

SBG STUDY

classmate

Date _____

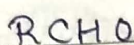
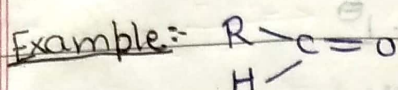
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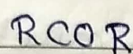
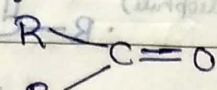
Aldehydes, Ketones and Carboxylic acid

Carbonyl compound

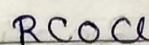
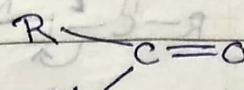
Compounds containing carbonyl group ($C=O$) are known as carbonyl compounds.



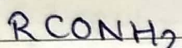
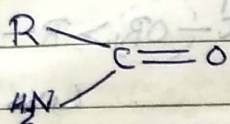
Aldehyde



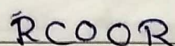
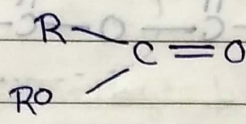
Ketone



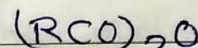
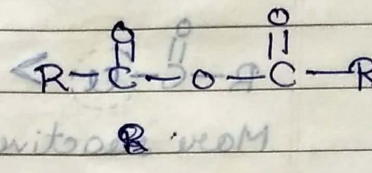
Acid chloride



Amide



Ester



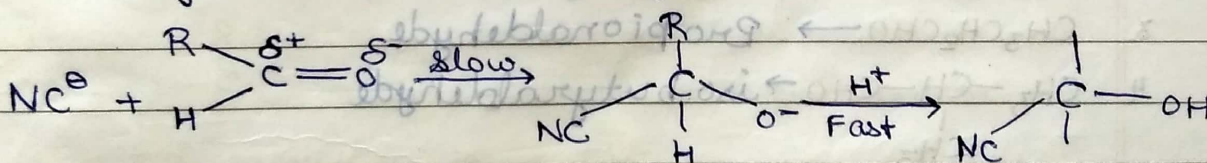
Acid anhydride

Reaction of Carbonyl group

There are two types of reaction takes place on carbonyl group:-

1. Nucleophilic addition reaction

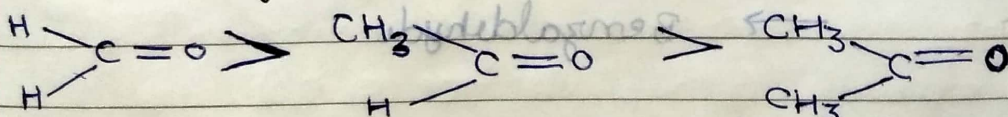
Aldehydes and ketones give this reaction.



Planar

Tetrahedral

Reactivity order of nucleophilic addition reaction



More reactive

Less reactive

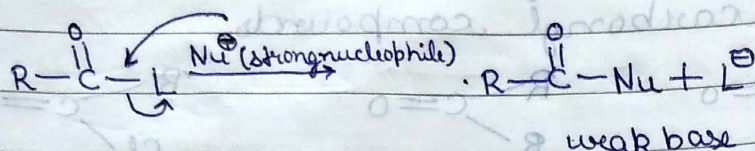
Reactivity of compound decrease with increase in size of alkyl group bonded with carbon atom

of carbonyl group.

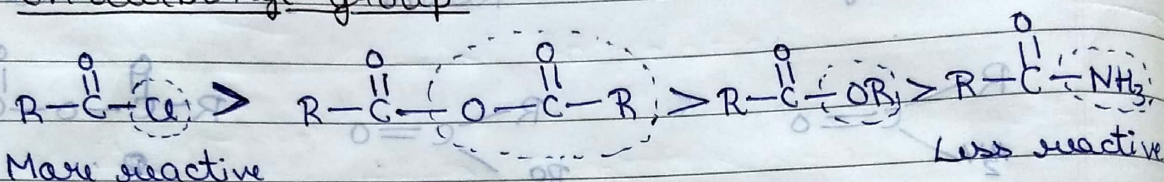
2. Nucleophilic substitution reaction

Carboxylic acid and its derivatives give this reaction.

