

## Unit - 12

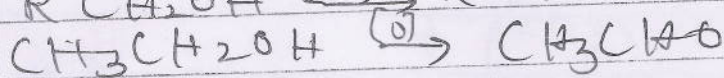
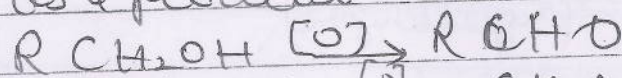
### Aldehydes, Ketones and Carboxylic Acids

Aldehydes & ketones or Carbonyl Compounds  
→ Method of preparation

- 1) From alcohol → Aldehyde & ketones can be prepared from alcohol by following methods →

• Oxidation →

1° alcohol on controlled oxidation with different oxidising agents such as acid  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{CrO}_3$  forms aldehyde as a product.



(Acetaldehyde)

Other oxidising agents such as

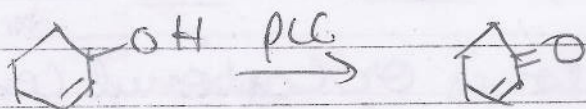
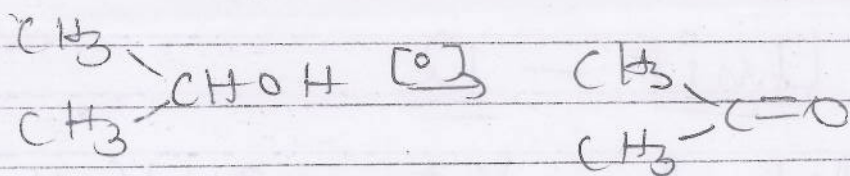
- (1) Collman's reagent
- (2) Corey's reagent
- (3) Jones reagent

Collman's reagent  $\rightarrow$  ( $\text{CrO}_3 + \text{Py. in CH}_2\text{Cl}_2$ )

Corey's reagent  $\rightarrow$  (PC) it is pyridinium chloro chromate.

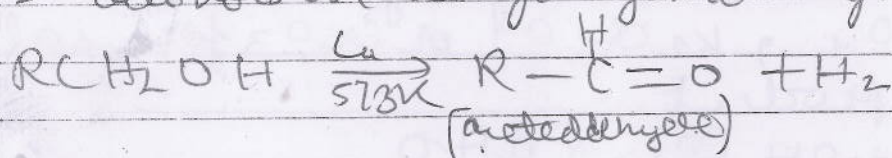
Jones reagent  $\rightarrow$  is chromium oxide in solution of  $\text{H}_2\text{SO}_4$  & acetone.

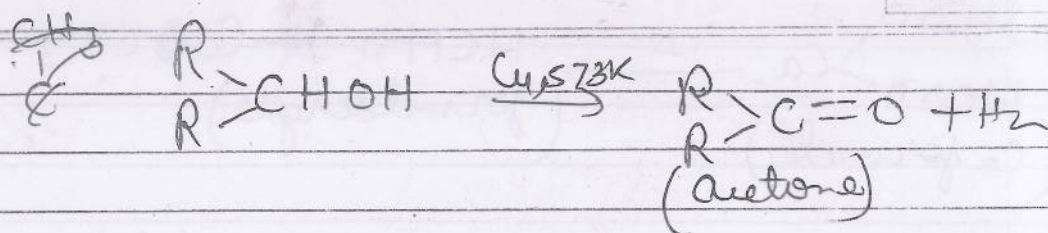
Whereas  $2^\circ$  alcohols on oxidation with different oxidising agent gives ketone as a product.



• By dehydrogenation  $\rightarrow$  Alcohol on dehydrogenation heating in presence of Cu at 573K forms carbonyl compound as a product.

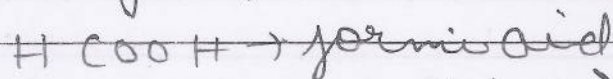
- $1^\circ$  alcohol on dehydrogenation gives aldehyde.
- $2^\circ$  alcohols on dehydrogenation gives ketone.



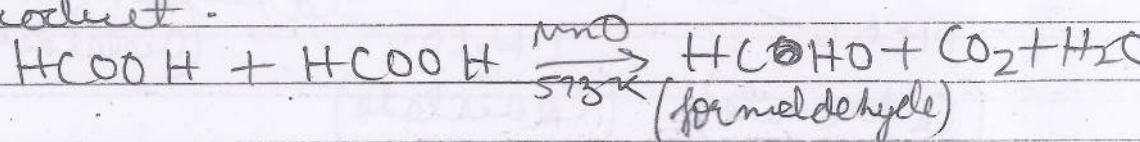


2) Form Carboxylic Acid  $\rightarrow$

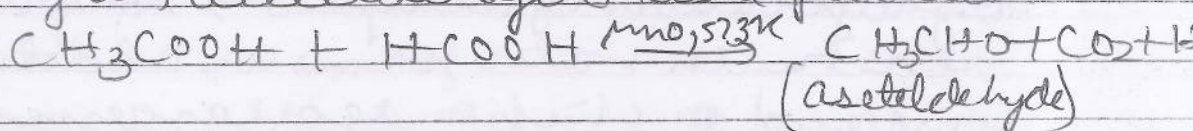
• By catalytic decomposition  $\rightarrow$  Carboxylic acid on heating to a temp.  $573\text{K}$  in pres. of  $\text{MnO}$  undergoes decomposition & forms aldehyde & ketone as a product.



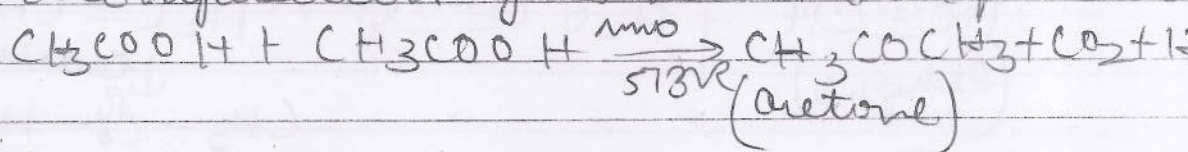
Two molecules of formic acid on catalytic decomposition gives formaldehyde as a product.



One molecule of formic acid & one molecule of acetic acid on catalytic decomposition gives acetaldehyde as a product.



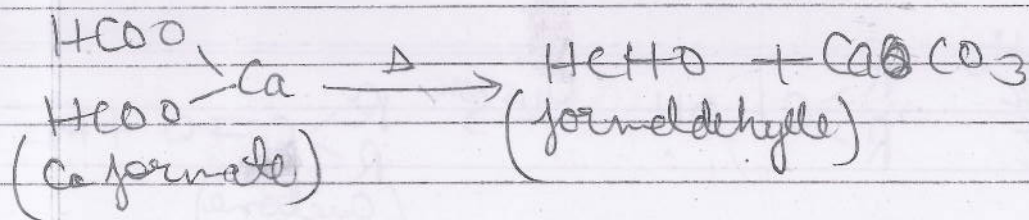
Two molecule of acetic acid on catalytic decomposition gives ketone as a product.



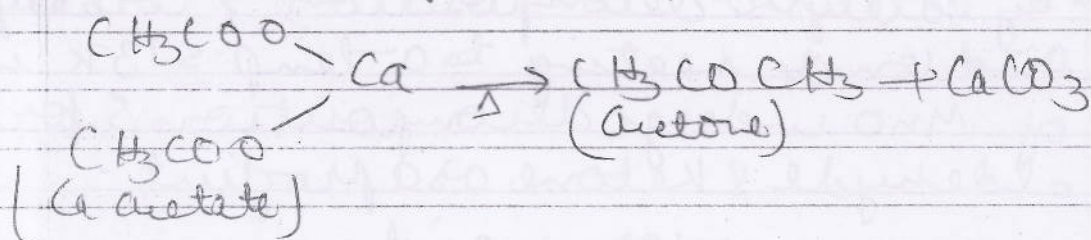
• By the distillation of Ca salt of Carboxylic acid  $\rightarrow$  Ca salt of Carboxylic acid on distillation gives Carbonyl compounds.

$\rightarrow$  Ca formate on distillation gives formaldehyde.

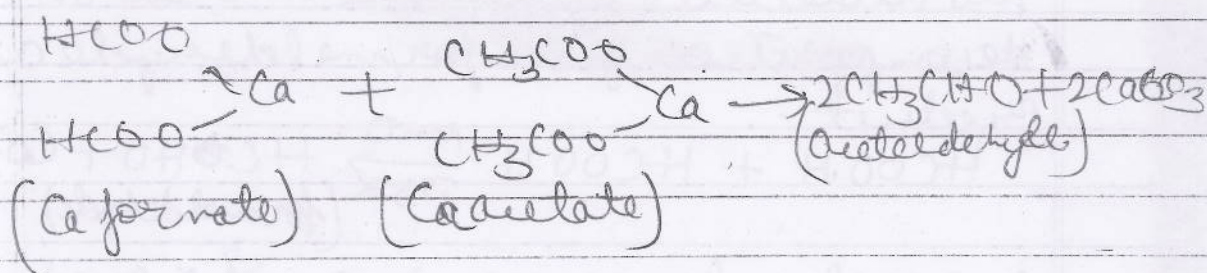
as a product.



⇒ Ca salt acetate on distillation gives acetone as a product.

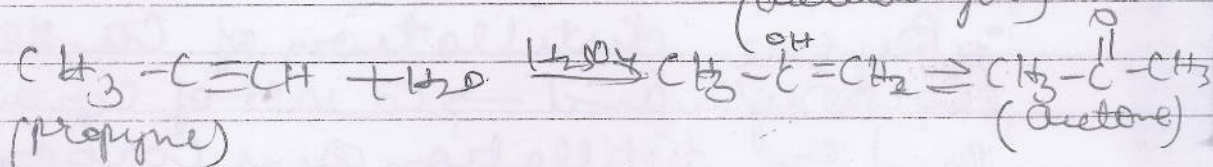
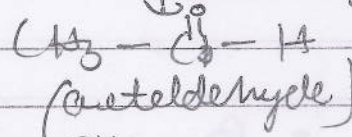
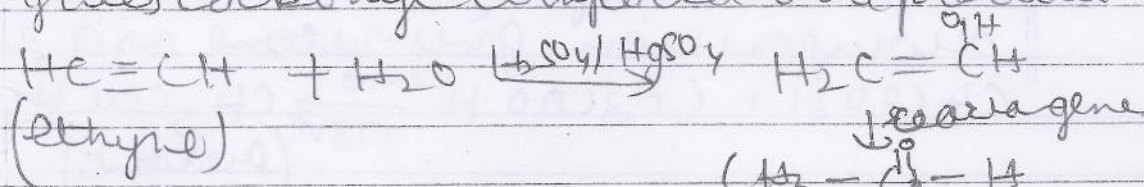


⇒ Ca acetate or Ca formate on distillation gives acetaldehyde as a product.

