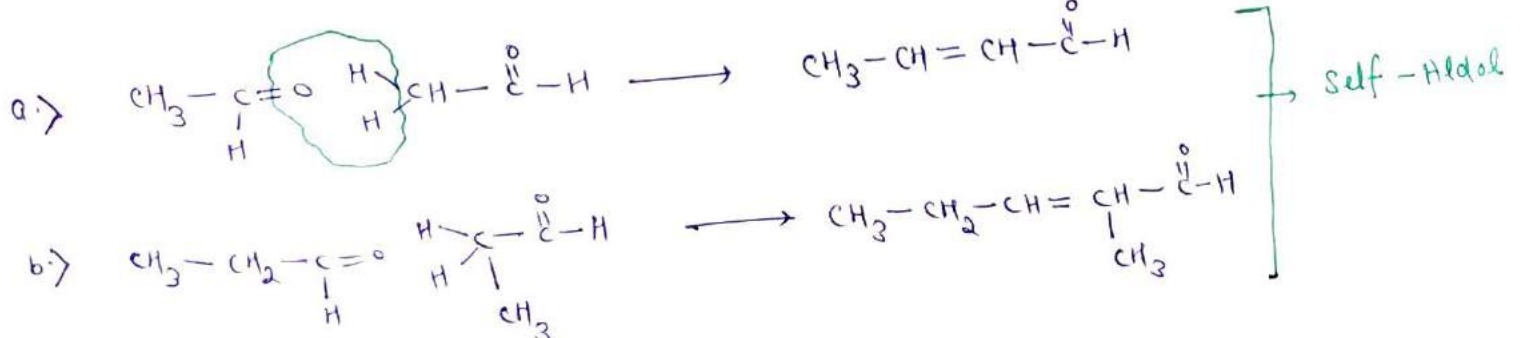
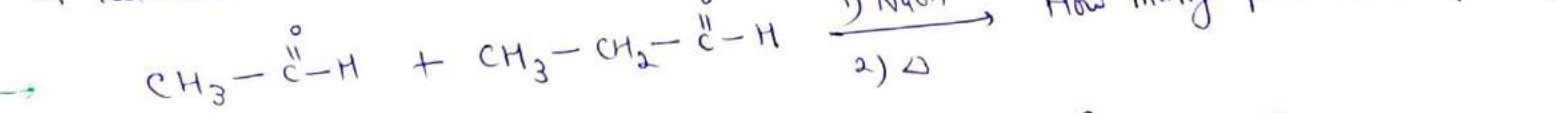
Aldehyde  $\xrightarrow{\text{dil NaOH}}$   $\beta$ -Hydroxyaldehyde : Aldol Reaction

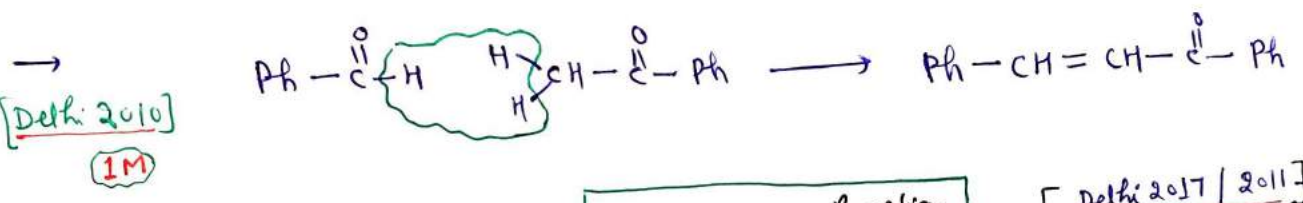
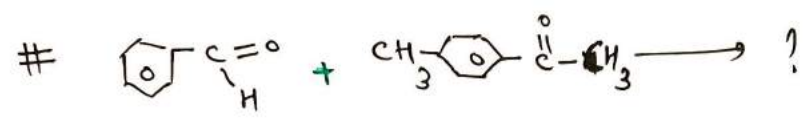
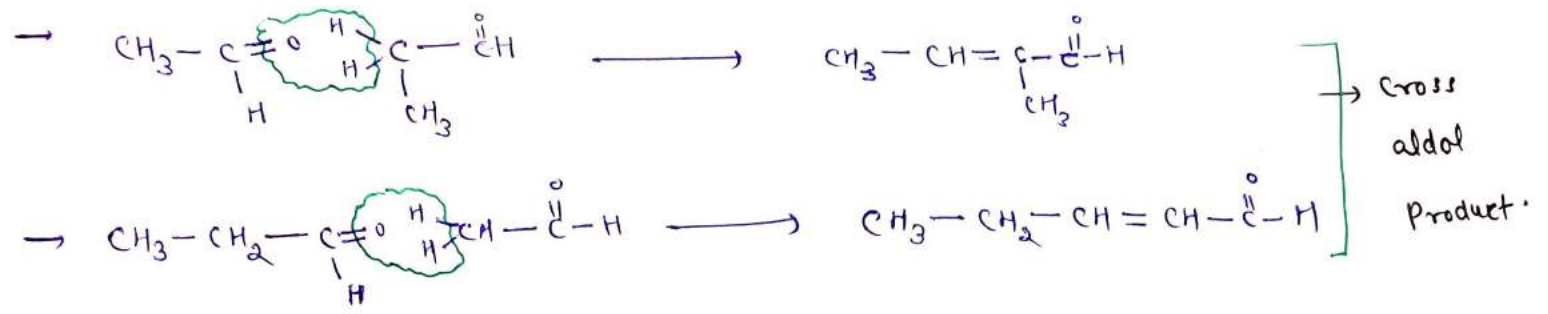
Aldehyde  $\xrightarrow[2) \Delta]{1) \text{dil NaOH}}$   $\alpha, \beta$ -unsaturated aldehyde : Aldol Condensation



[Delhi 2012] [1M]

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

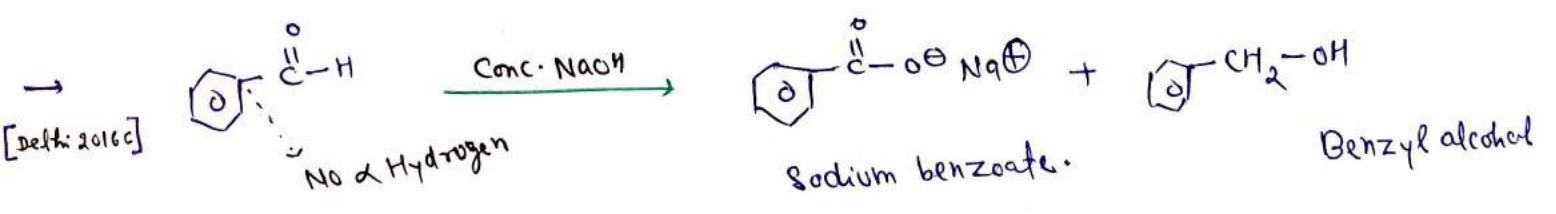
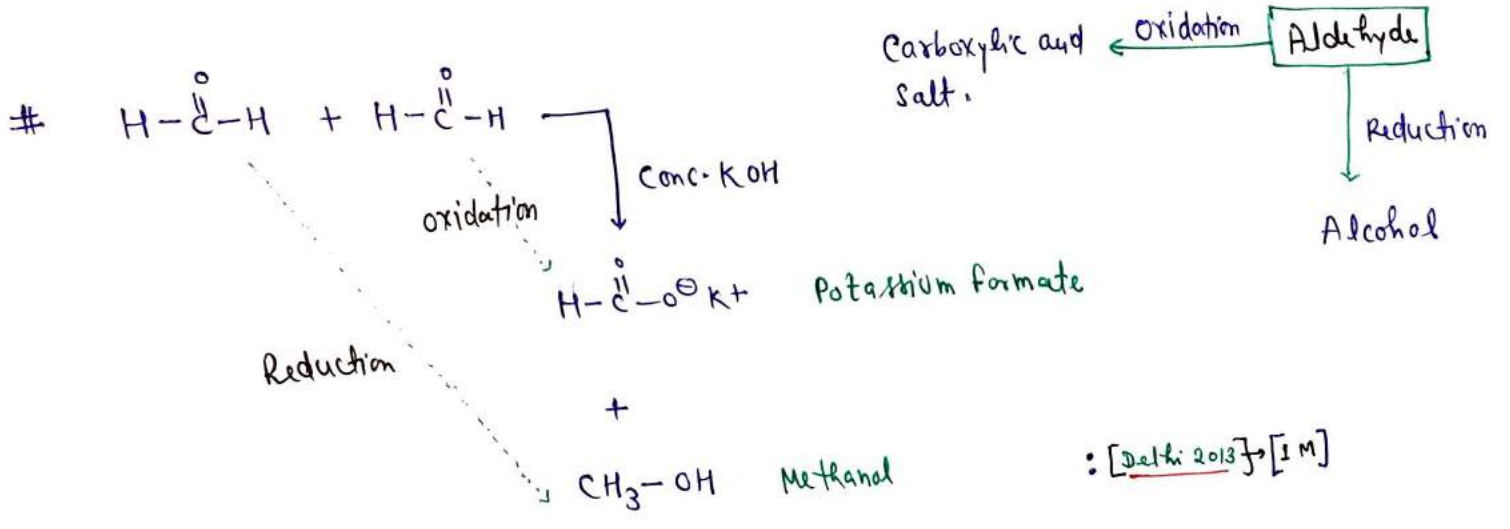




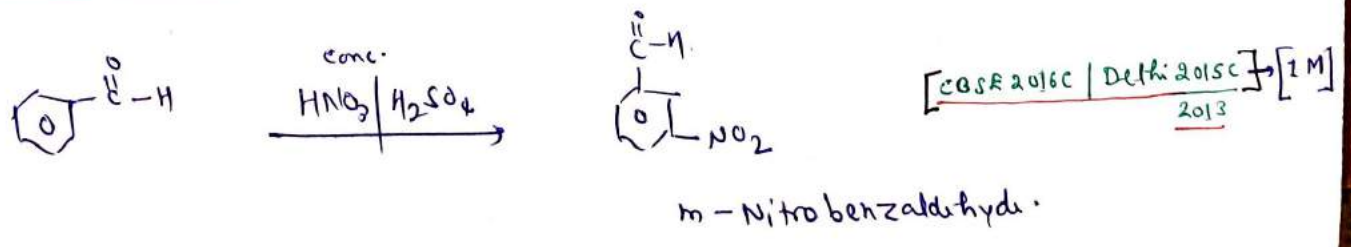
Cannizzaro Reaction

 [Delhi 2017 / 2011] (1M)

$\rightarrow$  Con. NaOH / KOH  $\rightarrow$  No,  $\alpha$ -Hydrogen  $\rightarrow$  Disproportionation Reaction



Electrophilic Substitution Reaction :- (-C(=O)-H : meta-directing in nature)



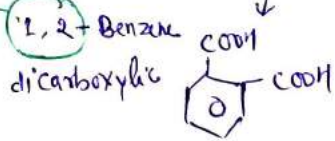
Question :-

$C_9H_{10}O \longrightarrow$  2, 4 - DNP Derivative : Presence of Carbonyl group

[CBSE 2012]

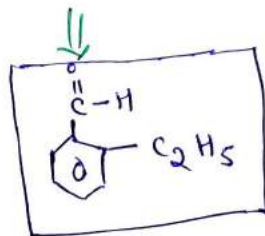
Reduces Tollen's Reagent : Presence of aldehyde  
 gives Cannizzaro Reaction : No,  $\alpha$  Hydrogen

Oxidation



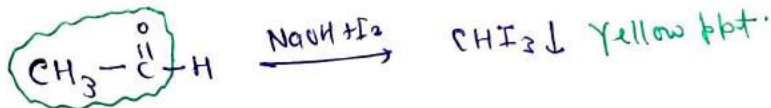
Then predict the structure.

means that  
substitution at 1, 2 position  
in reactant.