Mechanism - [L = leaving group]



Reactivity order of nucleophilic substitution reaction on carbonyl group



Hint:- Base $\Rightarrow \text{Cl}^- < \text{RCOO}^- < \text{RO}^- < \text{NH}_2^-$ (strong base)

Conjugate acid $\Rightarrow \text{HCl} > \text{RCOOH} > \text{ROH} > \text{NH}_3$

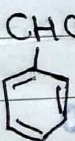
strong acid weak base

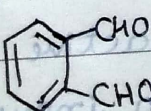
Common names of Aldehydes

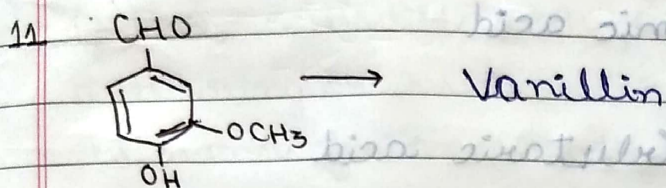
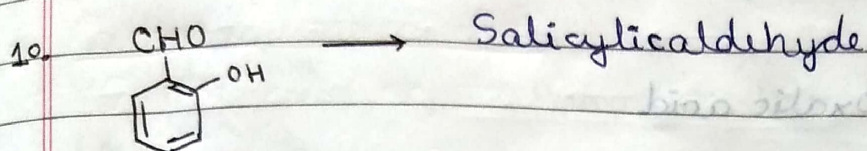
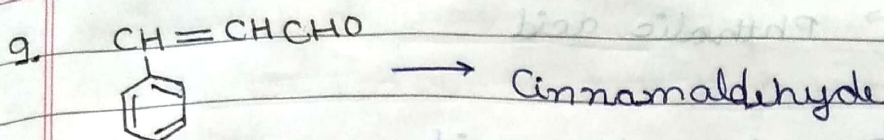
1. $\text{HCHO} \rightarrow$ Formaldehyde
2. $\text{CH}_3\text{CHO} \rightarrow$ Acetaldehyde
3. $\text{CH}_3\text{CH}_2\text{CHO} \rightarrow$ Propionaldehyde
4. $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CHO} \rightarrow$ isobutyraldehyde

5. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \rightarrow$ Valeraldehyde

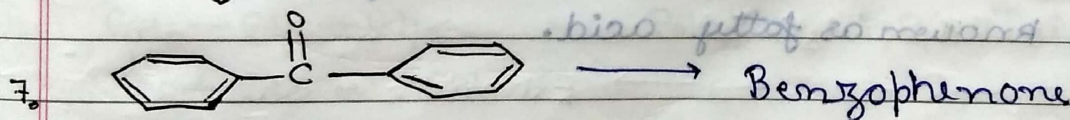
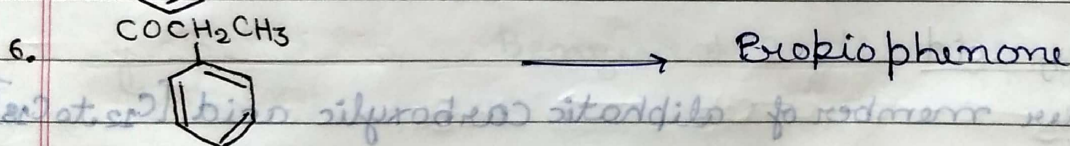
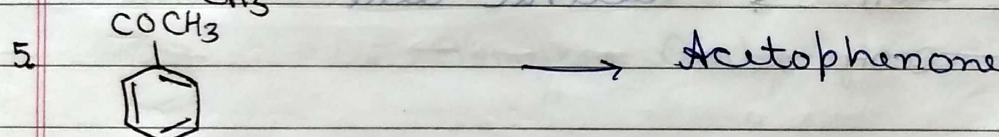
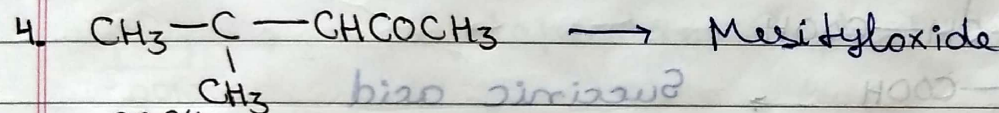
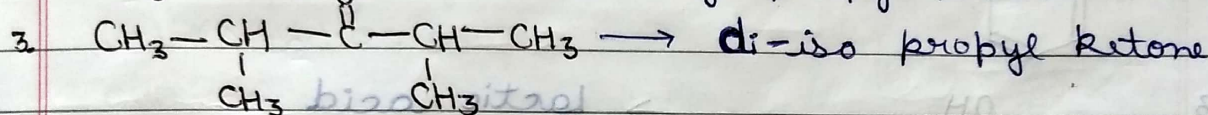
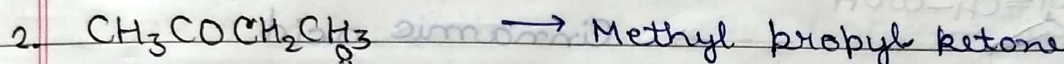
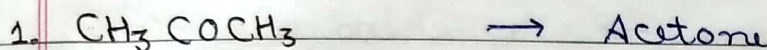
6. $\text{CH}_2=\text{CH}-\text{CHO} \rightarrow$ Acrolein