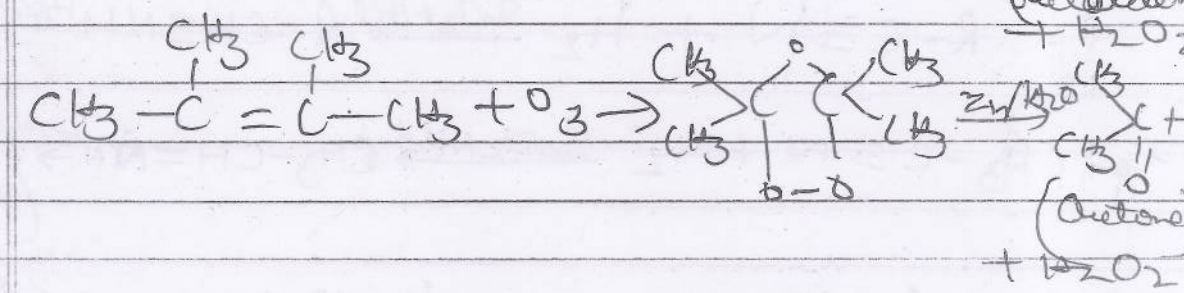
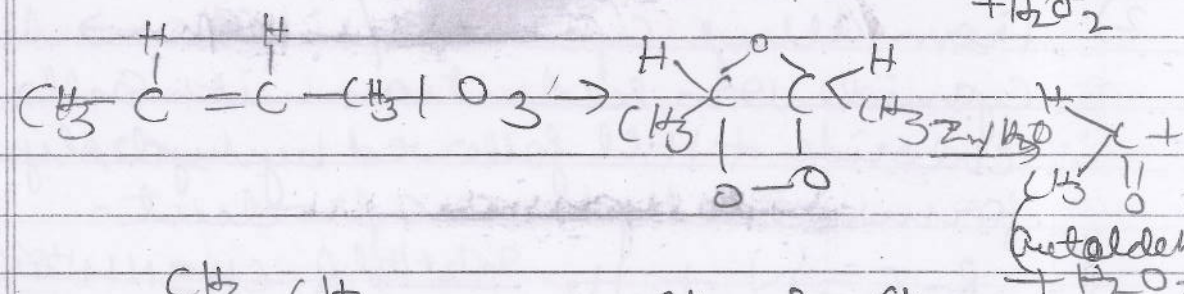
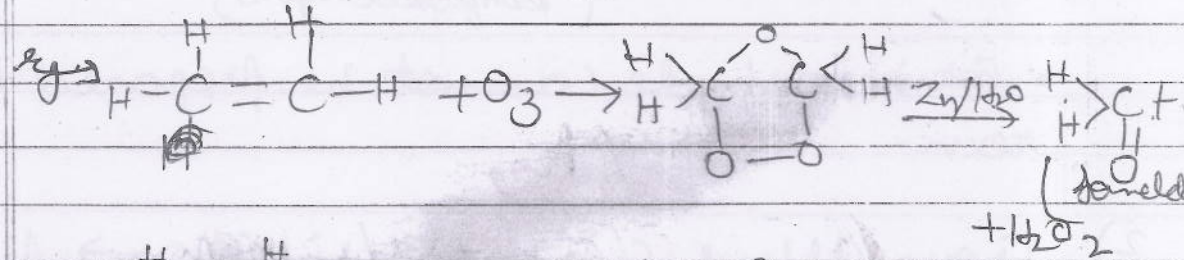
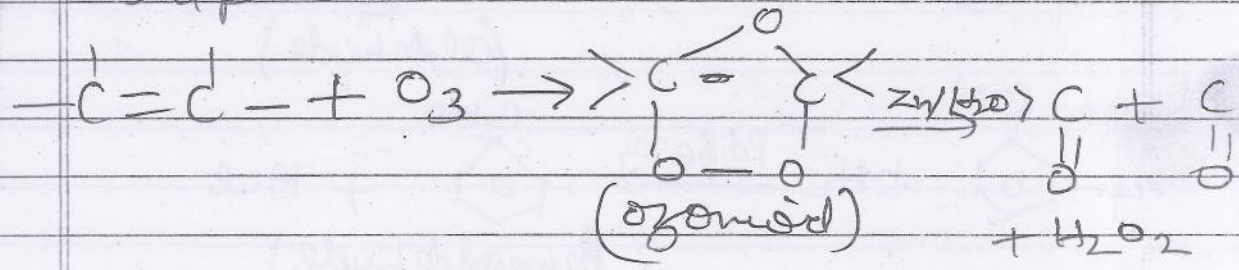


3) From hydrocarbons →

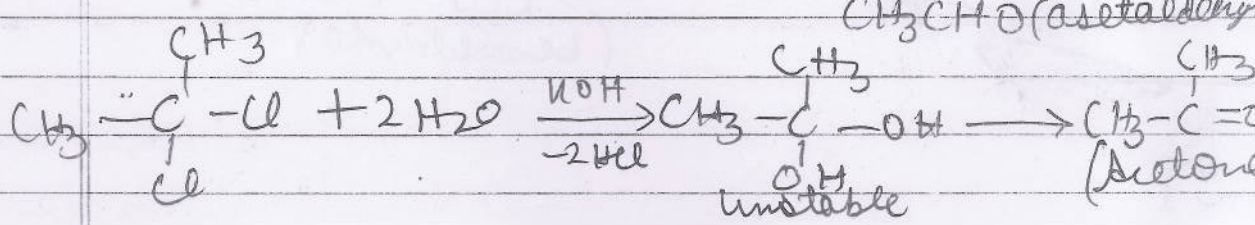
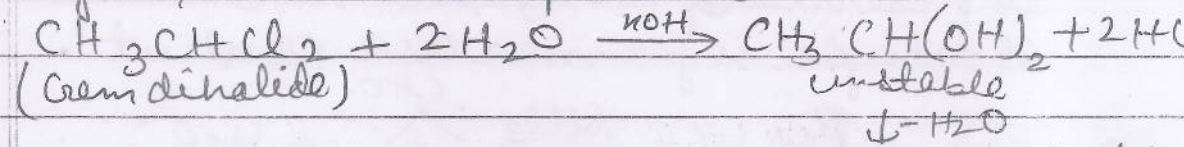
By hydration of alkynes → Alkynes when react with water forms an additional compound or which on rearrangement gives carbonyl compound as a product.



• By ozonolysis of alkenes → Alkenes when react with ozone forms an additional compound which when heat with Zn & H<sub>2</sub>O forms carbonyl compound as a product.

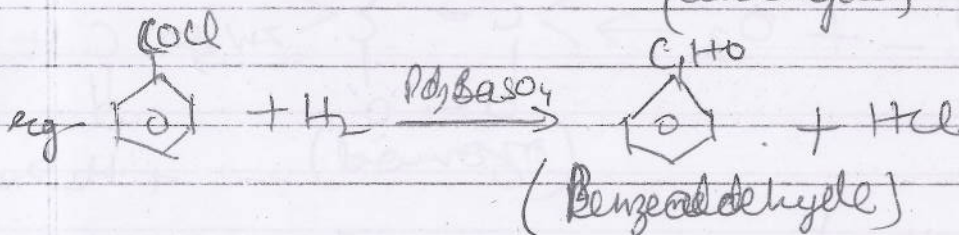
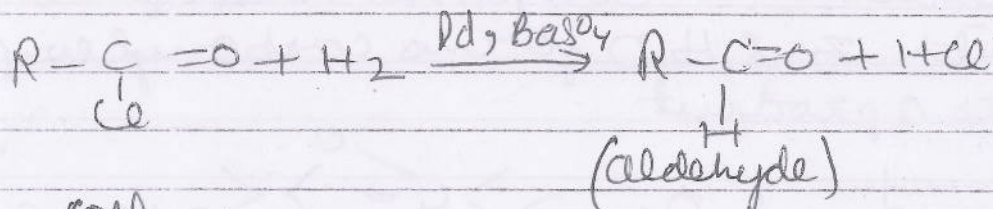


4) From gem dihalides → Gem dihalides on hydrolysis with aqueous KOH forms aldehyde & ketone as a product.



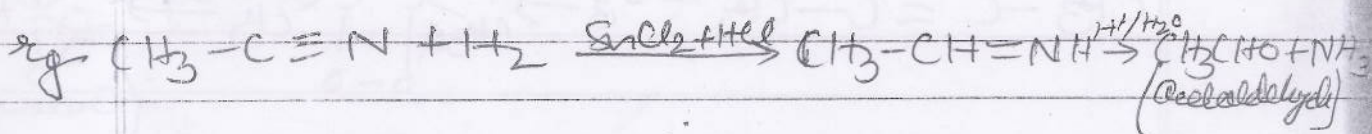
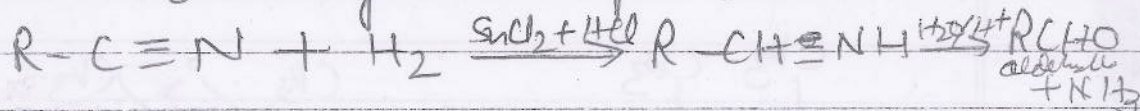
Method of preparation of aldehydes only  $\Rightarrow$

- 1) From acid chloride (By reduction)  $\rightarrow$  Acid chloride on reduction in presence of Pd &  $\text{BaSO}_4$  forms aldehydes as a product. This rxn is known as Rosenmunds Rxn.

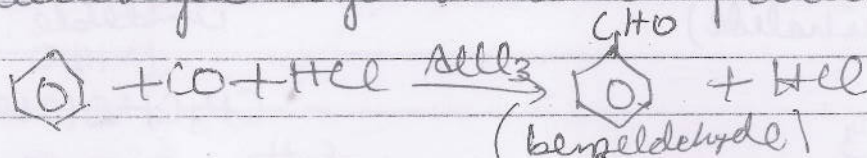


- Formaldehyde cannot be prepared by this rxn.

- 2) From Alkyl Cyanide/nitriles  $\rightarrow$  Alkyl Cyanide on reduction with  $\text{SnCl}_2$  (tin chloride) +  $\text{HCl}$  followed by hydrolysis forms aldehydes as a product.

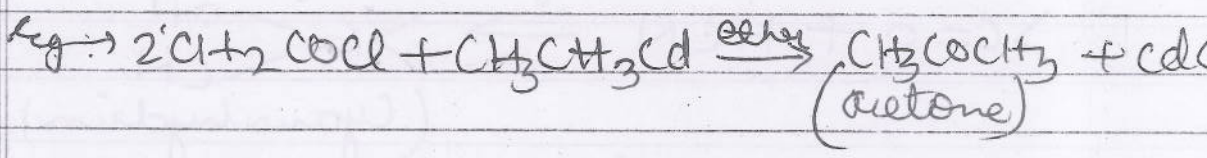
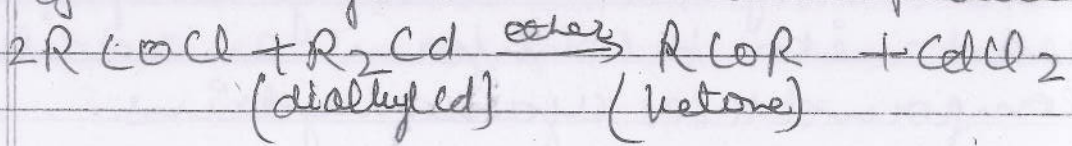


- 3) By Gattermanns Koch rxn  $\rightarrow$  When a mixture of carbon monoxide and  $\text{HCl}$  as gas is passed through benzene in presence of  $\text{AlCl}_3$  &  $\text{CuCl}_2$ , aromatic aldehyde is formed as a product.