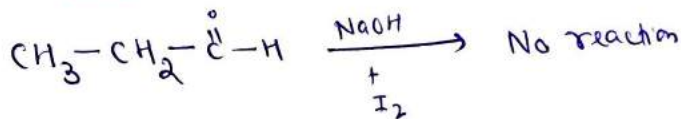


$\rightarrow$  Describe a chemical test to distinguish between  $\rightarrow$

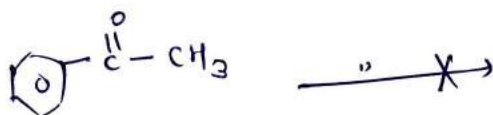
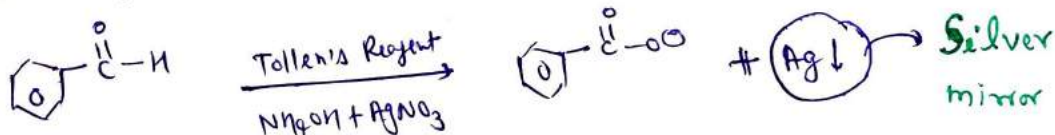
a) Ethanal and propanal :-



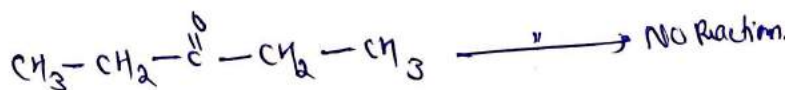
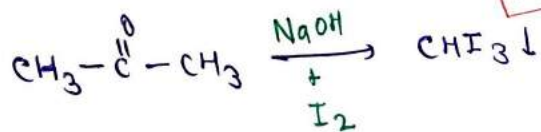
[Delhi 2010] [2M]



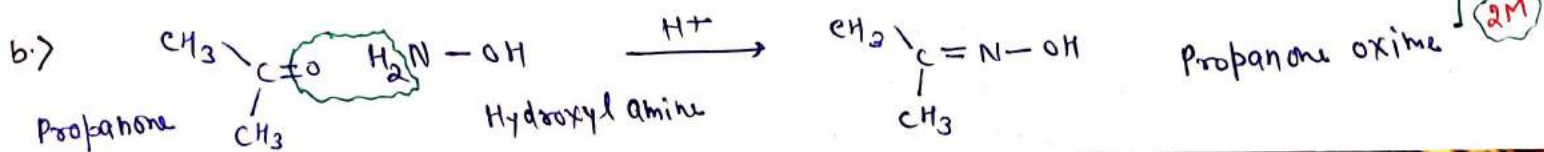
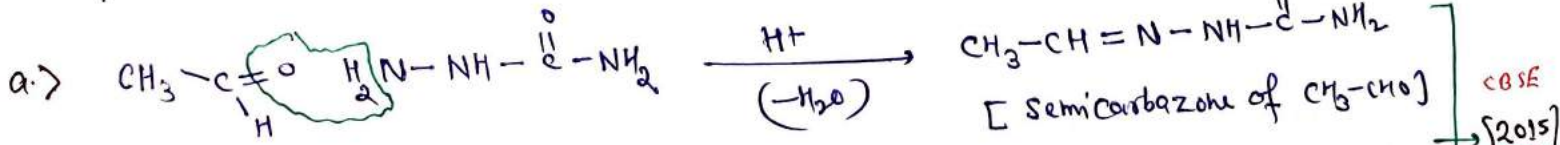
b) Benzaldehyde and acetophenone :-

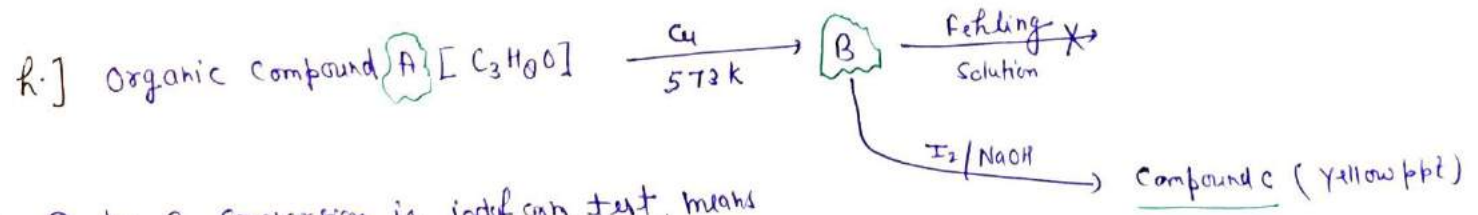
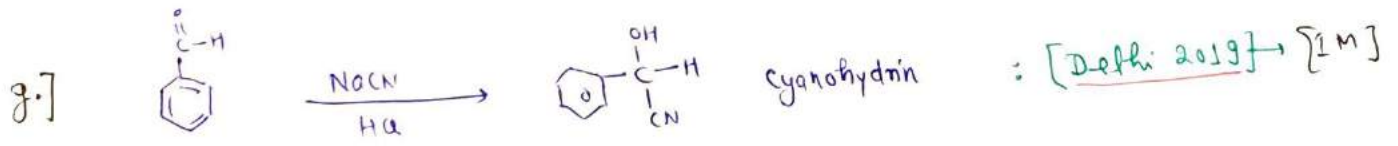
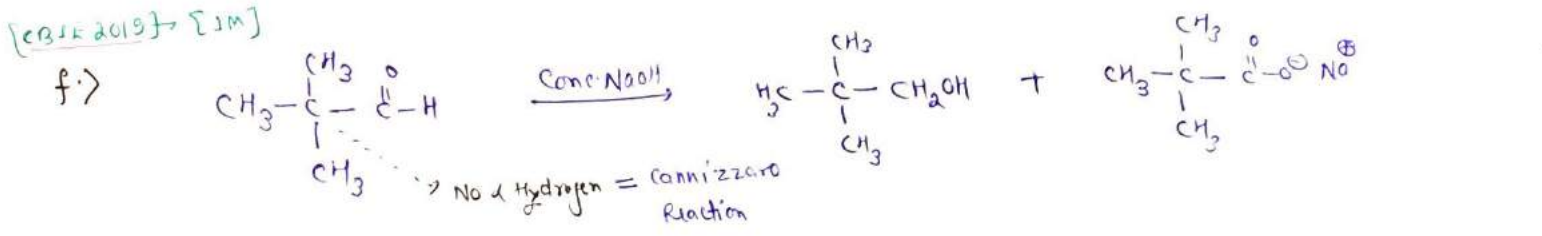
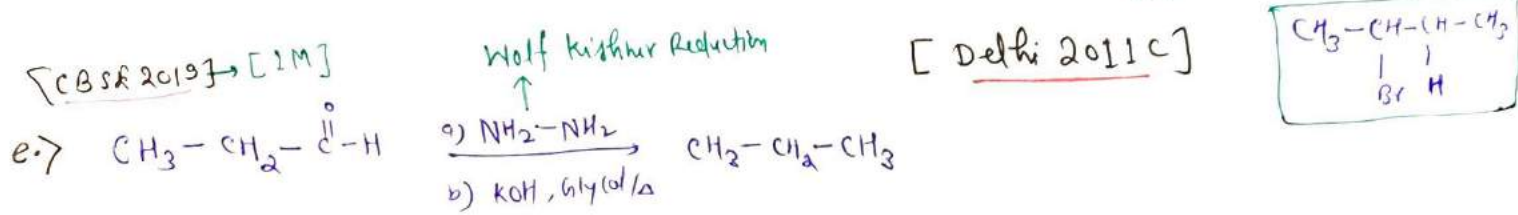
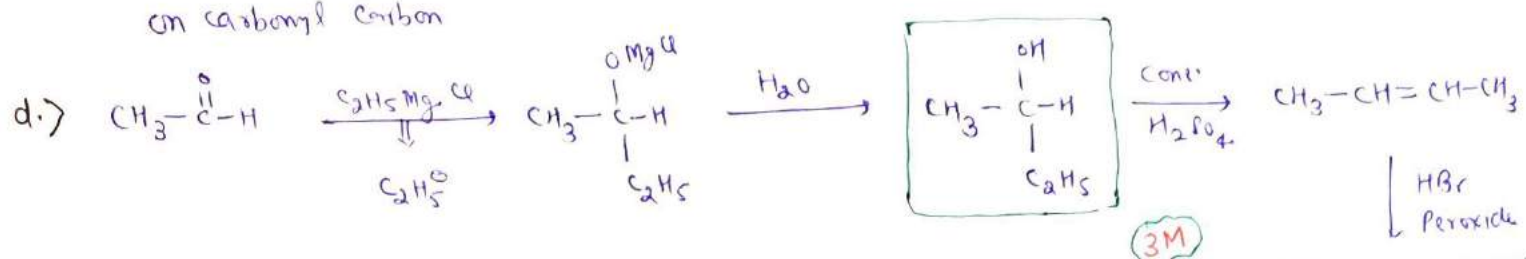
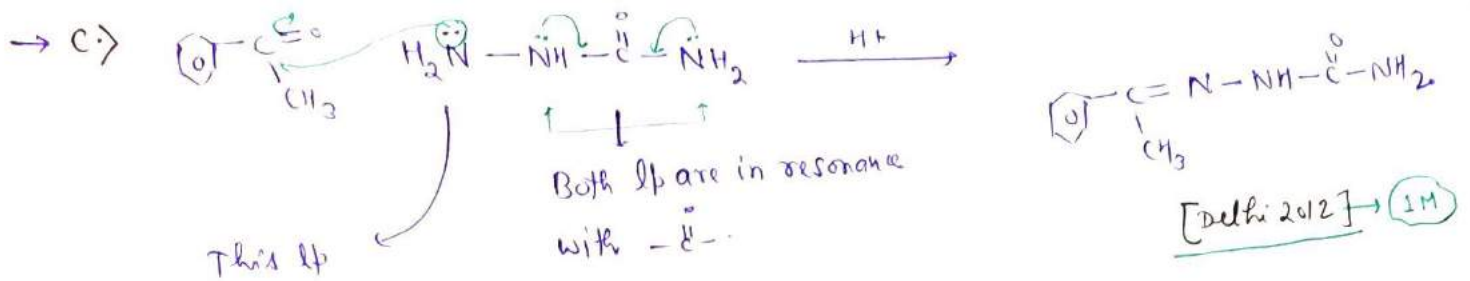