7.  $\rightarrow$ Benzaldehyde

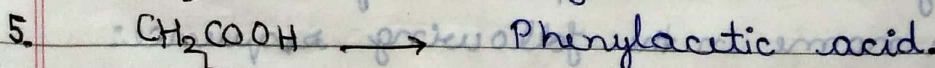
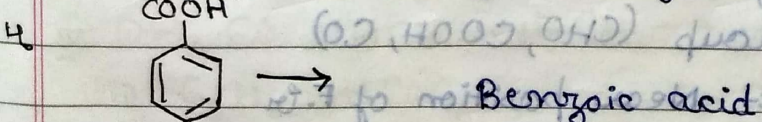
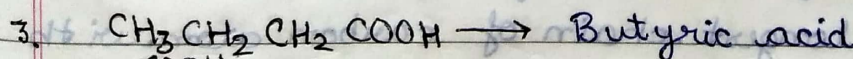
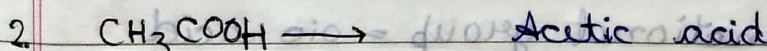
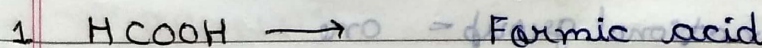
8.  $\rightarrow$ Phthalaldehyde

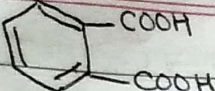
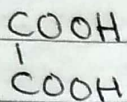
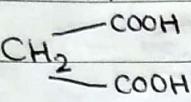
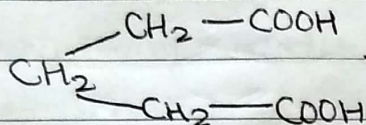
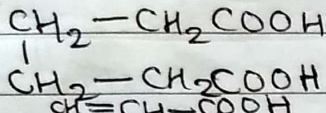
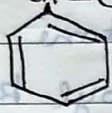
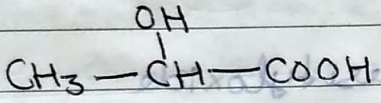
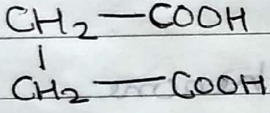


Common names of ketones



Common name of carboxylic acid



6.  $\rightarrow$ Phthalic acid
7.  $\rightarrow$ Tere-phthalic acid
8.  $\rightarrow$ Oxalic acid
9.  $\rightarrow$ Melanic acid
10.  $\rightarrow$ Truxetic acid
11.  $\rightarrow$ Adipic acid
12.  $\rightarrow$ Cinnamic acid
13.  $\rightarrow$ Lactic acid
14.  $\rightarrow$ Succinic acid

Fatty acid

Higher member of aliphatic carboxylic acid [C_{12} to C_{18}] are known as fatty acid.

I.U.P.A.C nomenclature of aldehyde, ketone and COOH

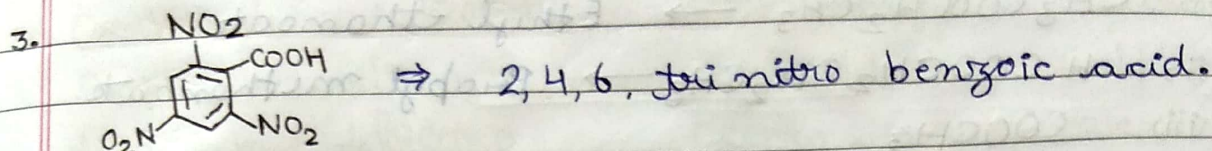
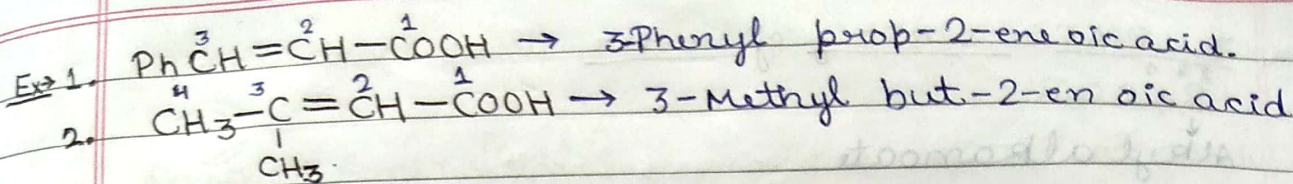
$\text{CHO} \Rightarrow$ As a functional group = al