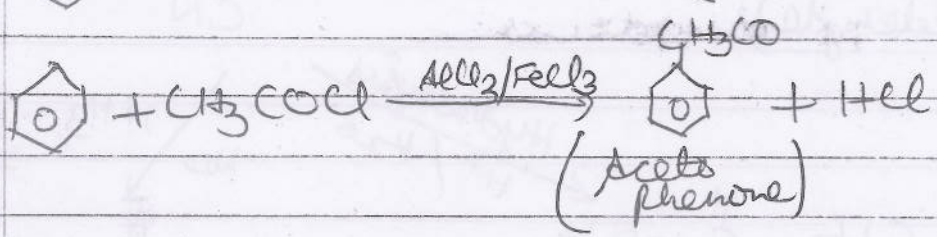
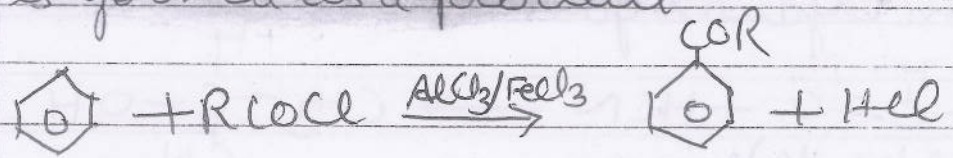


Method of preparation of ketones only  $\rightarrow$

1) From acid chloride  $\rightarrow$  Acid chloride when react with dialkyl cadmium in presence of an ether forms ketones as a product -

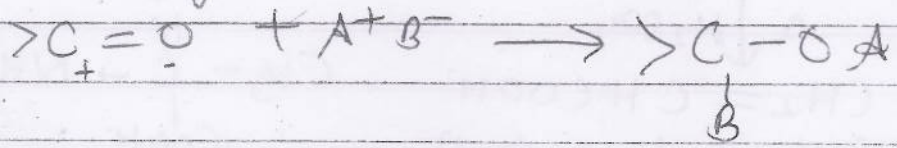


2) From benzene by Friedel-Crafts acylation  $\rightarrow$  when benzene react with acid chloride in presence of  $\text{AlCl}_3$  or  $\text{FeCl}_3$  aromatic ketone is formed as a product -



Properties  $\rightarrow$  (Carbonyl compounds)

1) Reactivity  $\rightarrow$  Carbonyl compounds mainly undergo nucleophilic addition rxn -



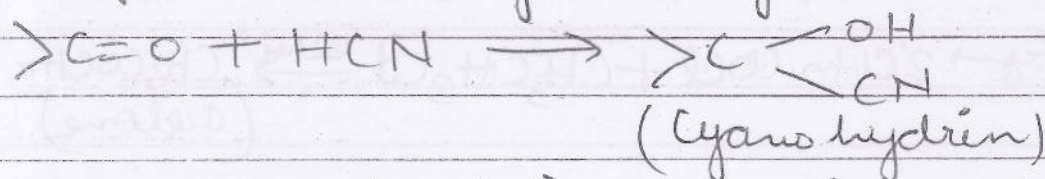
Reactions of carbonyl compounds  $\rightarrow$   
Carbonyl compounds gives following type of rxns  $\rightarrow$

A) Nucleophilic addition rxn

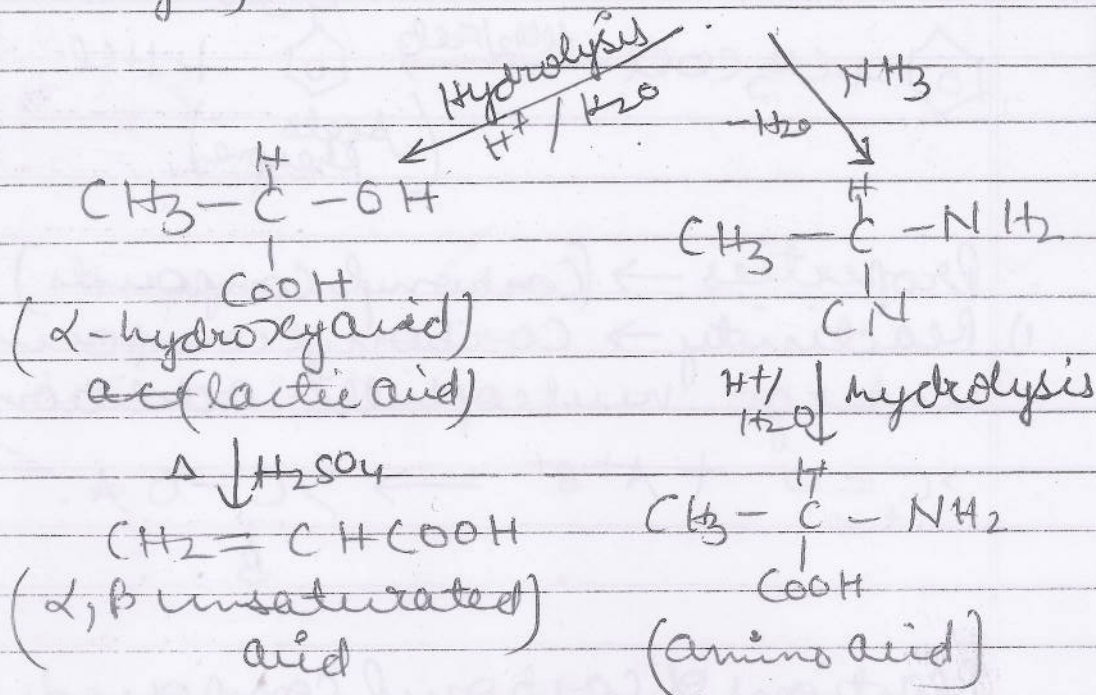
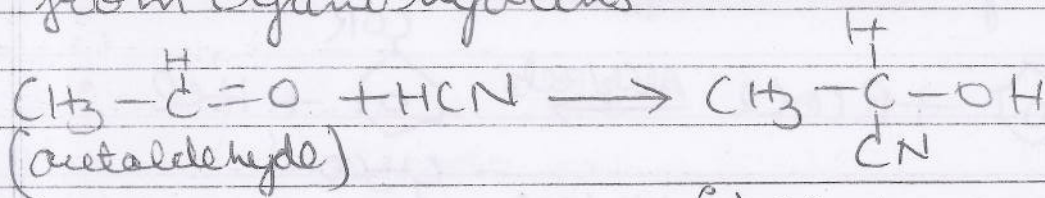
- B) Nucleophilic addition rxn with elimination  
 C) Oxidation rxn  
 D) Reduction  
 E) Miscellaneous (special rxns)

• Nucleophilic addition rxn  $\rightarrow$

1) Addition of HCN  $\rightarrow$  Carbonyl compounds react with HCN & forms an additional compound known as cyanohydrins.

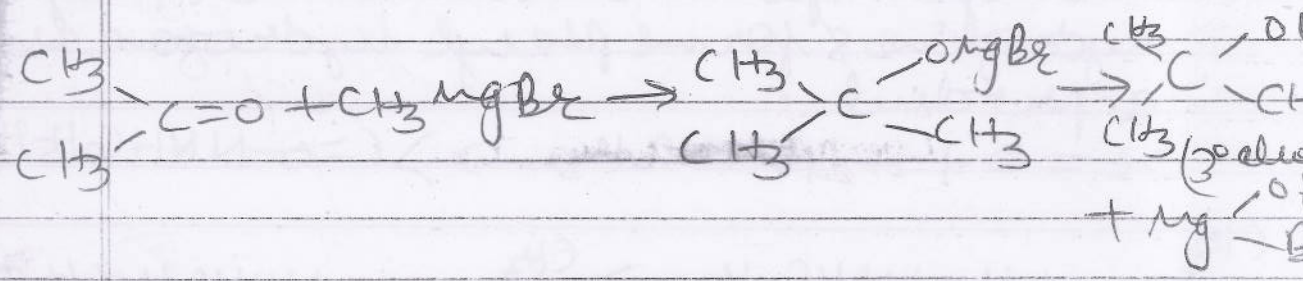
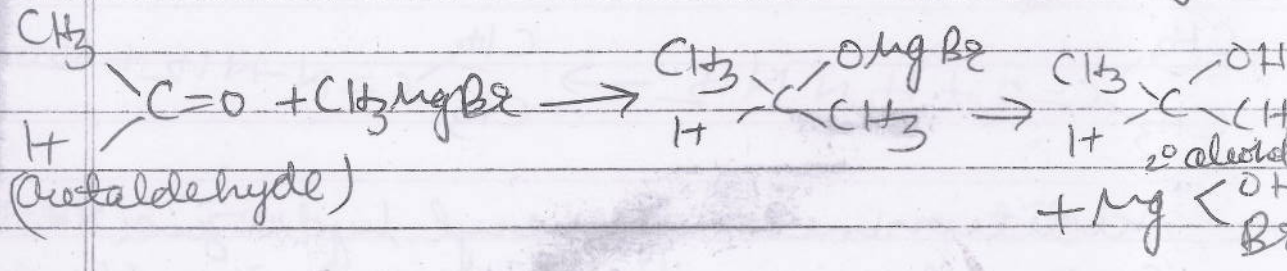
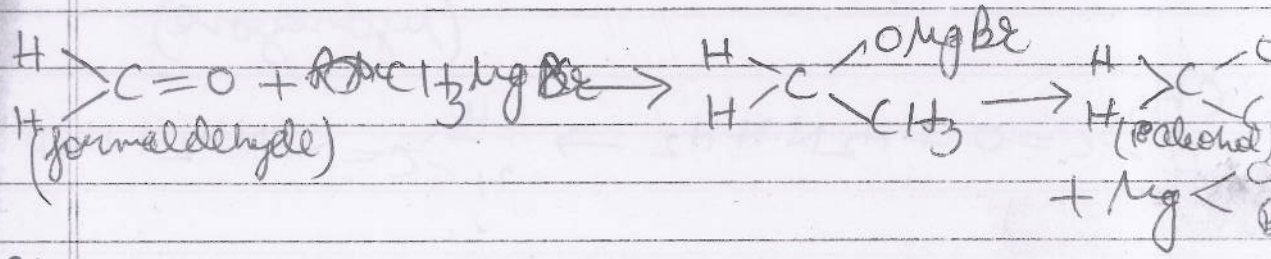
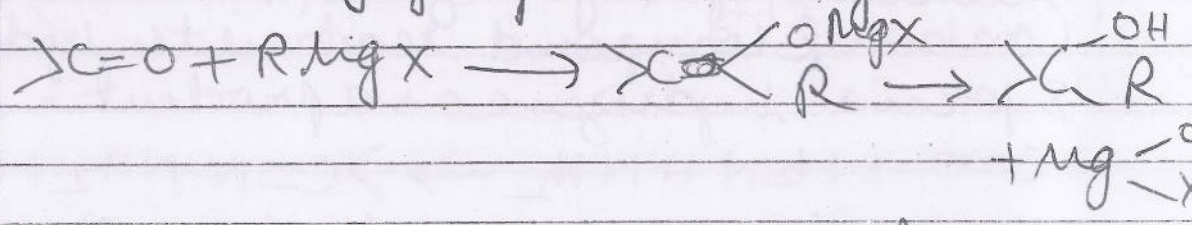


These cyanohydrins are important compounds and various other compounds such as  $\alpha$ ,  $\beta$  unsaturated acid, amino acid,  $\alpha$ ,  $\beta$  unsaturated acid can be formed from cyanohydrins.