c) Propan-2-one and pentan-3-one :-

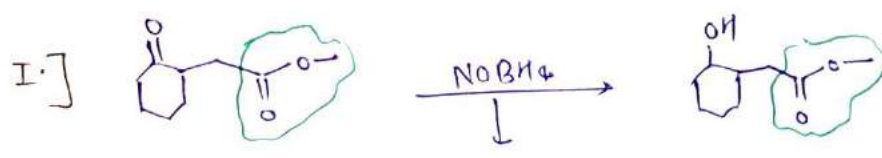
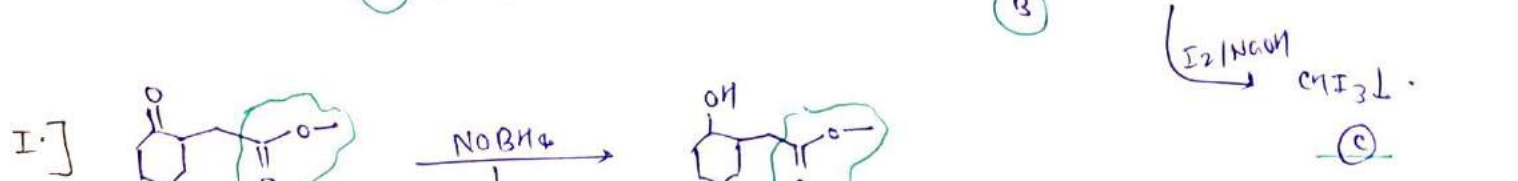
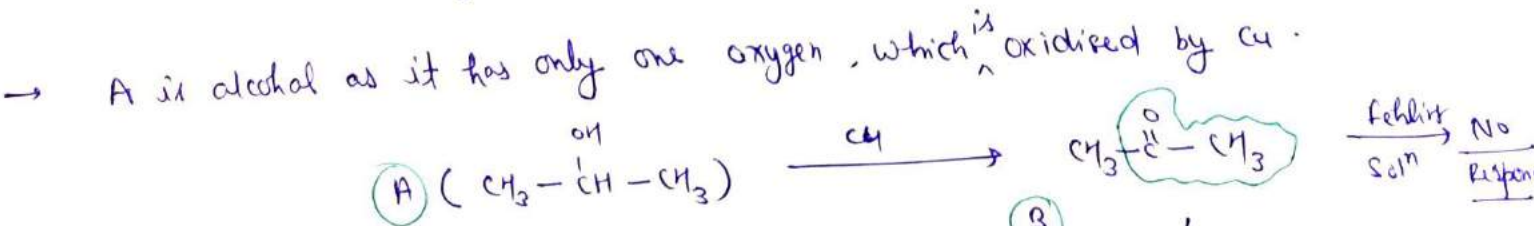


Complete the reactions :-





→ B to C conversion is iodoform test, means that B has  $-C(=O)CH_3$  group and  $e \Rightarrow (CHI_3 \downarrow)$ .

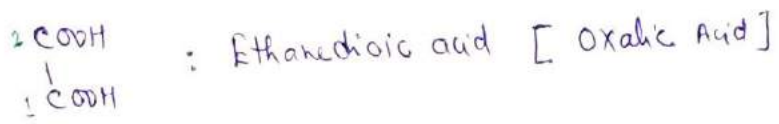
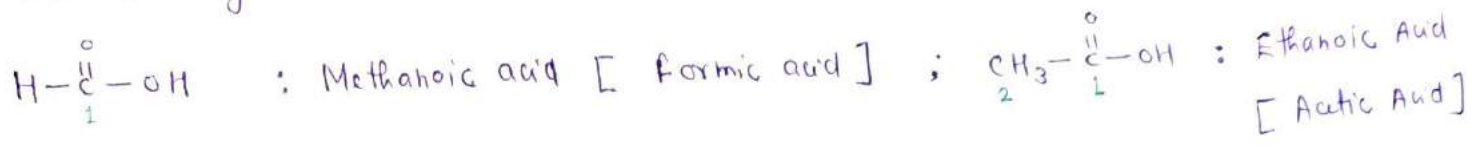


It reduces only aldehyde easily. So, No effect on ester.

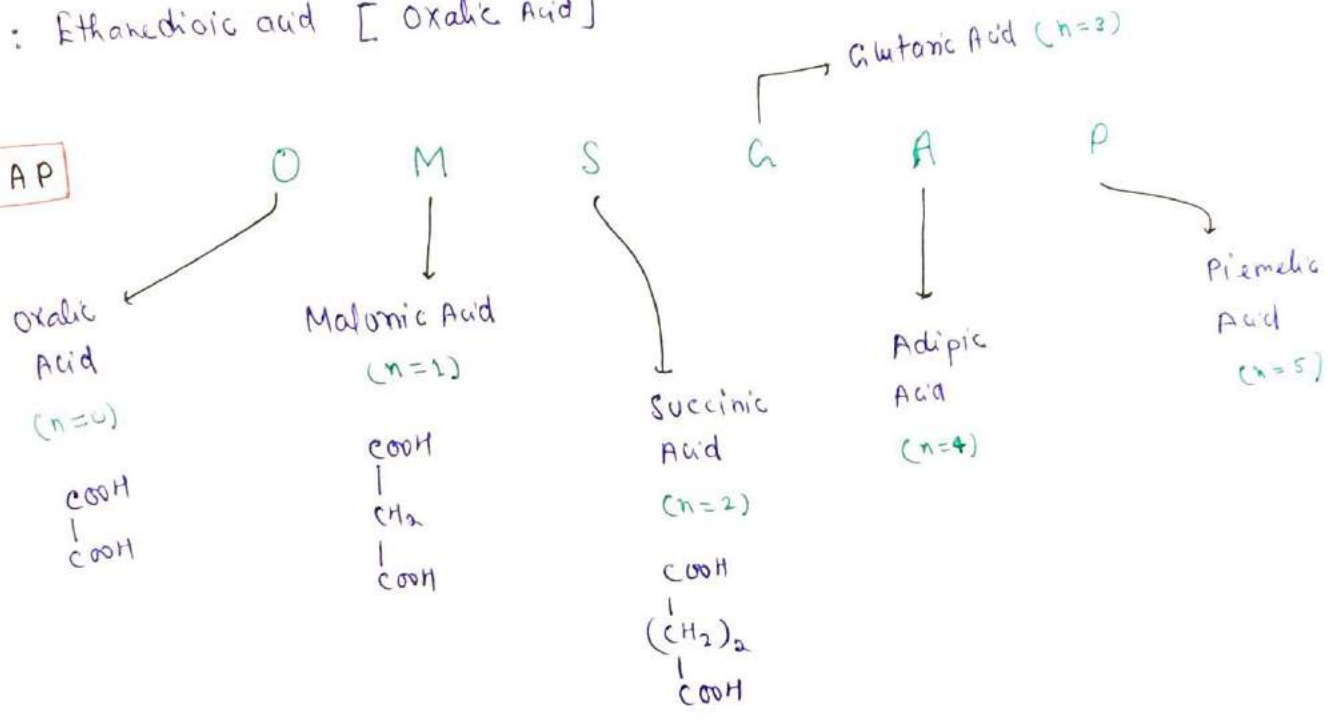
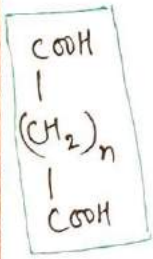


Nomenclature - : Alkane - e + oic acid = Alkanoic acid

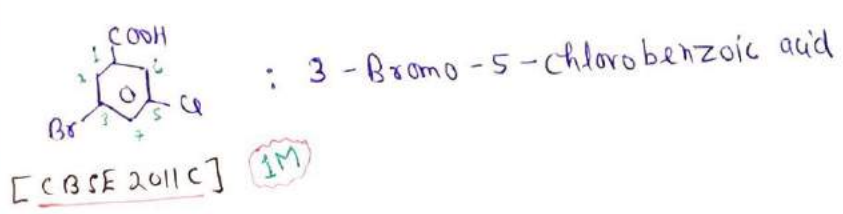
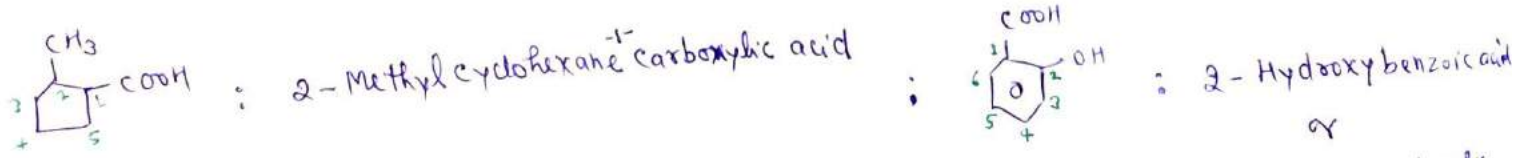
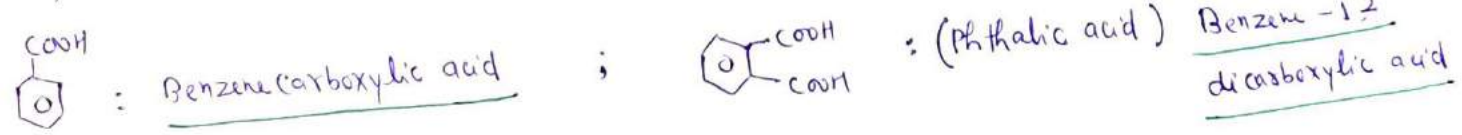
$\rightarrow$  In numbering the carbon chain, the carboxylic carbon is numbered one.



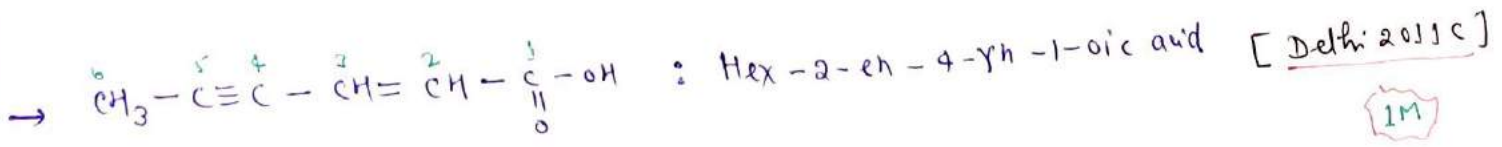
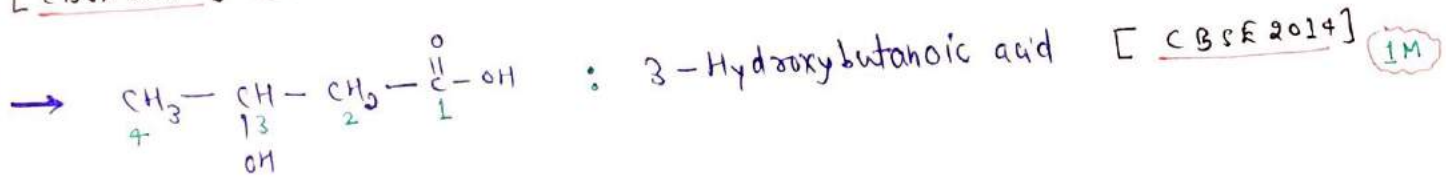
OMSGAP