$\text{CO} \Rightarrow$ As a functional group = one

$\text{COOH} \Rightarrow$ As a functional group = oic acid

1. Select the longest chain of carbon atom with functional group (CHO , COOH , CO)
2. Numbering order:- Near position of F.G
3. Write the name in the following sequence:

Side chain with + no. of carbon atom + types of bond between position and alphabetically in selected chain Carbon atom + F.G



** If CHO, COOH, CN, CONH₂, COCl group are directly bonded with ring or successive carbon atom of open chain then the name of compound is written in the form of alkane and name of these group, write in the last of the name as follows:-

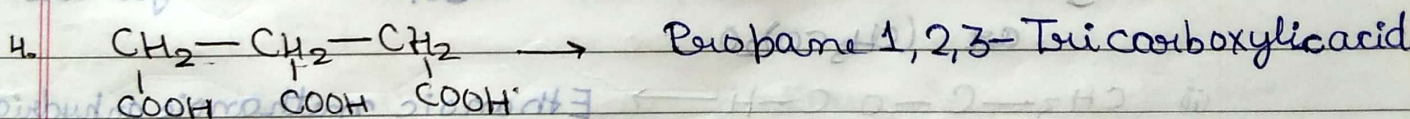
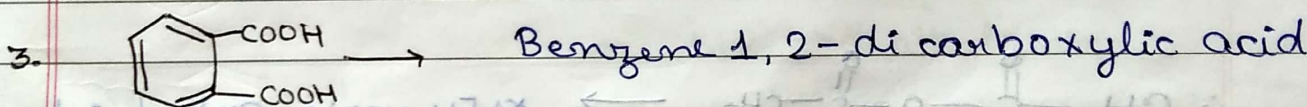
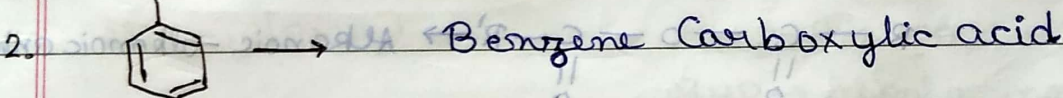
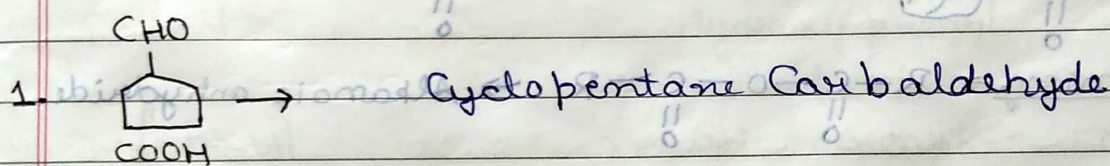
CHO $\rightarrow$ Carbaldehyde

CONH₂ $\rightarrow$ Carbamide

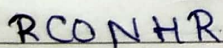
COOH $\rightarrow$ Carboxylic acid

COCl $\rightarrow$ Carbonyl chloride

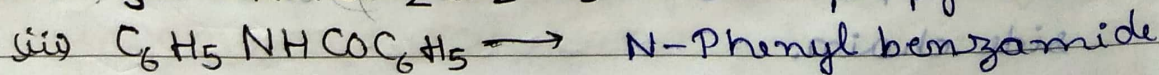
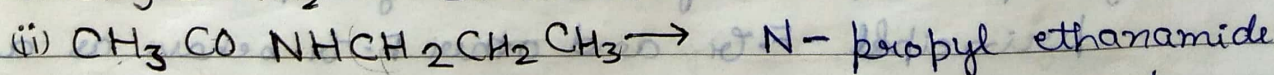
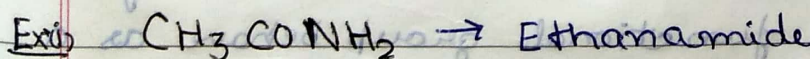
CN $\rightarrow$ Carbonitrile