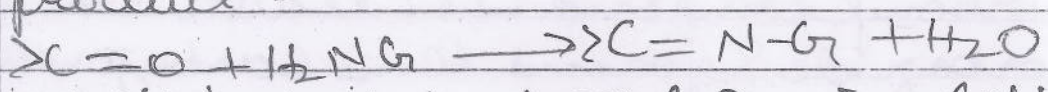


2) Addition of Grignard reagent  $\rightarrow$

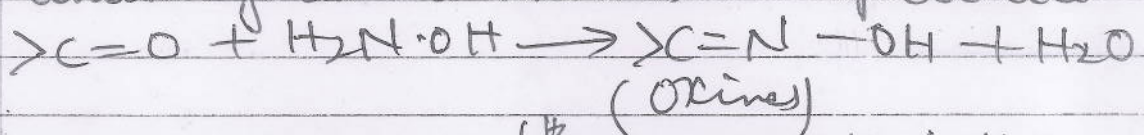


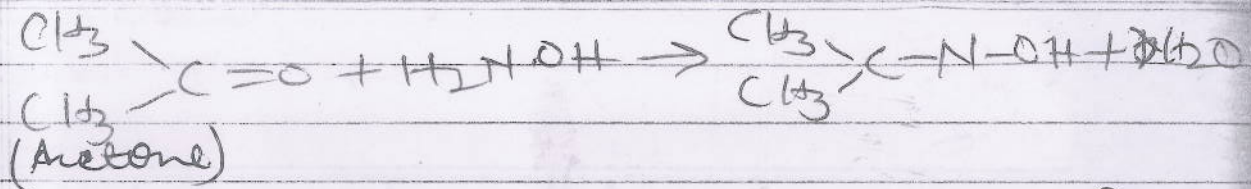
• Nucleophilic addition rxn with elimination  $\rightarrow$

1) Rxn with ammonia derivatives  $\rightarrow$   
Different types of ammonia derivatives react with carbonyl compounds & forms diff product.

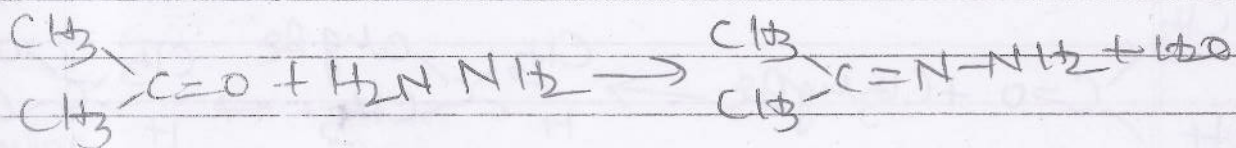
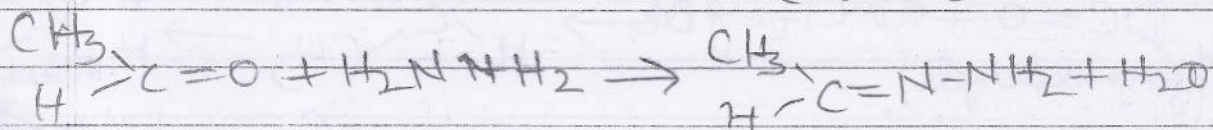
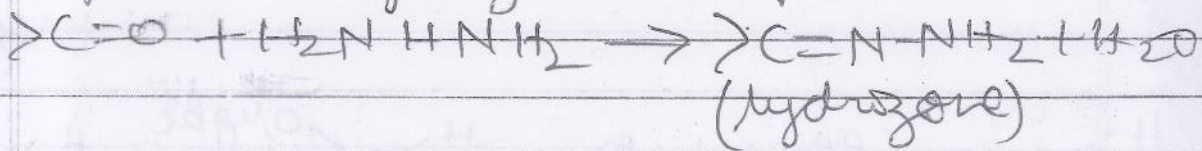


Addition of hydroxyl amine ( $NH_2 \cdot OH$ )  
Carbonyl compound react with hydroxyl amine formed oximes as a product.

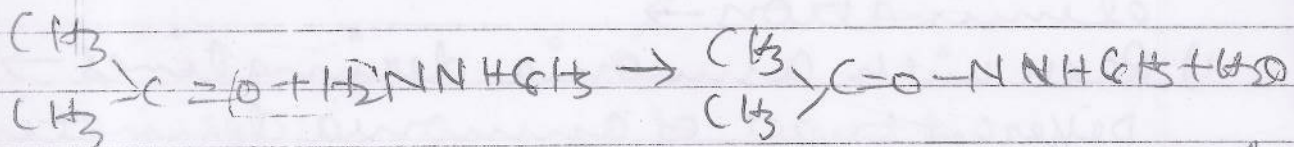
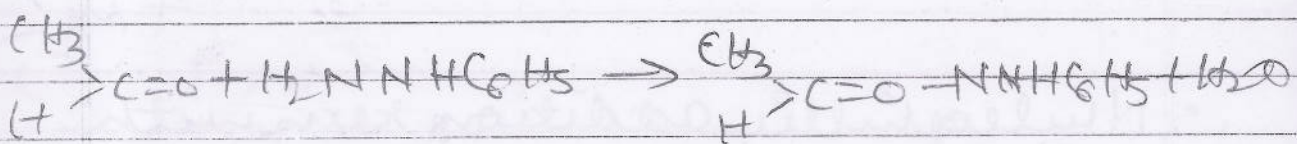




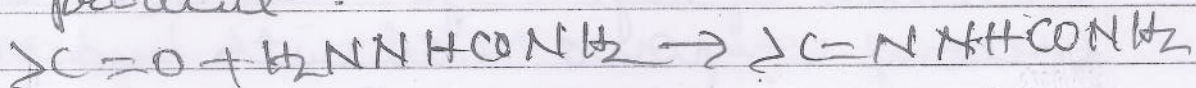
Addition of hydrazine ( $\text{NH}_2 \cdot \text{NH}_2$ )  
Carbonyl compound reacts with hydrazine & forms hydrazine as a product.

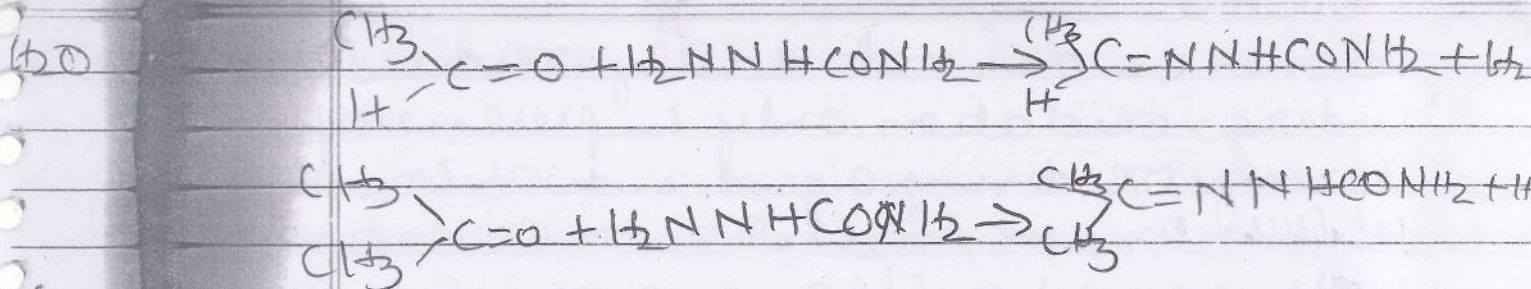


Addition of phenyl hydrazine ( $\text{NH}_2 \cdot \text{NHPh}$ )  
Carbonyl compound when reacts with phenyl hydrazine & forms phenyl hydrazine as a product.

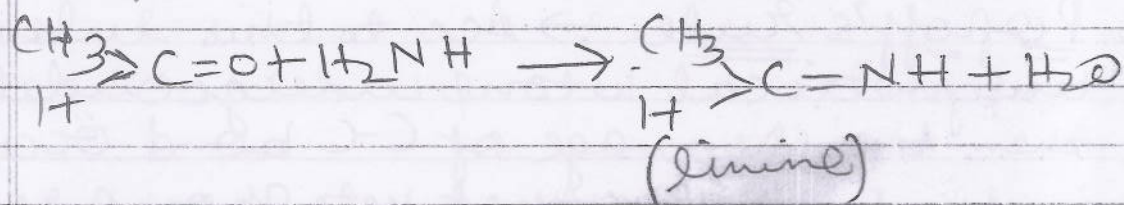


Addition of semi carbazide ( $\text{NH}_2 \cdot \text{NHCONH}_2$ )  
Carbonyl compound when reacts with semi carbazide & forms semi carbazon as a product.

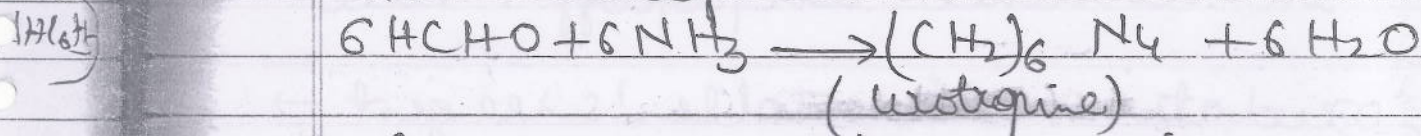




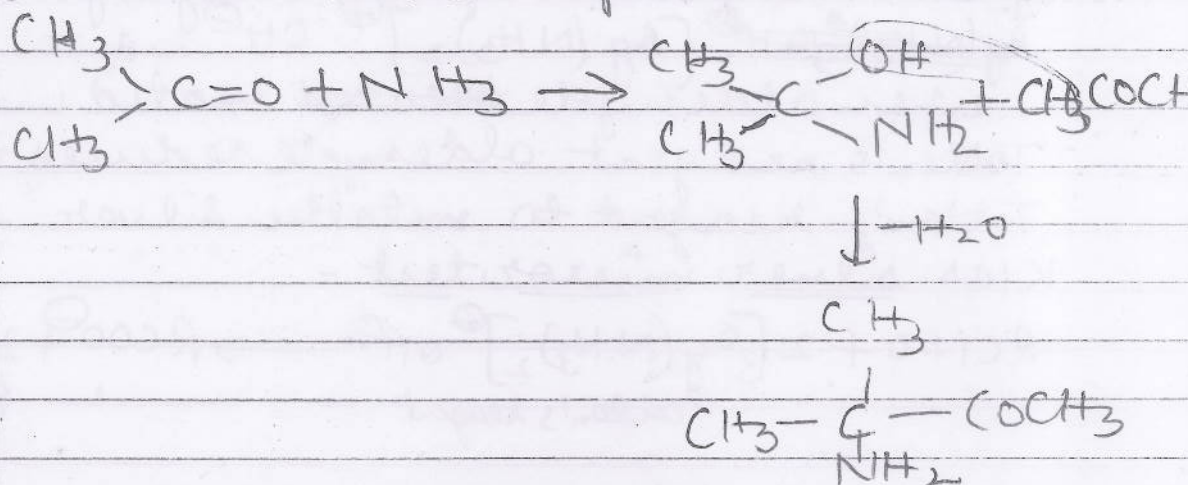
Reaction with ammonia  $\rightarrow$  Aldehyde (except formaldehyde) react with ammonia and forms imine as a product.



Formaldehyde react with ammonia to form hexamethylenetetra amine also known as urotropine.