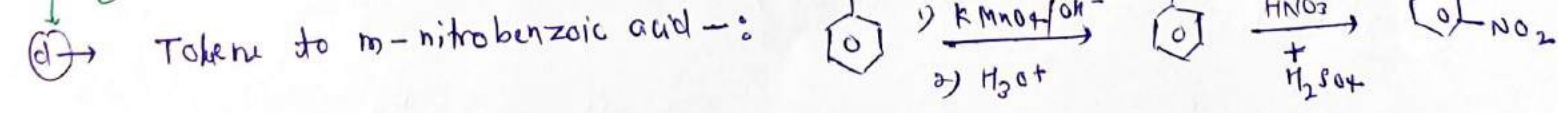
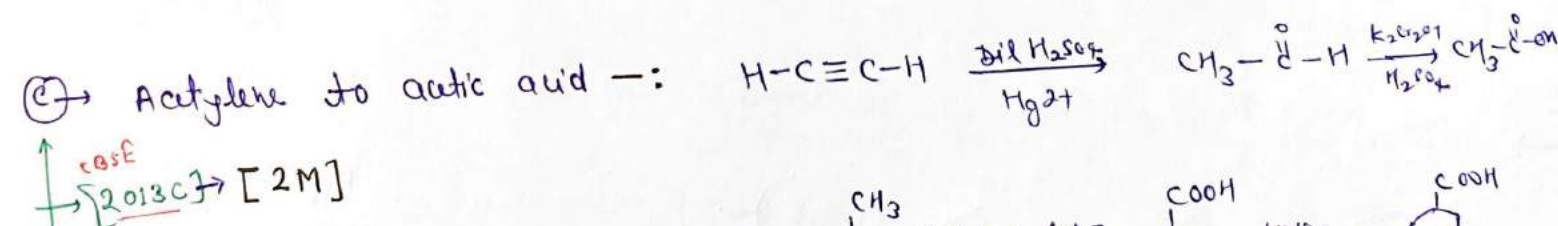
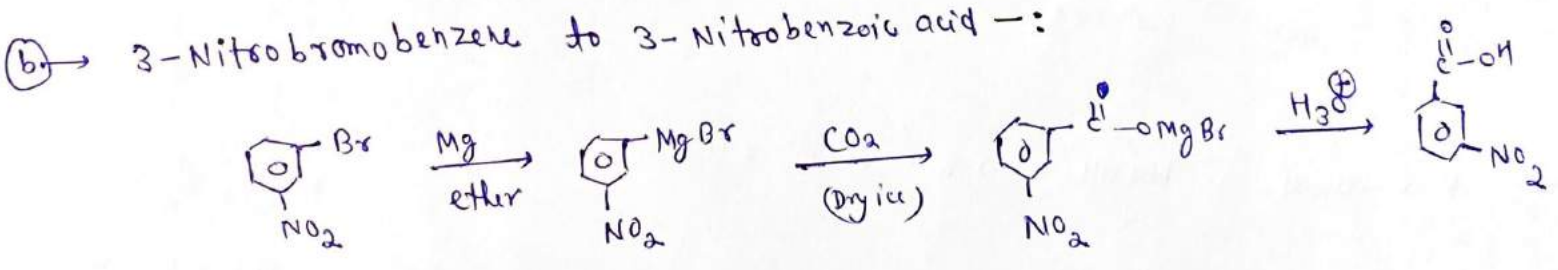
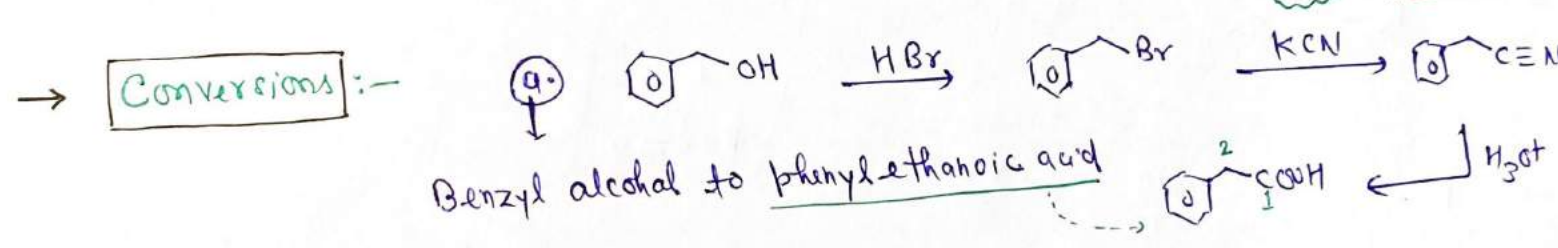
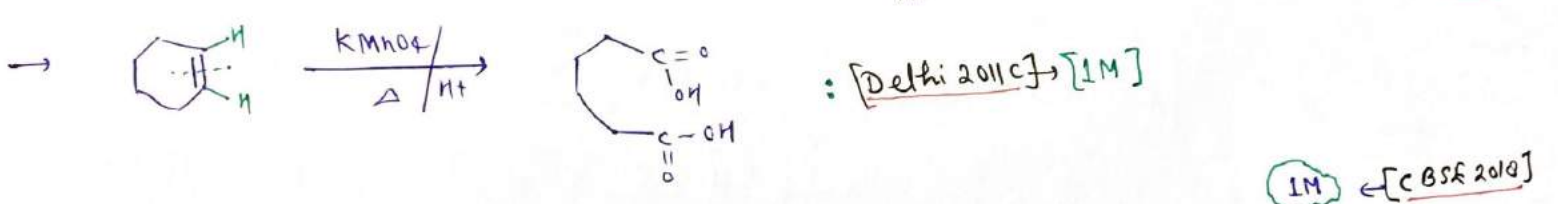
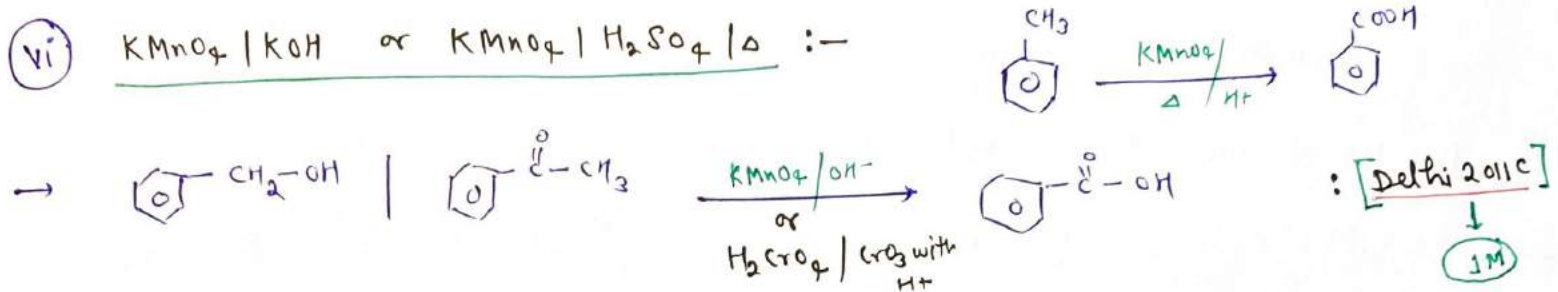
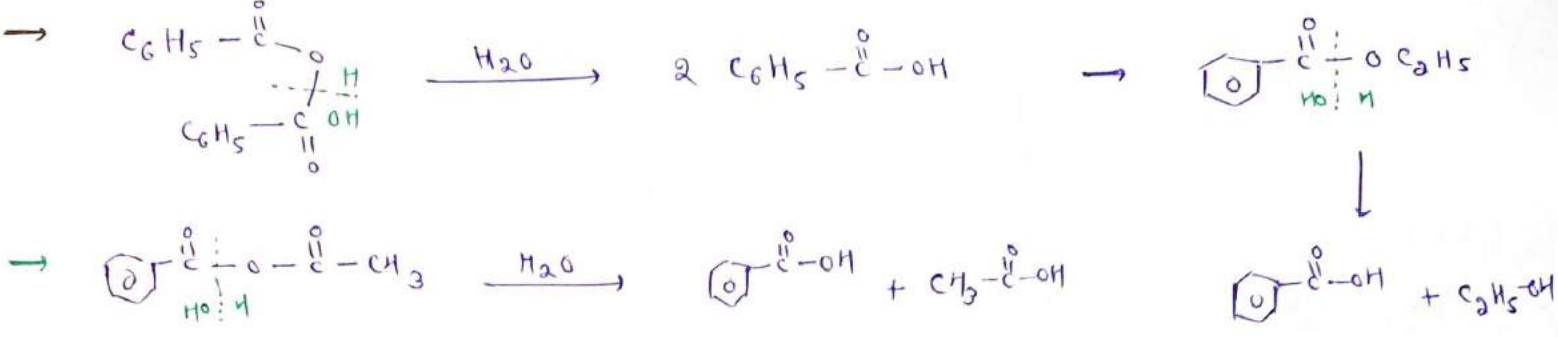
$\rightarrow$  If  $-\overset{\overset{O}{\parallel}}{C}-OH$  group is present on ring then suffix : carboxylic acid