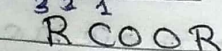


I.U.P.A.C naming of Amide

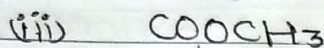
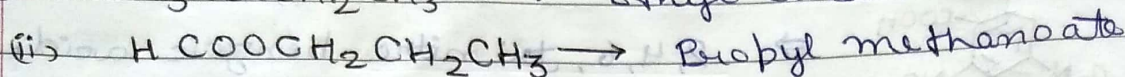
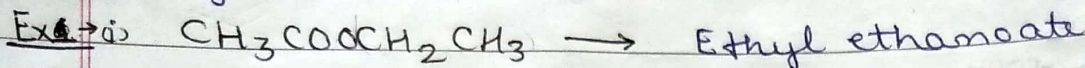


$\nwarrow$
N-alkyl alkanamide



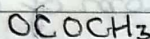
I.U.P.A.C naming of ester

Alkyl alkanoate

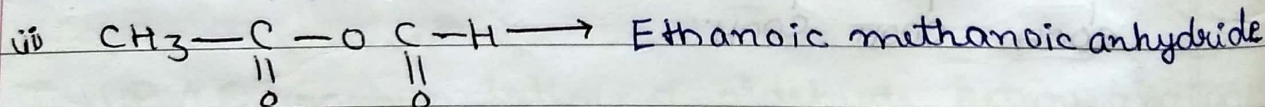
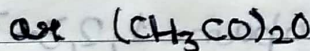
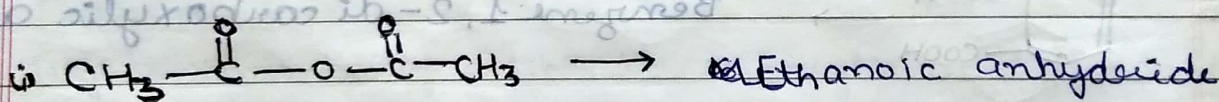
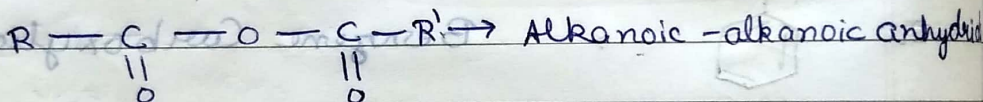
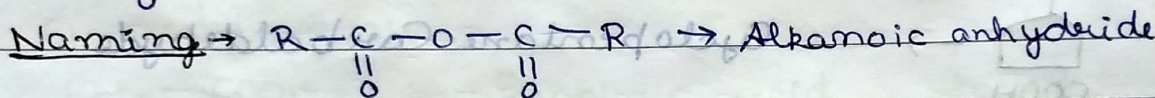
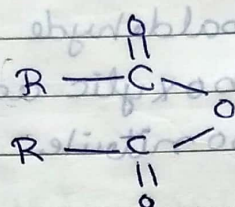
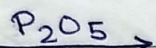
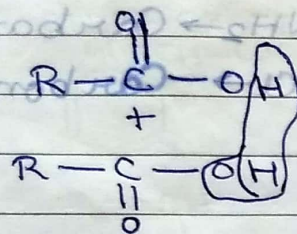


Methyl benzoate

(iv)



Phenyl ethanoate

Acid AnhydrideI.U.P.A.C nomenclature of polyfunctional group containing

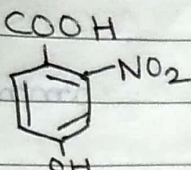
If a compound contains more than one functional group then one functional group behave as a principal F.G. and other F.G. behave as a side chain.