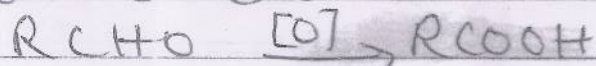


Ketones react with ammonia and forms di keto amines as a product.

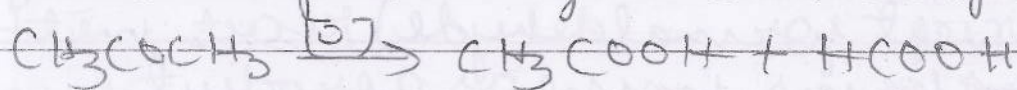


- oxidation  $\rightarrow$  aldehyde easily undergo oxidation to form carbonyl compounds carboxylic acid. On treatment with oxidising agents such as dilute HNO<sub>3</sub>, KMnO<sub>4</sub>

$K_2Cr_2O_7$ , Tollen's reagent, Fehling's reagent solution etc.



ketones are not easily oxidised. Ketones undergo oxidation only in presence of strong oxidising agent such as conc.  $HNO_3$ ,  $H^+/KMnO_4$ ,  $H^+/K_2Cr_2O_7$ . On oxidation there occurs a cleavage of C-C to form mixture of carboxylic acid as a product.

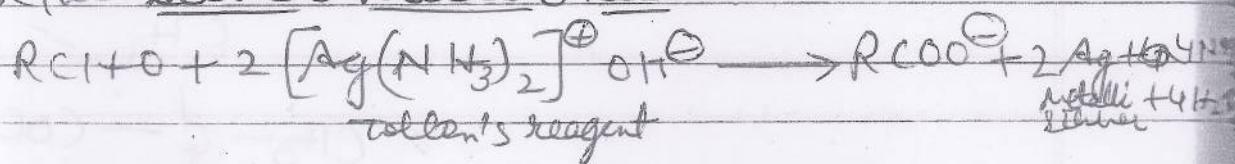


Popoff's Rule  $\Rightarrow$  Acc. to this rule when unsymmetrical ketone undergoes oxidation then the cleavage of C-C bond occurs in such a way that keto group remains with the smaller alkyl group.  
 eg  $\Rightarrow CH_3CH_2COCH_3 \xrightarrow{[O]} CH_3COOH + CH_3COOH$   
 in accordance with Popoff's rule.

oxidation with Tollen's reagent  $\rightarrow$

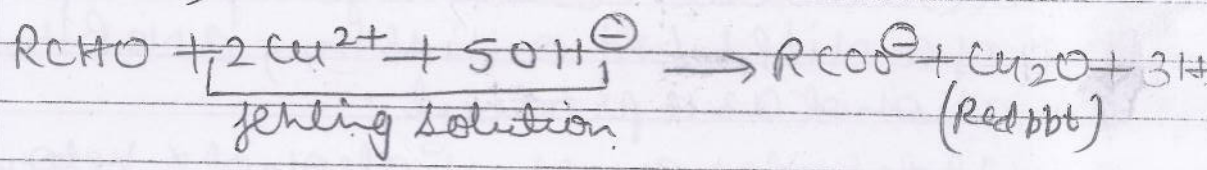
Tollen's reagent is a ammoniacal solution of silver nitrate represented by  $AgNO_3 + NH_4OH$   
 $Ag(NH_3)_2^+ OH^-$   $[Ag(NH_3)_2]^+ OH^-$

when aldehyde is heated with Tollen's reagent aldehyde reduces the Tollen's reagent to metallic silver. This is known as silver mirror test.



ketones do not react with Tollen's reagent.

oxidation with fehling solution  $\rightarrow$  Alkaline solution of  $\text{CuSO}_4 / \text{OH}^-$  or  $\text{Cu}^{2+}$   
 When aldehydes react with fehling solution aldehyde reduces the fehling sol to red phosphorus precipitates of copper oxide ( $\text{Cu}_2\text{O}$ )



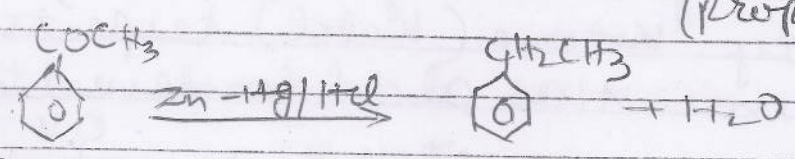
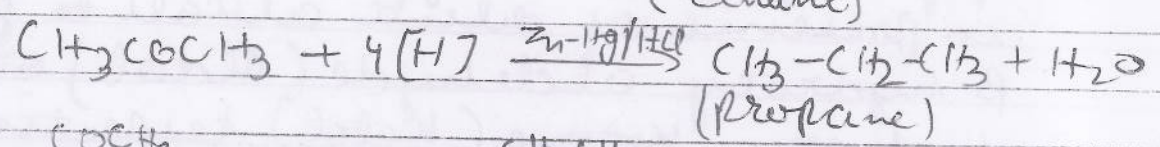
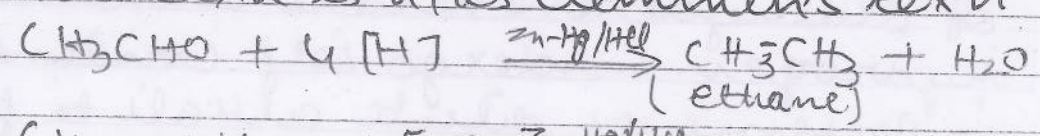
ketones do not react with fehling solution

Reduction  $\rightarrow$

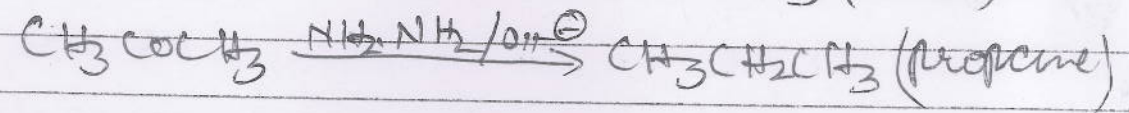
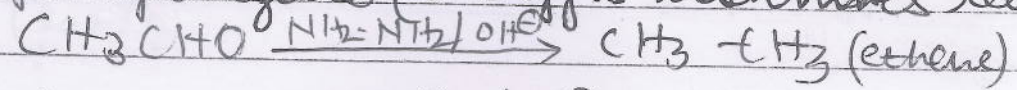
i) Reduction to hydrocarbons (alkane)  $\rightarrow$  Carbonyl compounds on reduction and forms alkane as a product using different reducing agents.

ii) Reduction with Zn-amalgam & HCl (Clemmensen's reduction)  $\rightarrow$  Carbonyl compound in presence of Zn amalgam and HCl undergo reduction and forms alkane as a product.

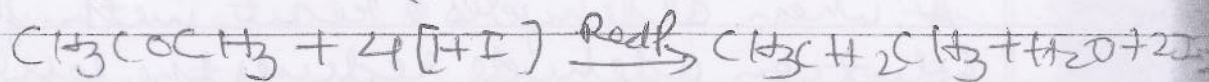
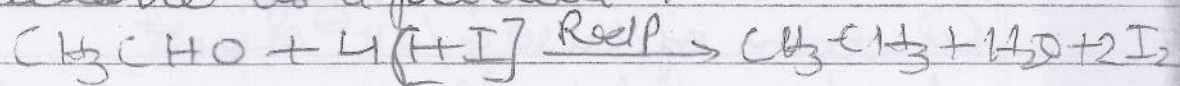
This rxn is called Clemmensen's rxn



ii) Reduction with alkaline/basic solution of hydrazine (Wolff's reid reduction)

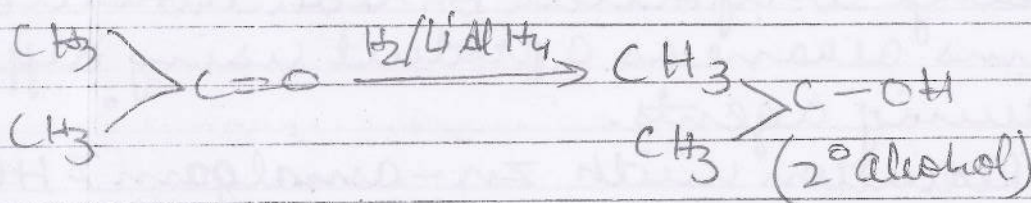
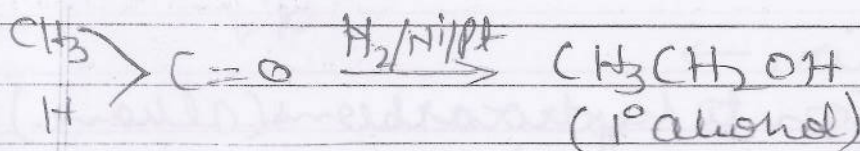


iii) Reduction with HI in red phosphorus  
 → Carbonyl compounds on reduction with HI in presence of a red phosphorus form alkane as a product.



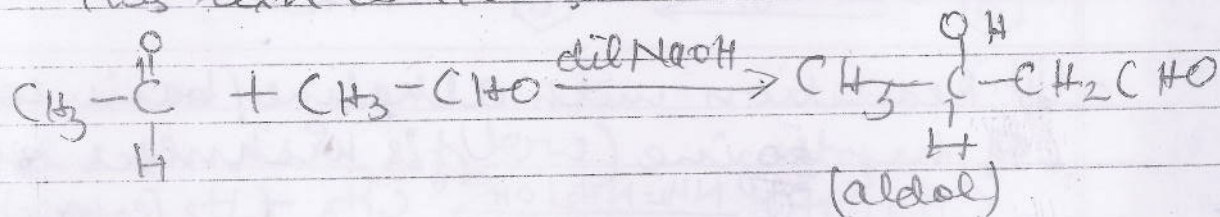
(2) Reduction to alcohol → Carbonyl compounds on reduction with hydrogen in presence of a Ni/Pt/Pd or  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$ , forms alcohol as a product.

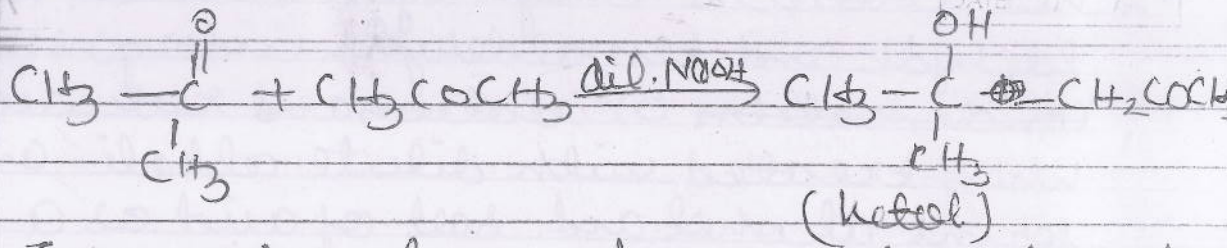
Aldehydes gives  $1^\circ$  alcohol & ketones give  $2^\circ$  alcohol.