[ Delhi 2014 ] 1M



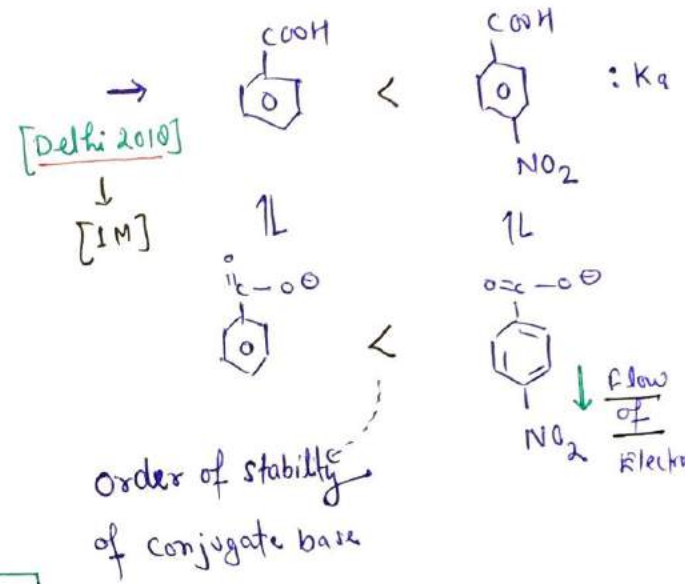
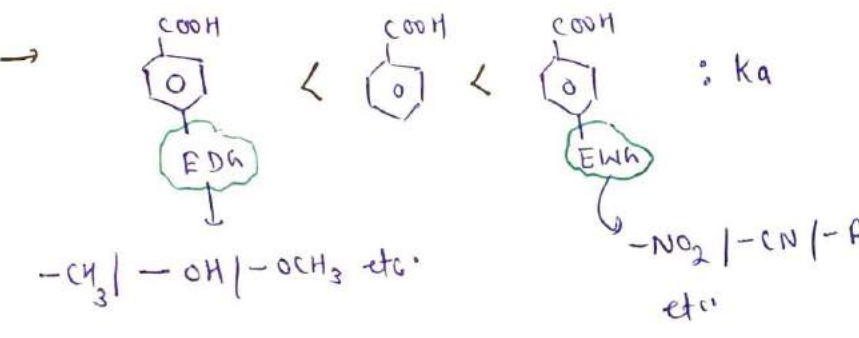
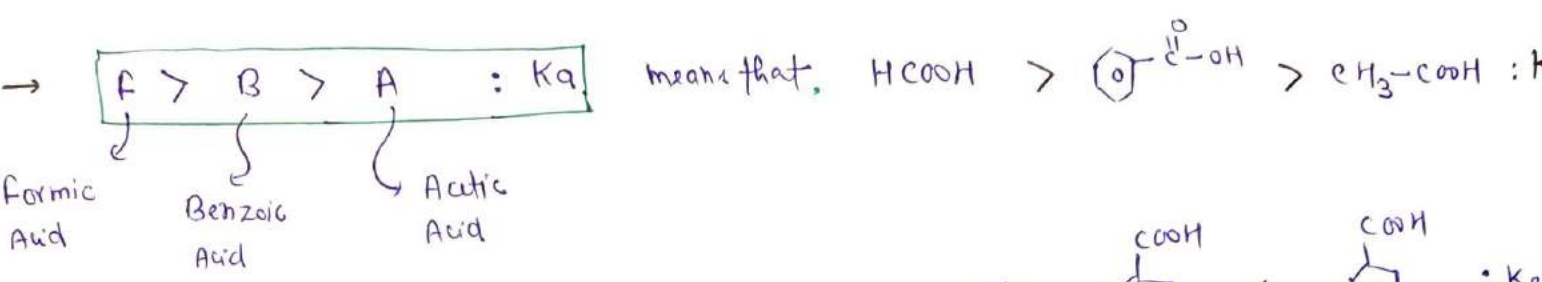
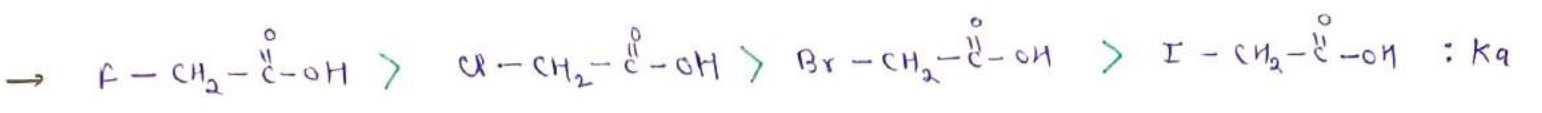
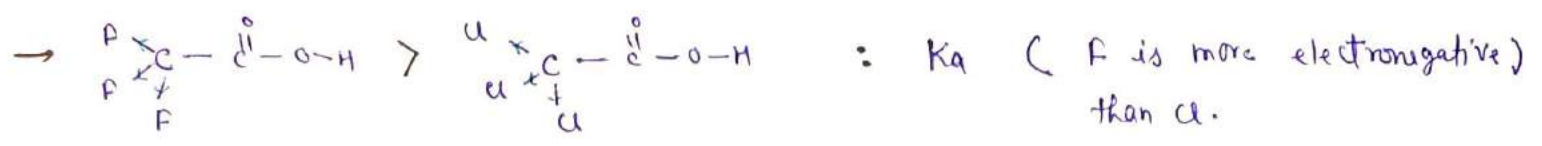




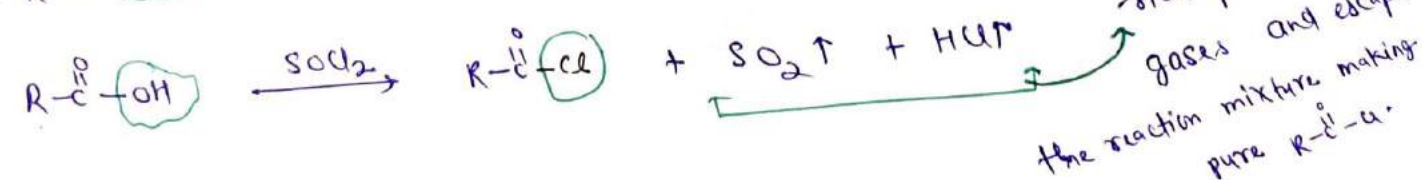
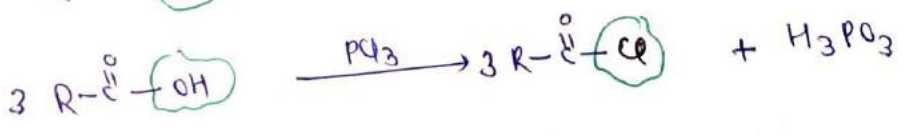
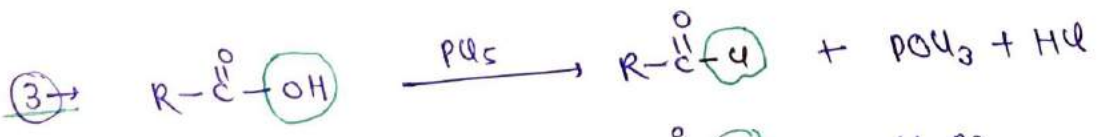
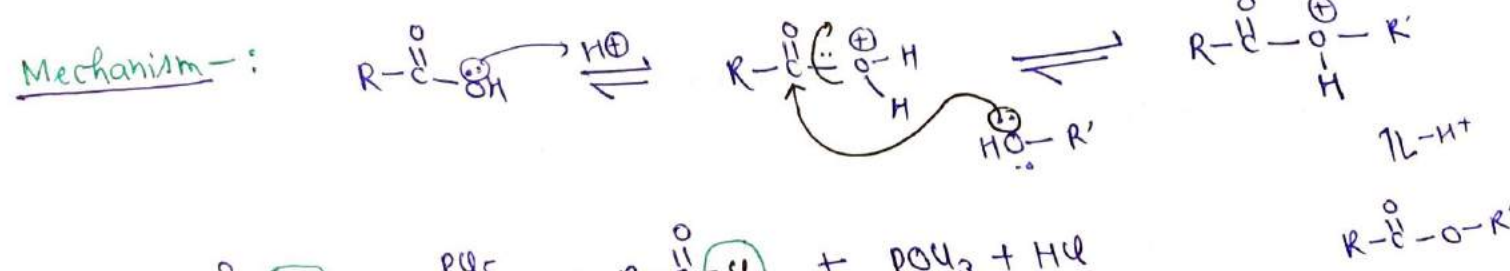
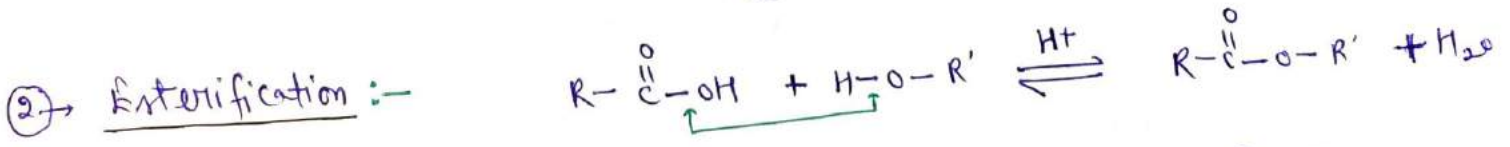
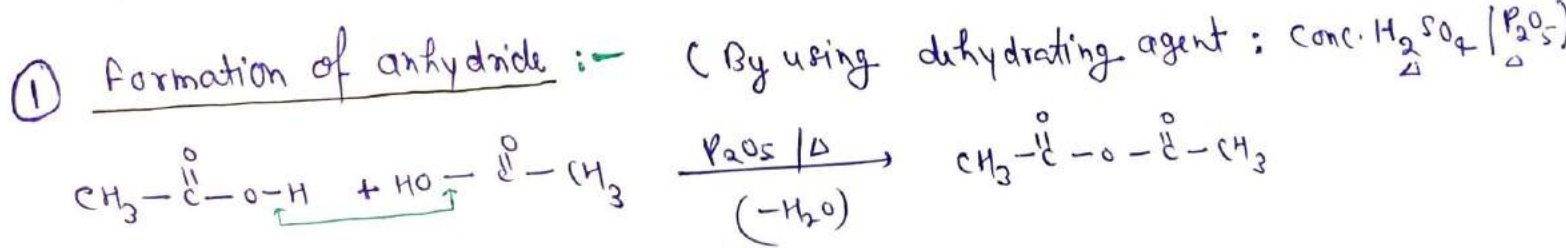
**Physical Properties**

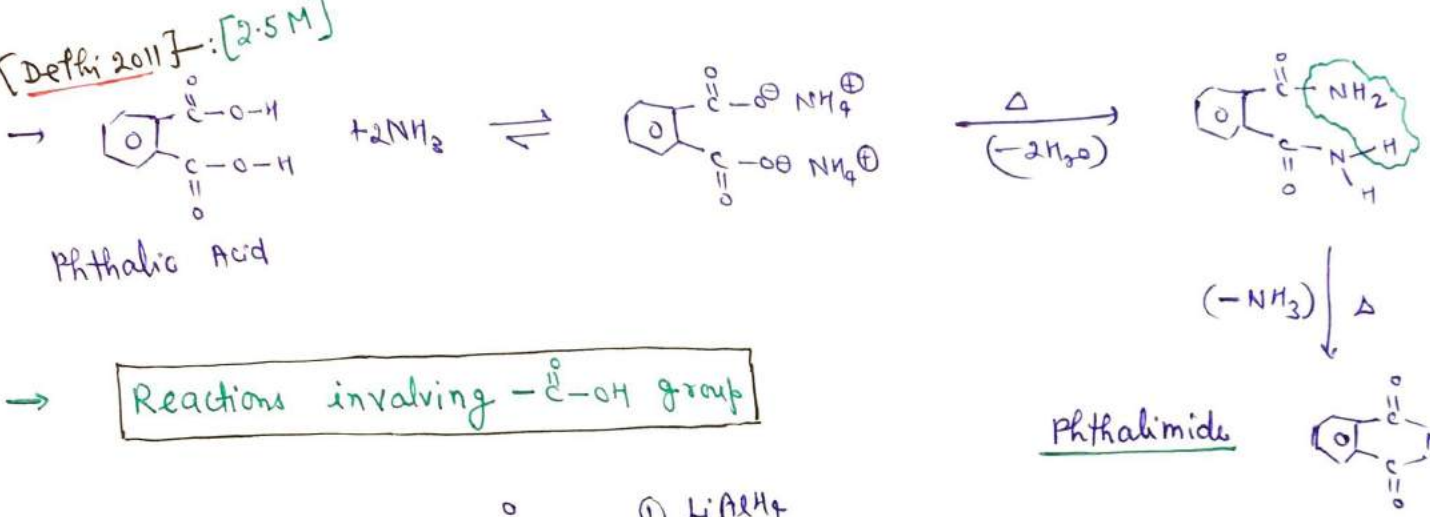
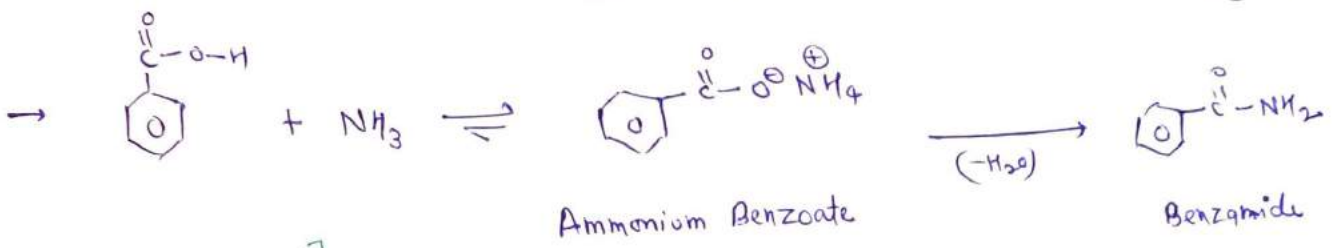
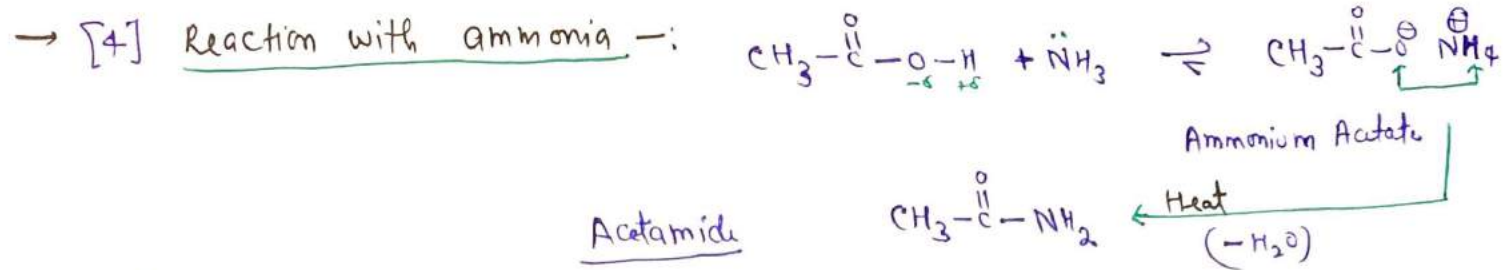
Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable mass. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.



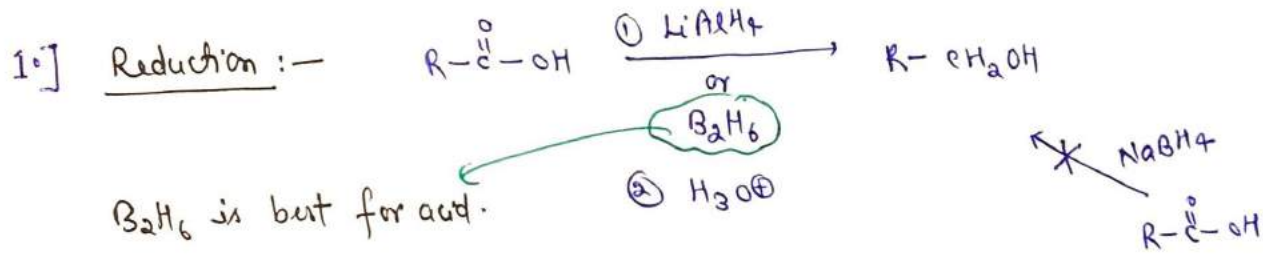


**Reactions involving breaking of C-OH bond**

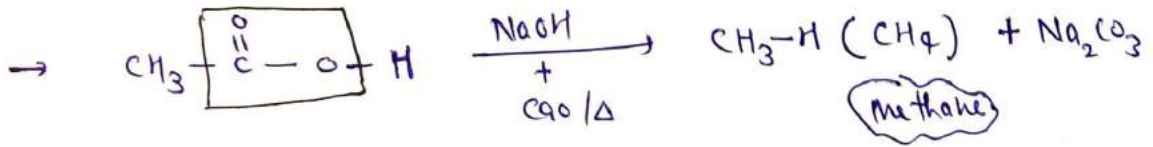
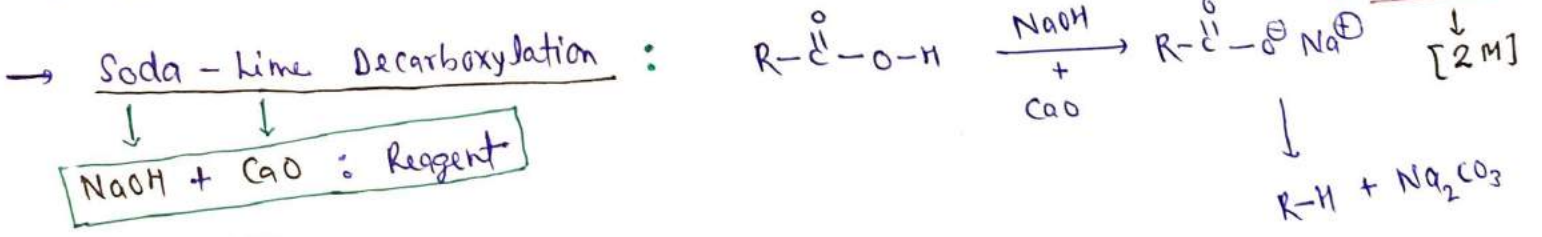




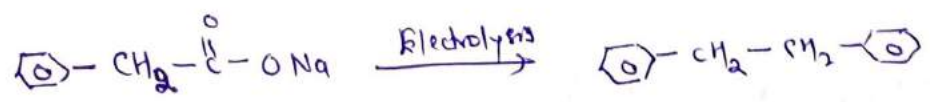
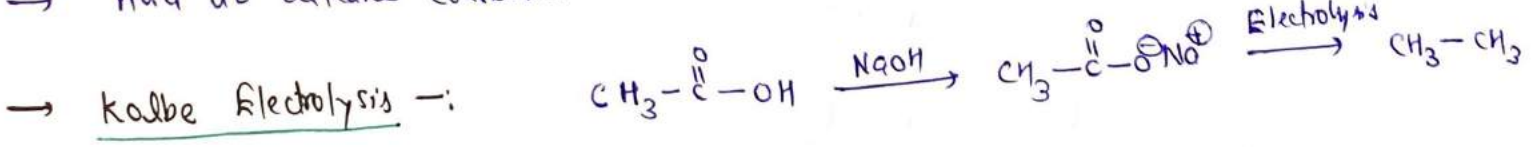
→ Reactions involving -C(=O)OH group



2.] Decarboxylation :- [Removal of CO<sub>2</sub>]



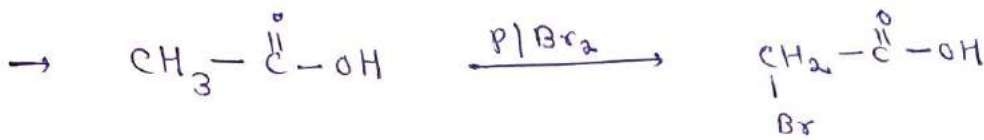
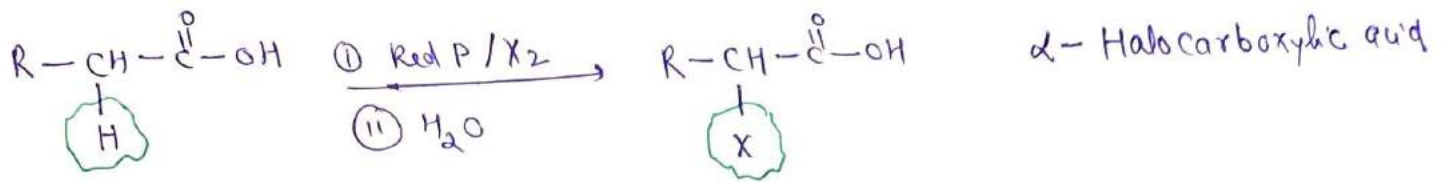
→ Acid to alkane Conversion



# Reaction on hydrocarbon part

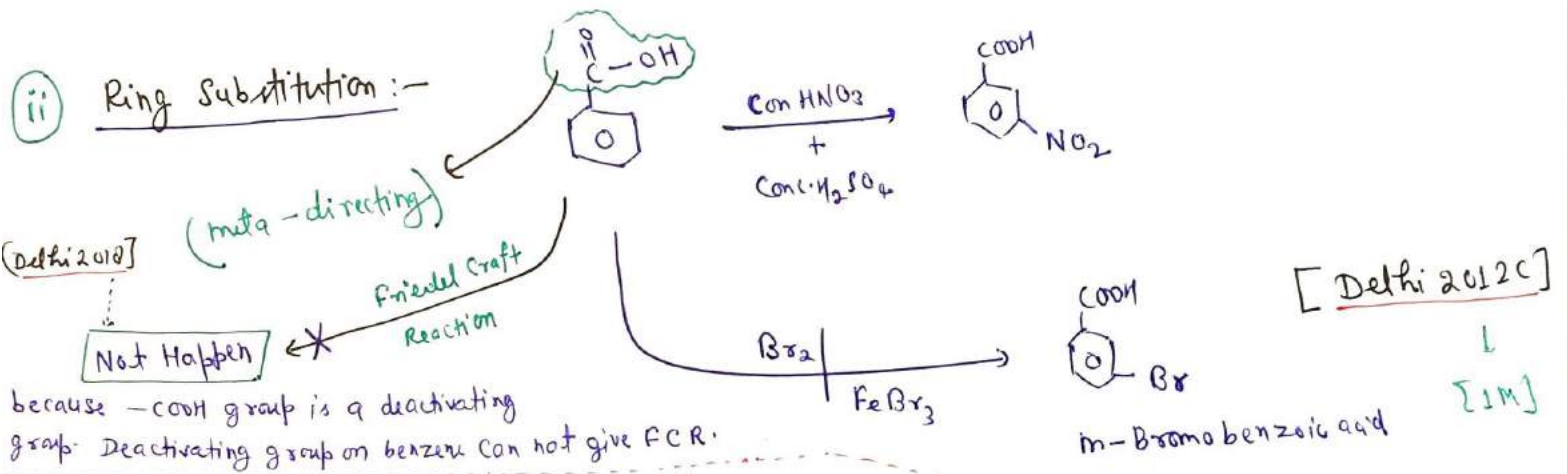
[Delhi 2017] - [2M]  
[CBSE 2010]