• miscellaneous rxns / special rxns →

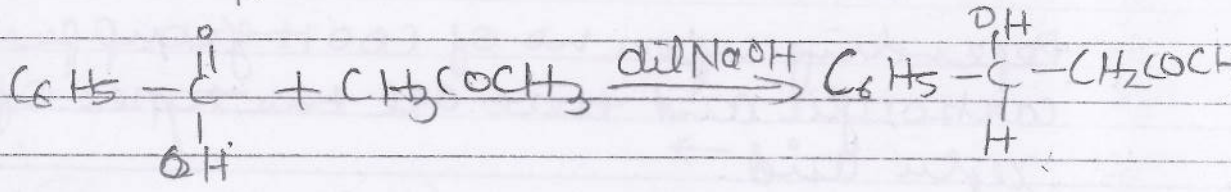
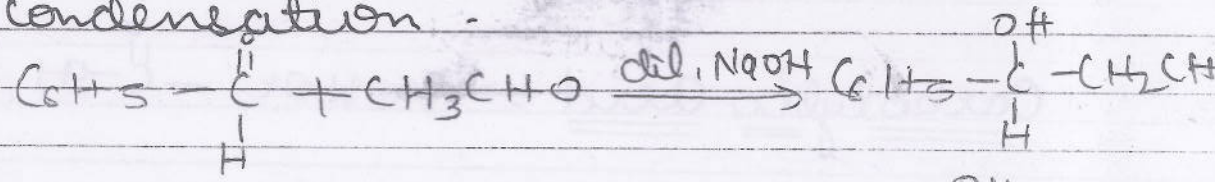
1) Aldol condensation → Two molecules of aldehyde and ketone containing  $\alpha$ -hydrogen undergo self condensation in presence of dilute alkali to form  $\beta$  hydroxy aldehyde (Aldol) or  $\beta$ -hydroxy ketone (Ketal) respectively. This rxn is called aldol condensation.



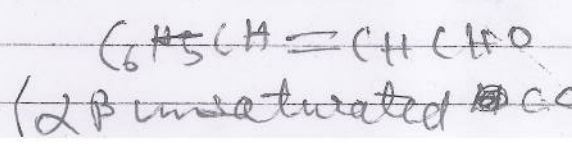
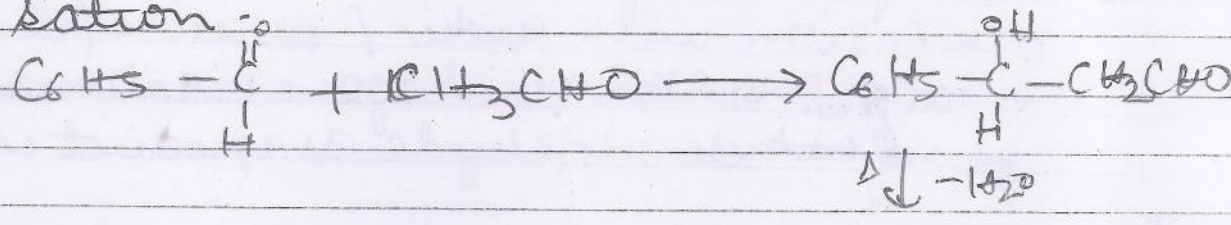


Formaldehyde and benzaldehyde do not contain  $\alpha$  hydrogens therefore they do not undergo aldol condensation.

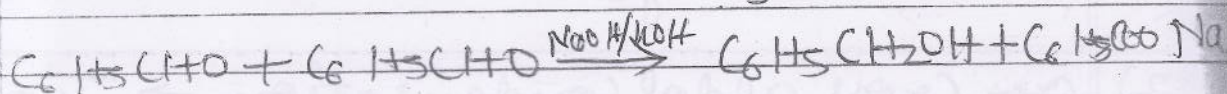
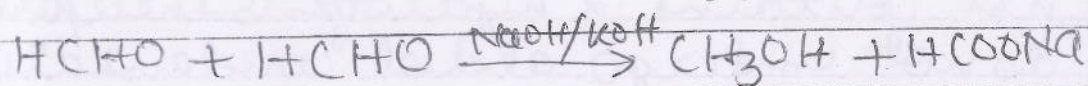
2) ~~or~~ Cross aldol condensation  $\rightarrow$  Two different molecules of a carbonyl compound at least one containing  $\alpha$  hydrogens undergo self condensation in presence of dilute alkali. This rxn is known as cross aldol condensation.



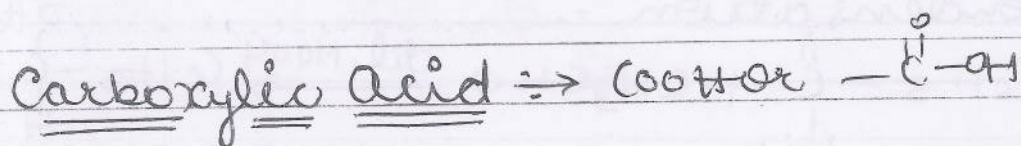
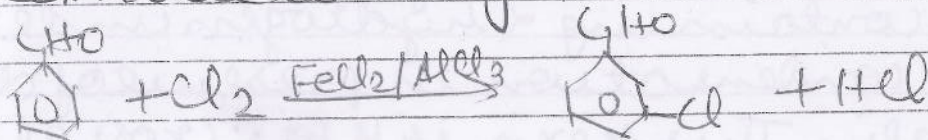
3) Claisen's Condensation / Claisen's Schmitt  $\rightarrow$  when an aromatic carbonyl compound and an aliphatic carbonyl compound at least one containing  $\alpha$  hydrogens undergo self condensation and forms  $\alpha, \beta$  unsaturated carbonyl compound as a product. This rxn is known as Claisen's condensation.



4) Cannizzaro's rxn  $\rightarrow$  Aldehydes which do not contain  $\alpha$  hydrogen such as formaldehyde and benzaldehyde undergo self condensation oxidation and reduction when treated with dilute alkali and forms alcohol and salt of acid as a product. This rxn is known as Cannizzaro's rxn.



Rxn due to ring  $\rightarrow$



Depending upon no. of  $\text{COOH}$  group present in carboxylic acid there are two types of carboxylic acid  $\rightarrow$

1) Monocarboxylic acid  $\rightarrow \text{CH}_3\text{COOH}, \text{C}_6\text{H}_5\text{COOH}$

2) Dicarboxylic acid  $\rightarrow \begin{array}{c} \text{COOH} \\ | \\ \text{COOH} \end{array}$  oxalic acid

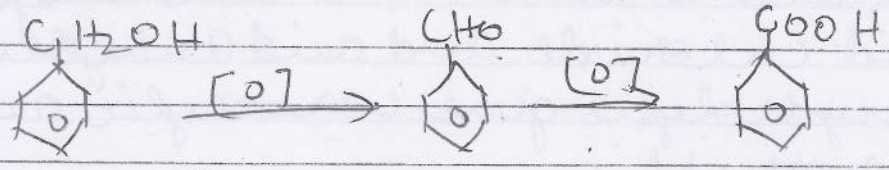
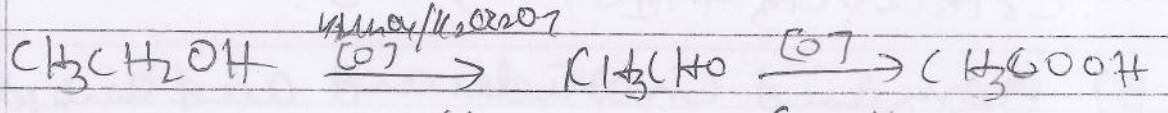
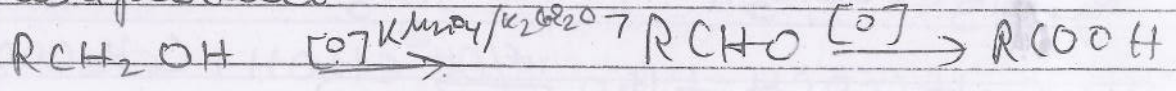
$\text{CH}_2\text{COOH}$  succinic acid  
 $\begin{array}{c} | \\ \text{CH}_2\text{COOH} \end{array}$

Methods of preparation  $\rightarrow$

1) From primary alcohol  $\rightarrow$   $1^\circ$  alcohol on oxidation with aeri / alkaline / neutral  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$  undergo oxidation and forms ~~etc~~ aldehyde as a product which

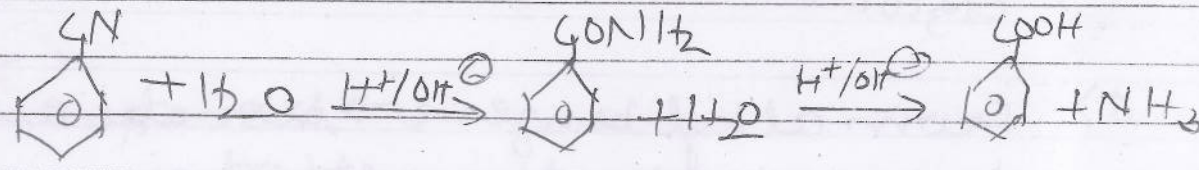
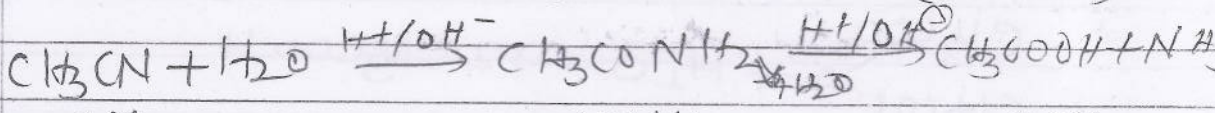
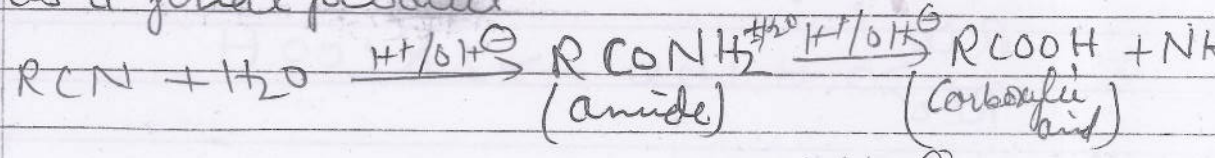


further oxidation forms carboxylic acid as a product.

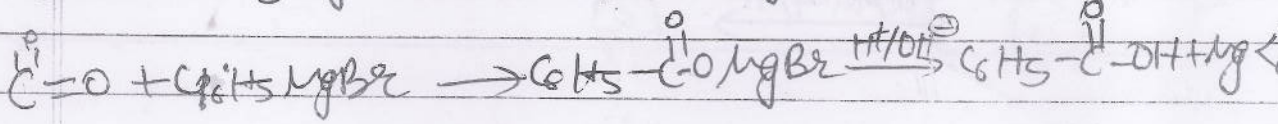
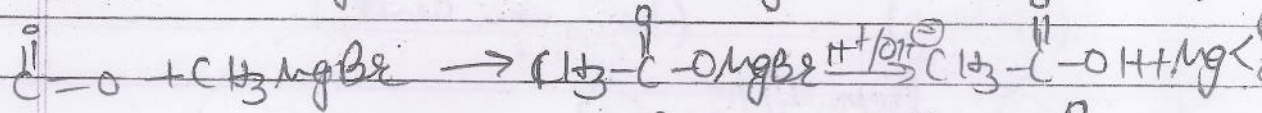
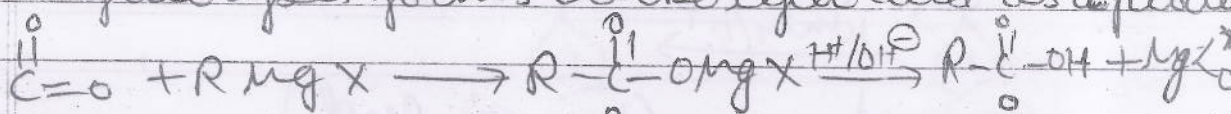


The oxidation also takes place in presence of  $CrO_3 / H_2SO_4$ .