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

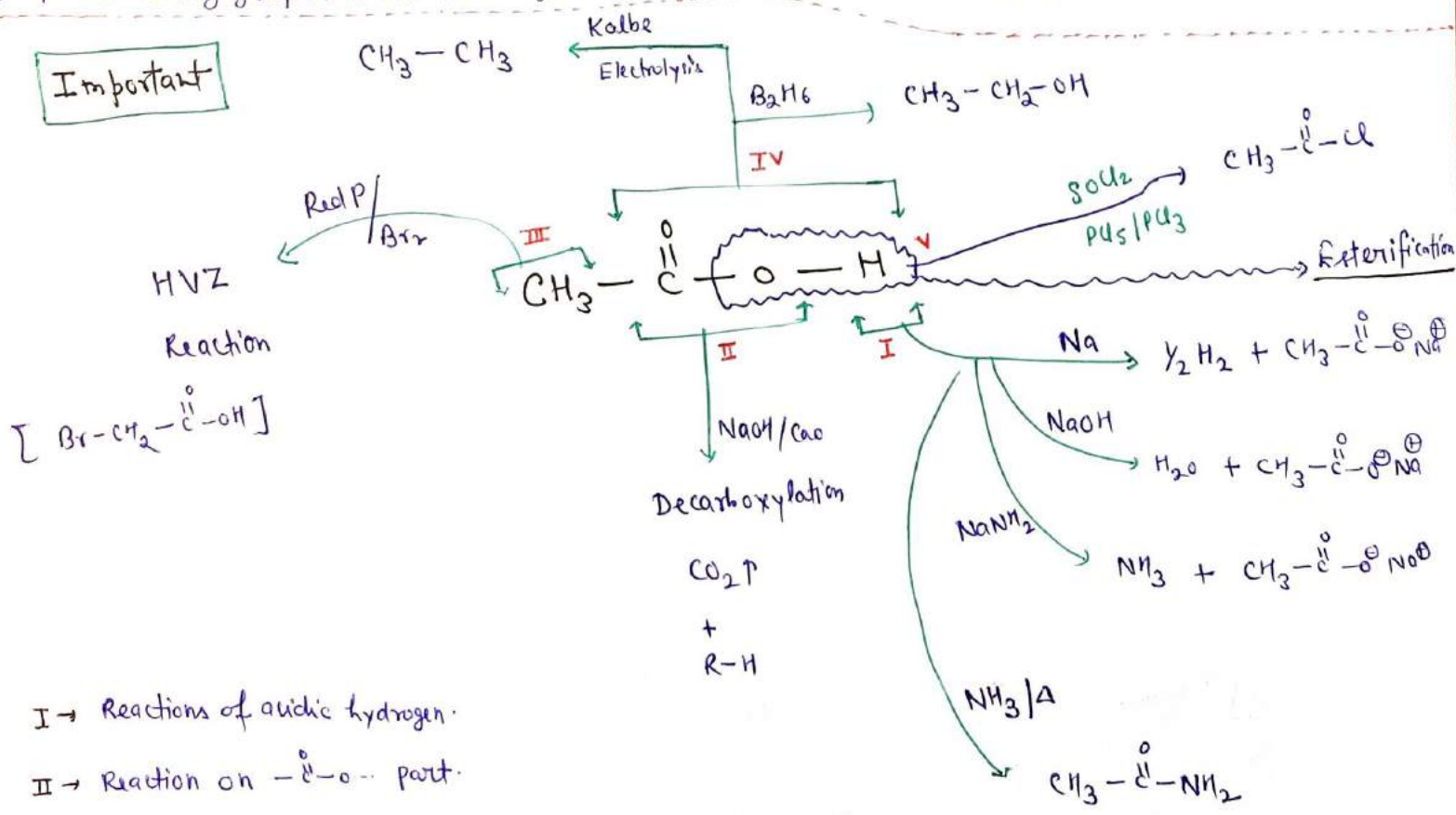


[Delhi 2014] → [1M]  
[Delhi 2013C] → [1M]  
[CBSE 2016] → [1M]

(ii) Ring Substitution :-

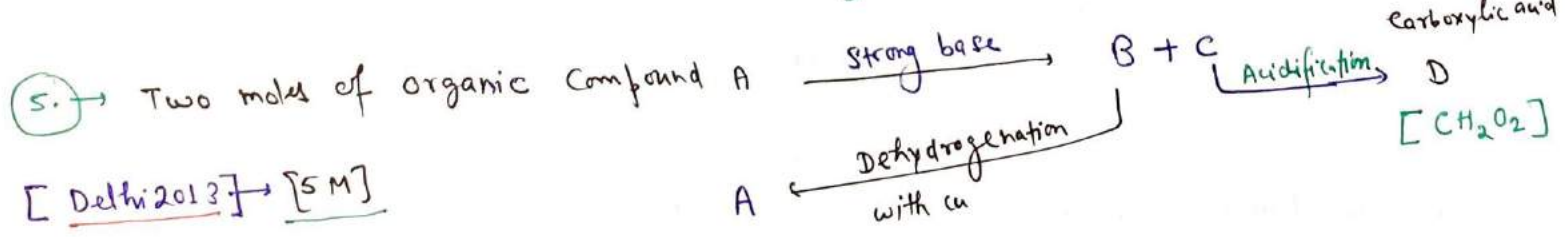
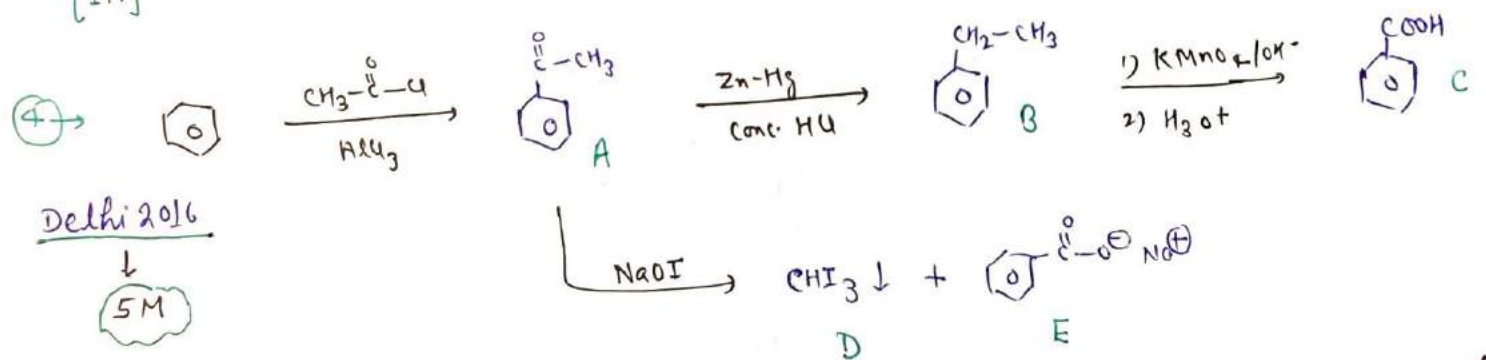
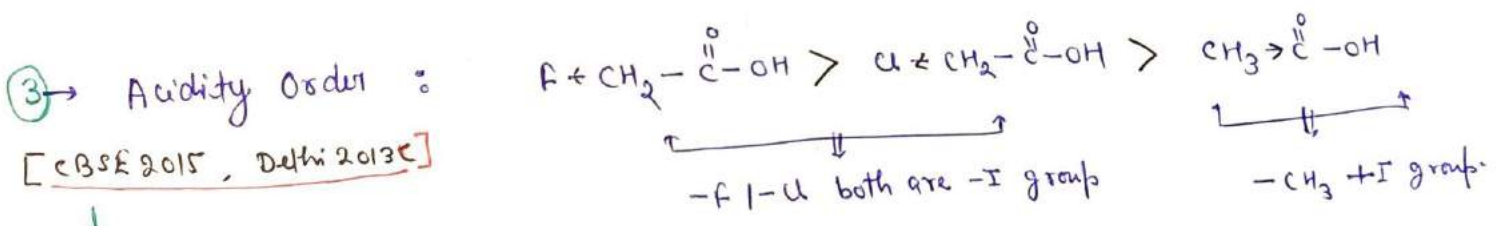
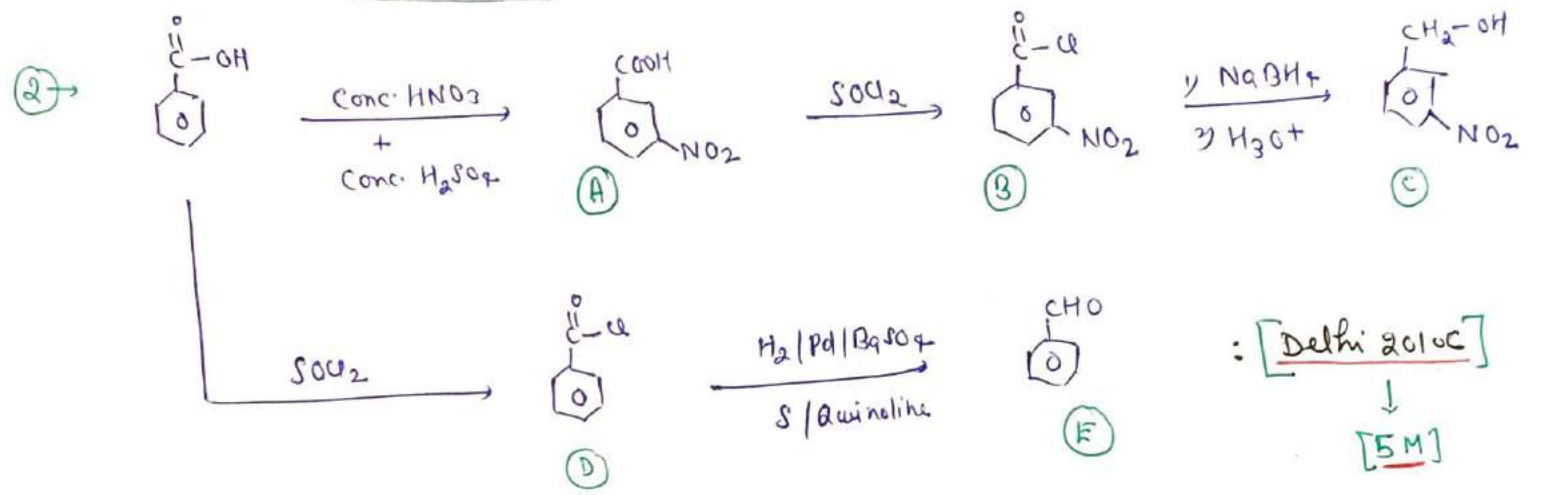
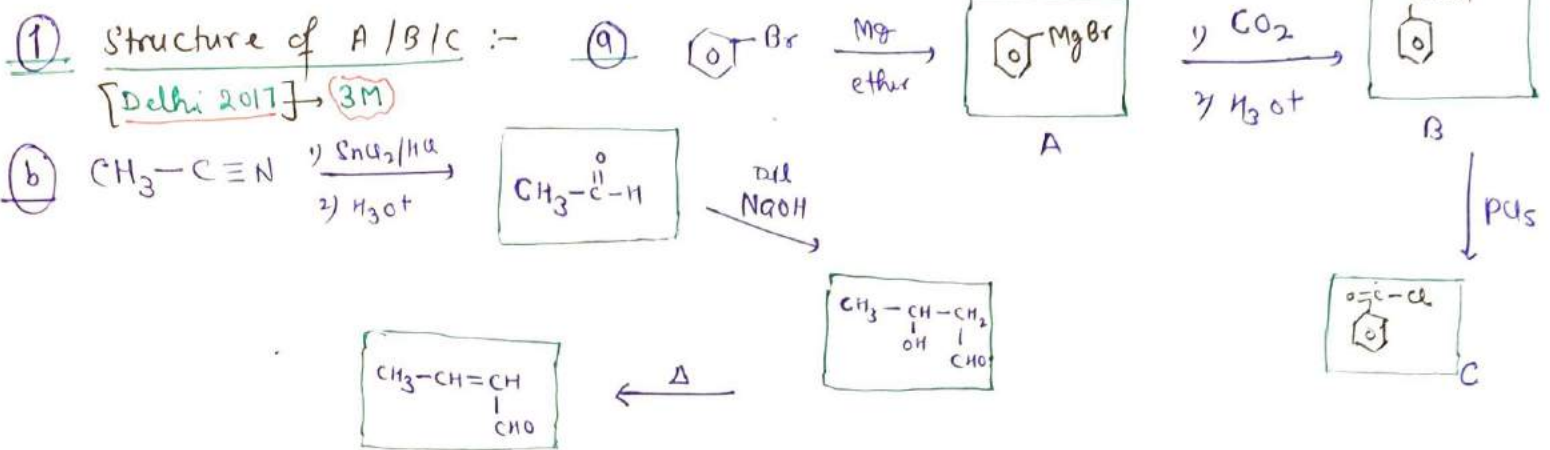