2) From nitriles / cyano compounds  $\rightarrow$  Nitriles or cyano compound on hydrolysis in acidic or basic medium forms carboxylic acid as a final product.

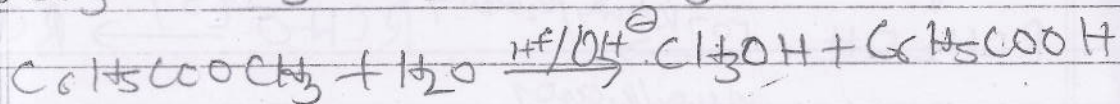
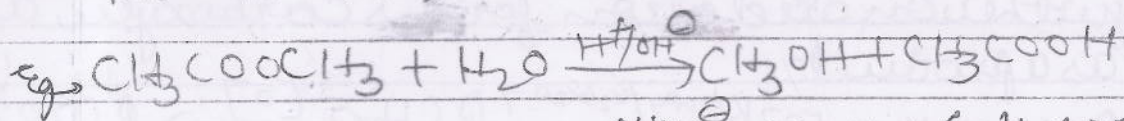
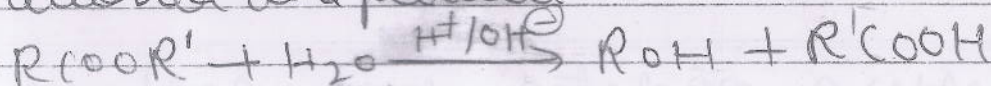


3) From Grignard reagent  $\rightarrow$  Grignard reagent when react with  $CO_2$  forms an additional compound which on hydrolysis forms carboxylic acid as a product.



4) From ester  $\rightarrow$  Ester on hydrolysis in presence

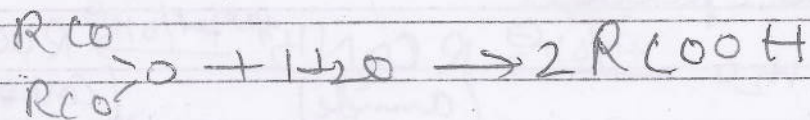
of a acid or a base forms carboxylic acid and alcohol as a product -



5) From acid chlorides and acid anhydride  
 → acid chloride and acid anhydride  
 on hydrolysis gives carboxylic acid  
 as a product -

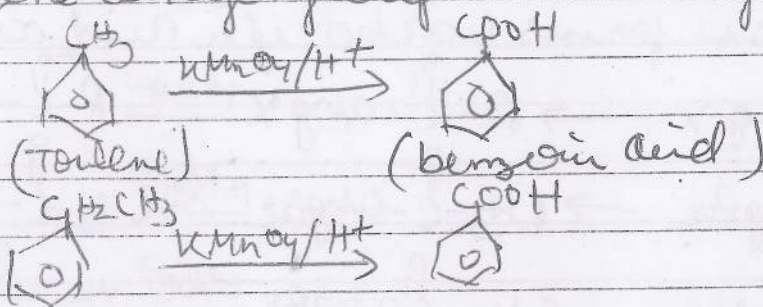


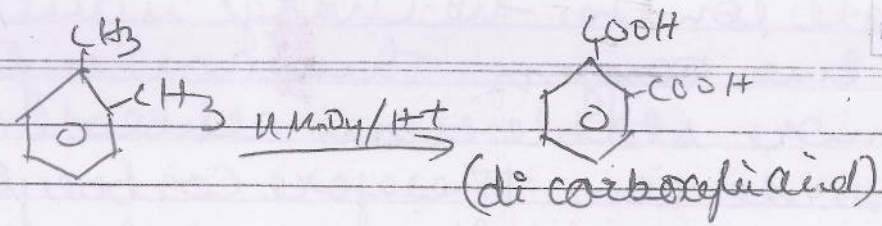
Acid anhydrides →



6) From alkyl benzene → aromatic acid. can  
 be prepared by this method -

Alkyl benzene in presence of acidic  
 or alkaline  $\text{KMnO}_4$  or conc.  $\text{HNO}_3$  oxidised  
 the alkyl group to carboxylic group.



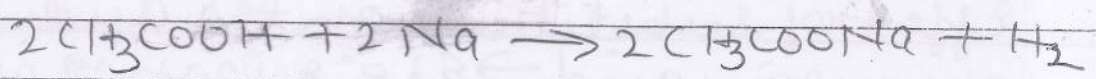
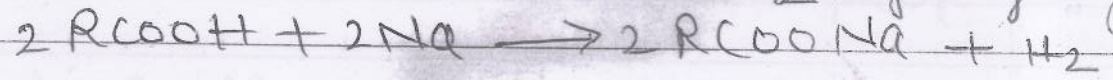


Carboxylic acid gives following types of rxn

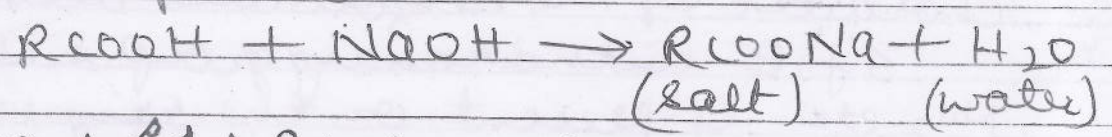
- A) Rxn due to H
- (B) Rxn due to O-H
- (C) Rxn due to COOH
- (D) Rxn due to alkyl or aryl group

• Rxn due to H →

1) Rxn with metal → Carboxylic acid reacts with metal and liberate  $\text{H}_2$  hydrogen gas

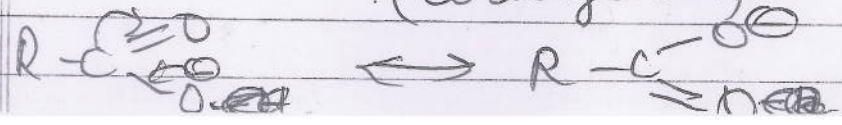
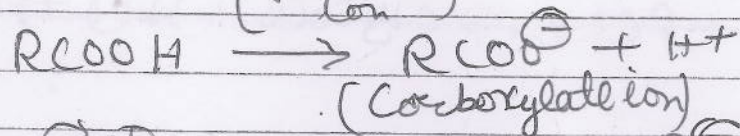
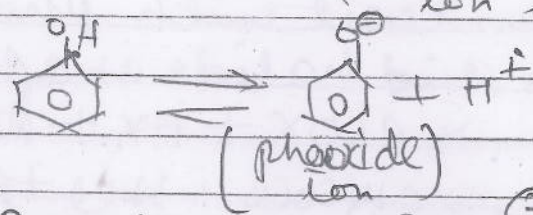
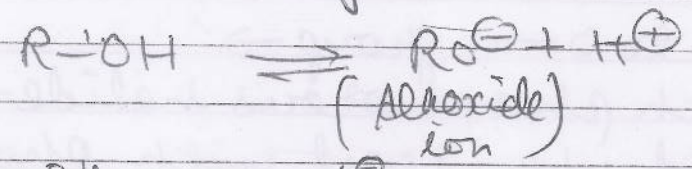


2) Rxn with alkali → Carboxylic acid reacts with base/alkali and forms salt and water as a product.



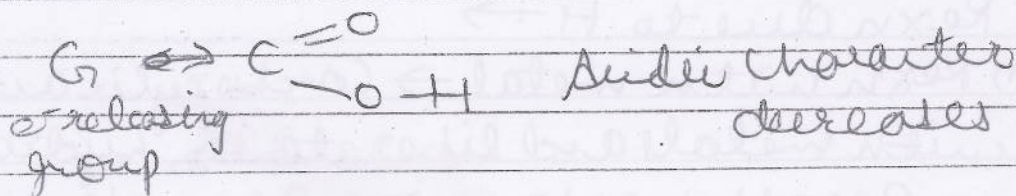
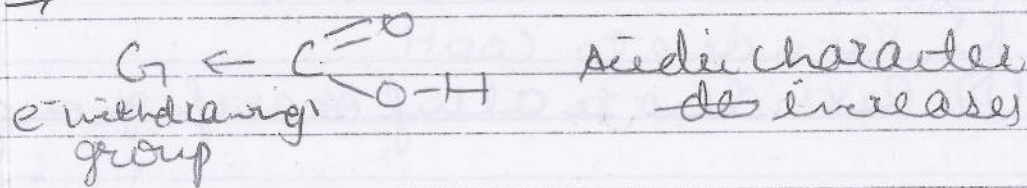
3) ~~Acid~~ Acidic character →

Carboxylic acids are more acidic than alcohol and phenol.



Due to resonating structures of carboxylate ion the  $-ve$  charge is distributed b/w two oxygen. Thus carboxylate ion is more stable than alkoxide and phenoxide ion. Therefore carboxylic acids are more acidic than alcohol and phenol.

Effect of substituent on acidic character



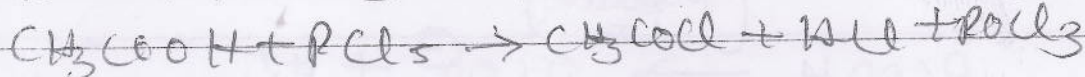
Effect of substituent on the acidic character of benzoic acid  $\rightarrow$  If  $e^-$  releasing group

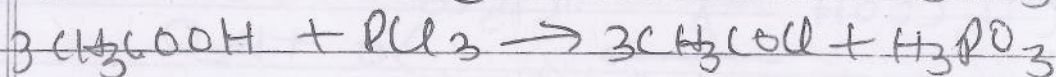
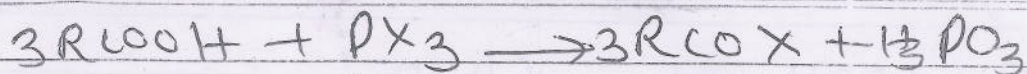
such as  $\text{Cl}$ ,  $\text{OH}$ ,  $\text{NH}_2$  etc. present on the benzene ring. The acidic character of the benzoic acid decreases.

If  $e^-$  withdrawing group such as  $\text{Cl}$ ,  $\text{NO}_2$  etc. is present on the ring then the acidic character of the benzoic acid increases.

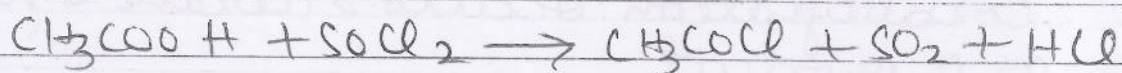
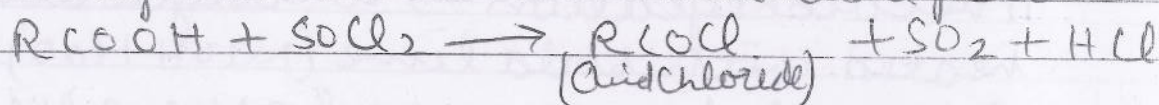
• Rxn due to  $\text{O-H}$  group  $\rightarrow$

1) Rxn with phosphorus halide  $\rightarrow$  Carboxylic acid when react with phosphorus halide forms acid halide as a product.



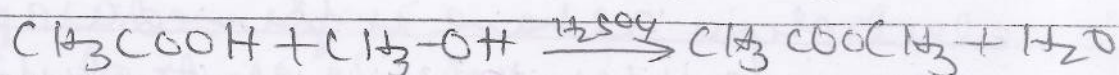
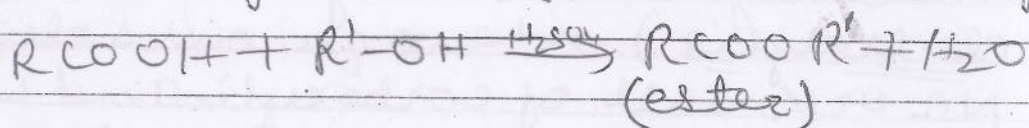


2) Rexn with thionyl chloride  $\rightarrow$  Carboxylic acid react with thionyl chloride and forms acid chloride as a product.

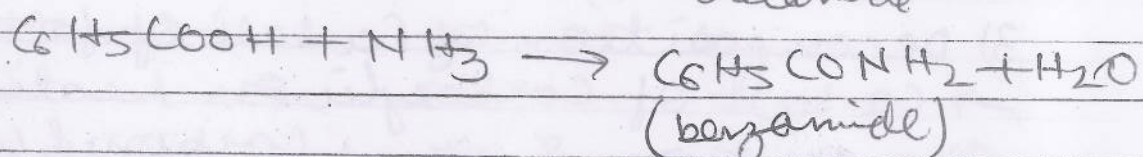
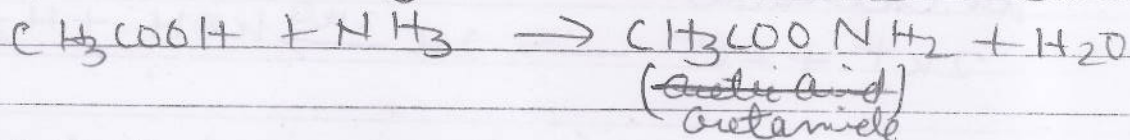
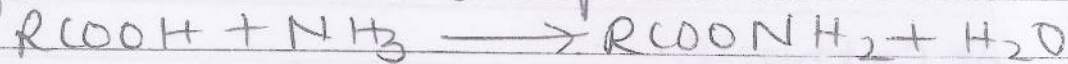


3) Rexn with alcohol  $\rightarrow$  (esterification)

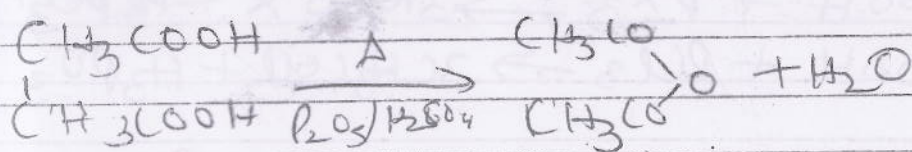
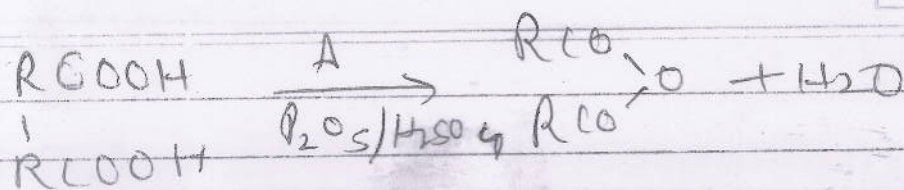
Carboxylic acid react with alcohol in presence of  $\text{H}_2\text{SO}_4$  & forms ester as a product.



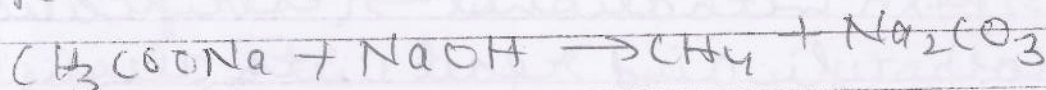
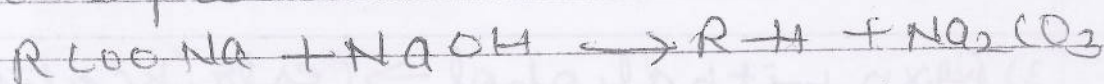
4) Rexn with ammonia  $\rightarrow$  (formation of amide)  
Carboxylic acid react with ammonia and forms amides as a product.



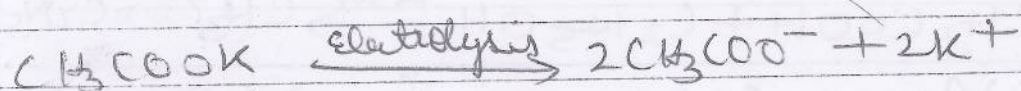
5) Action of heat (dehydration)  $\rightarrow$  Carboxylic acid on heating in presence of  $\text{P}_2\text{O}_5 / \text{H}_2\text{SO}_4$  forms acid anhydride as a product



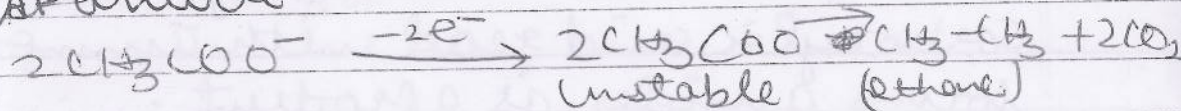
- Rxn due to COOH group  $\rightarrow$ 
  - 1) Decarboxylation  $\rightarrow$  <sup>Na salt of</sup> carboxylic acid when heated with soda lime (NaOH + CaO) decarboxylation occurs & alkane is formed as a product.



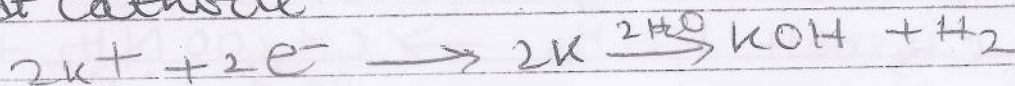
- 2) Electrolytic decarboxylation  $\rightarrow$  (Kolbe's electrolysis)  $\rightarrow$  when aqueous solution of Na or K salt of carboxylic acid undergo electrolysis alkane is formed as a product. This rxn is called Kolbe's electrolysis.



At anode

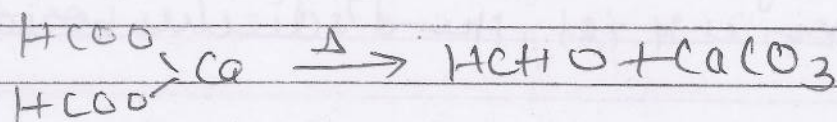


At cathode

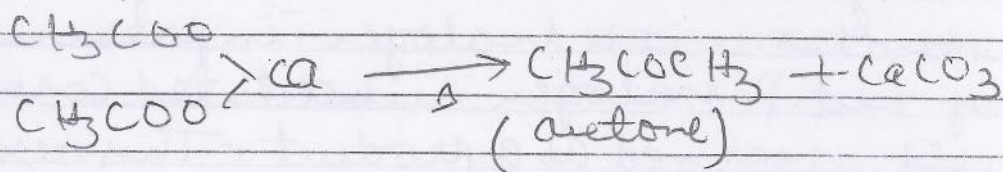


- 3) Decomposition of Ca salt of fatty acids  $\rightarrow$  Ca salt of carboxylic on heating undergo decomposition & forms carbonyl compound as a product.

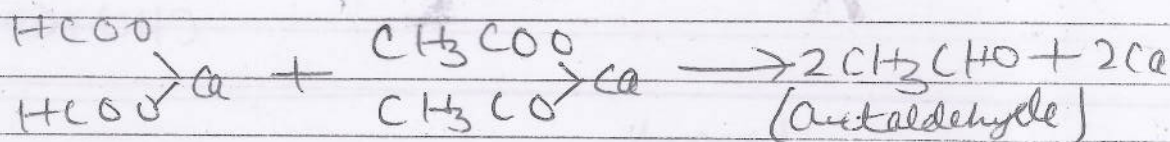
Ca formate on decomposition forms formaldehyde as a product.



Ca acetate on decomposition forms acetone as a product

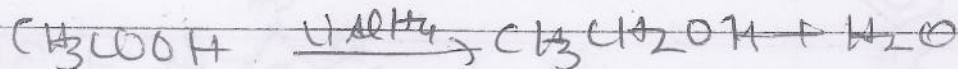
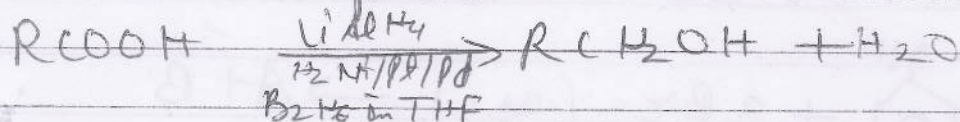


A mixture of Ca formate and Ca acetate forms acetaldehyde as a product.

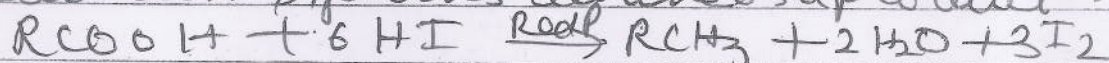


4) Reduction  $\rightarrow$  Carboxylic acid undergoes two types of reduction

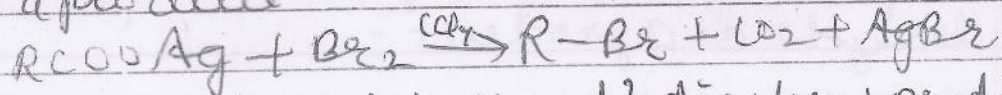
Partial reduction  $\rightarrow$  in presence of  $\text{LiAlH}_4$  or  $\text{H}_2/\text{Ni/Pt/Pd}$  or  $\text{B}_2\text{H}_6$  in THF carboxylic acid undergoes partial reduction & forms alcohol as a product.



Complete reduction  $\rightarrow$  with HI in presence of a Red P carboxylic acid undergoes complete reduction & forms alkane as a product.

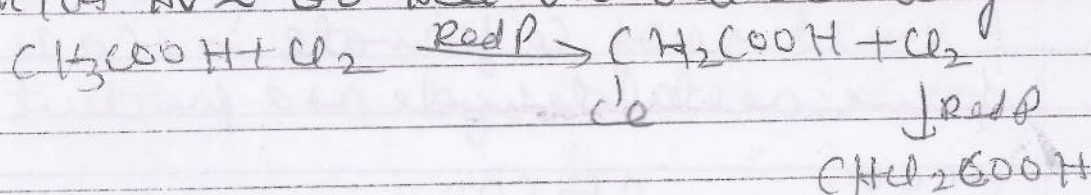


Reaction with bromine  $\rightarrow$  Silver salt of carboxylic acid is treated with bromine in presence of a CCl<sub>4</sub> bromo alkane is formed as a product.



This rxn is known as Hunsdiecker bromination rxn.

- Rxn due to alkyl or aryl group  $\rightarrow$  Halogenation  $\rightarrow$  when carboxylic acid is treated with halogen in presence of Red P halogen substituted carboxylic acid is formed as a product. This rxn is known as H<sub>2</sub> or Hell Volhard Zelinisky rxn.



### Reactions