**Important**

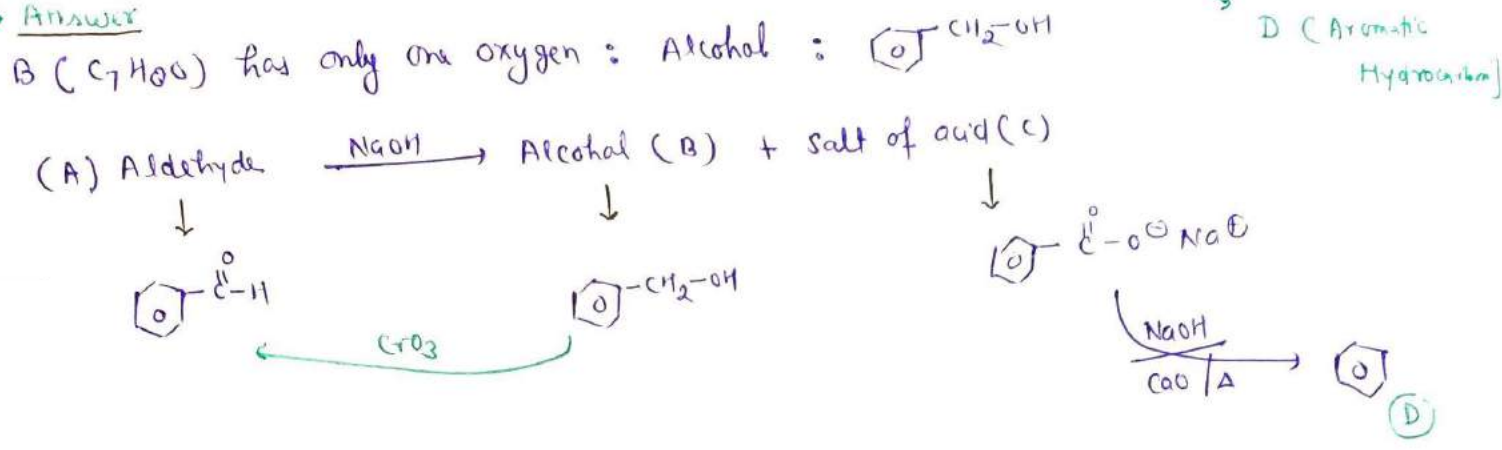
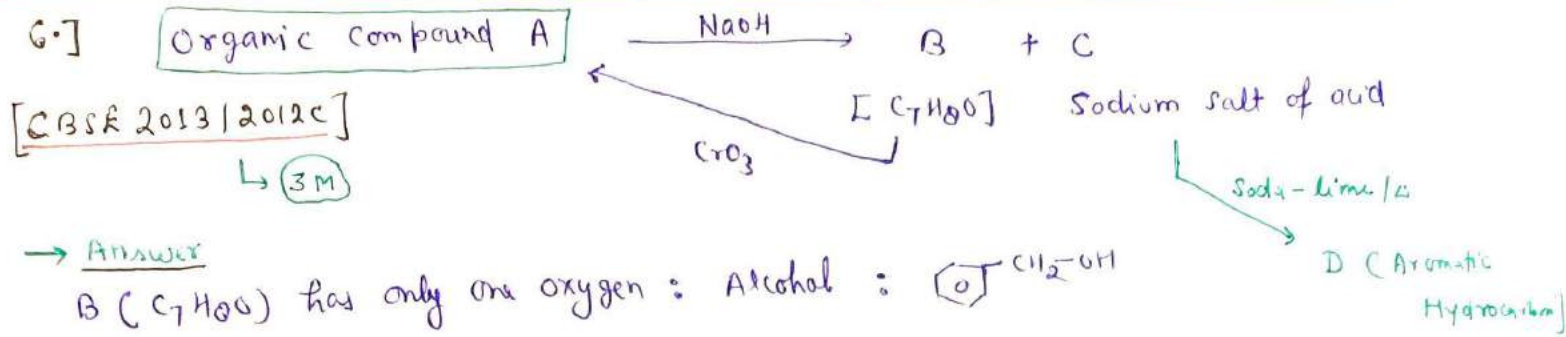


- I → Reactions of acidic hydrogen.
- II → Reaction on -C(=O)-O- part.
- III → Reaction on hydrocarbon part.
- IV → Reaction on -C(=O)-OH.
- v → Reactions on -OH part.

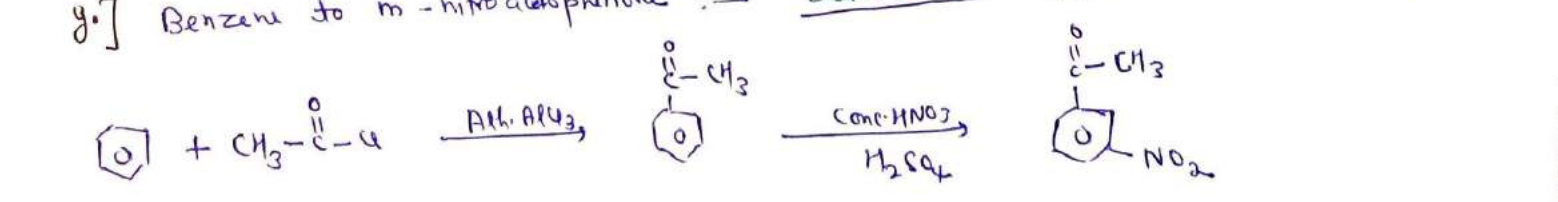
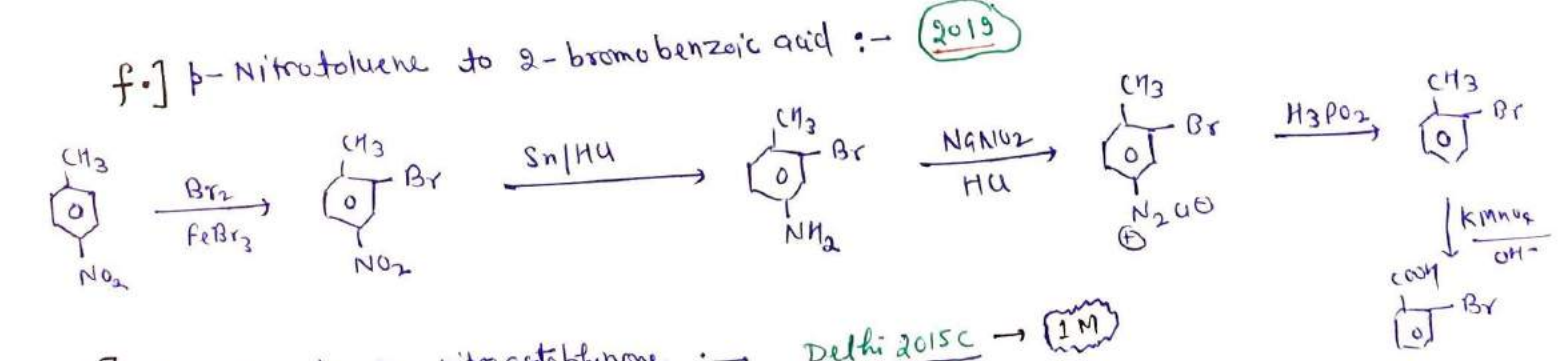
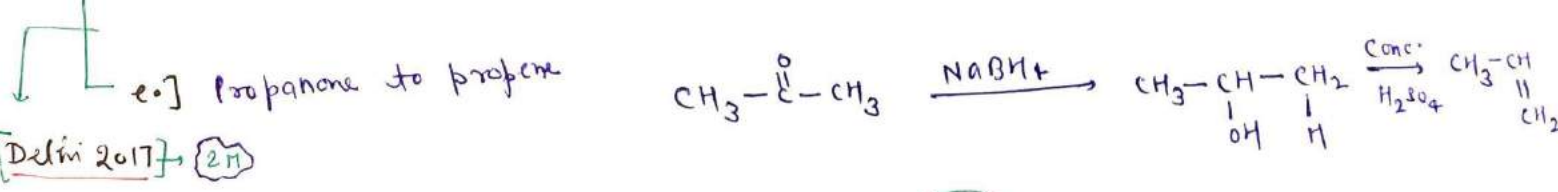
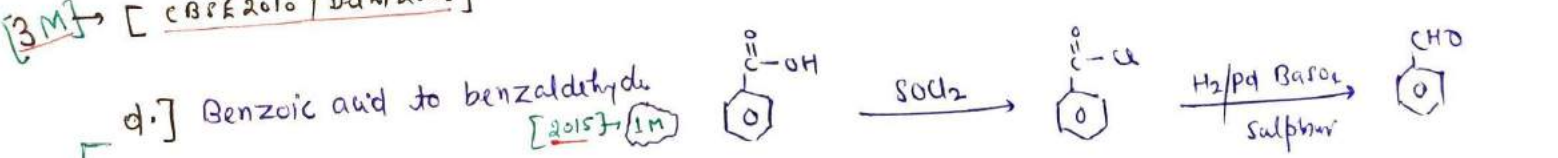
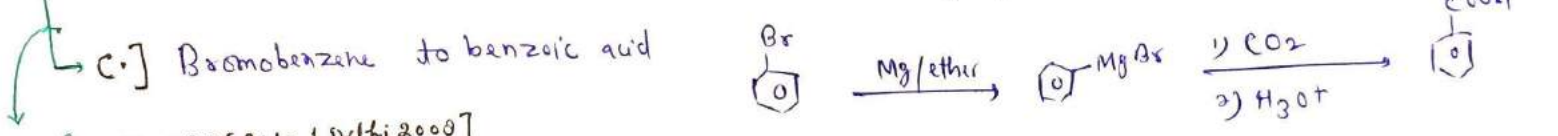
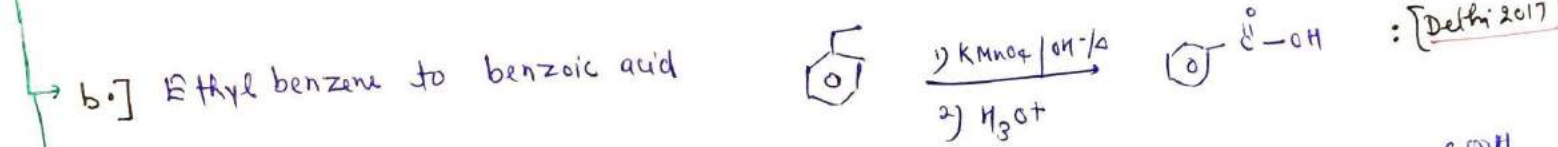
# Important Previous Year Questions



Answer :-   
 D ⇒ Carboxylic acid → H-C(=O)-OH      B → Alcohol → CH\_3-OH   
 C → H-C(=O)-O^-   
 Then A must be H-C(=O)-H as strong base represent Cannizzaro.   
 A (H-C(=O)-H)



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



Benzene

m-Nitroacetophenone