The order of preference of principle F.G. are as follows:-

Order of preference	Functional group	As a side chain	As a principle F.G.
1.	Salts of Amines $[R_4N^+X^-]$	—	ammonium halide
2.	Carboxylic acid $[RCOOH]$	$COOH \rightarrow$ Carboxy	oic acid
3.	Sulphonic acid $[RSO_3H]$	$SO_3H \rightarrow$ sulpho	sulphonic acid
4.	Acid Anhydride $[(RCO)_2O]$	$OCOCH_3 \rightarrow$ Acetoxy	oic anhydride
5.	Ester $[RCOOR]$	$COOR \rightarrow$ Alkoxy carbonyl	oate
6.	Acid chloride $[RCOCl]$	$COCl \rightarrow$ Chloro carbonyl	oyl chloride
7.	Acid amide $[RCONH_2]$	$CONH_2 \rightarrow$ Carbonyl	amide
8.	Nitrile $[RCN]$	$CN \rightarrow$ Cyano	nitrile
9.	Aldehyde $[RCHO]$	$CHO \rightarrow$ Formyl	al
		$O \rightarrow (oxo)$	
10.	Ketone $[RCOR]$	$O \rightarrow$ oxo or keto	one
11.	Alcohol $[ROH]$	$OH \rightarrow$ Hydroxy	ol
12.	Phenol	Hydroxy phenyl with position	Phenol
13.	Thiol $[RSH]$	$SH \rightarrow$ mercapto	Thiol
14.	Amines $[RNH_2]$	$NH_2 \rightarrow$ amino	
		$NHR \rightarrow$ alkyl amino	Amine
		$NR_2 \rightarrow$ di alkyl amino	
15.	Alkene $[R=]$	—	—
16.	Alkyne $[R\equiv]$	—	—
17.	Haloalkane $[RX]$	$F \rightarrow$ Fluoro	—
		$Cl \rightarrow$ Chloro	—
		$Br \rightarrow$ Bromo	—
		$I \rightarrow$ Iodo	—
18.	Nitroalkane $[RNO_2]$	$NO_2 \rightarrow$ Nitro	—

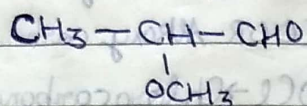
1. Write the I.U.P.A.C name of the following compound:
- (i) $CH_3COCH_2CH_2COOCH_3 \rightarrow$ Methyl-4-oxopentanoate.
- (ii) $CH_3-\underset{\substack{| \\ OH}}{CH}-\underset{\substack{|| \\ CH_2}}{C}-CH_2-COOH \rightarrow$ 4-Hydroxy-3-methylenepentanoic acid

3. $\text{PhCOPh} \rightarrow$ 1,1-diphenyl methanone

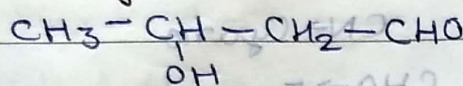
4.  $\rightarrow$ 4-hydroxy-2-nitro benzoic acid.

5. Draw Structure

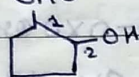
i. 2-Methoxy propionaldehyde



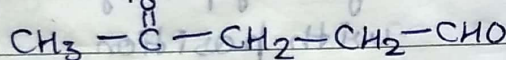
ii. 3-hydroxy butanaldehyde



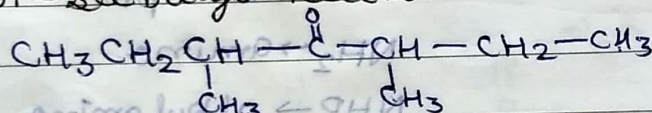
iii. 2-hydroxy cyclopentane carbaldehyde



iv. 4-oxo-pentanal



v. Di-secbutyl ketone



Carboxylic acid (Fatty acid)

Higher member of aliphatic carboxylic acid $[\text{C}_{12} \text{ to } \text{C}_{18}]$ are known as fatty acid.

Isomerism in Carboxylic acid

1. Chain isomers

2. Position isomers

3. Functional group isomers.

* General formula:- $\text{C}_n\text{H}_{2n}\text{O}_2 \rightarrow$ Carboxylic acid and ester
In case of benzene ring $\rightarrow [\text{C}_6\text{H}_5 + \text{C}_n\text{H}_{2n-1}\text{O}_2]$

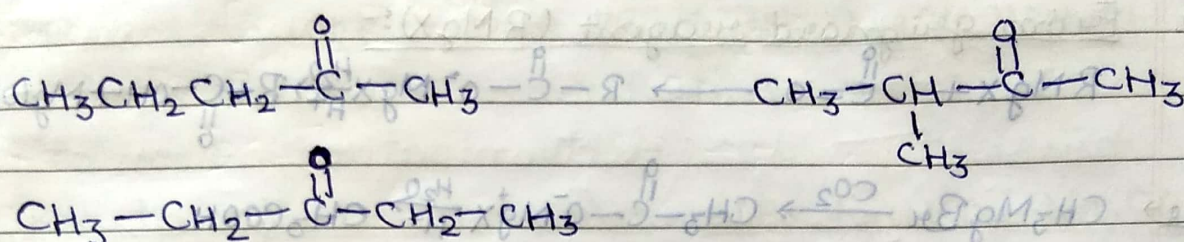
Aldehyde or Ketone

1. Chain isomers
2. Position isomers
3. Functional group isomers.

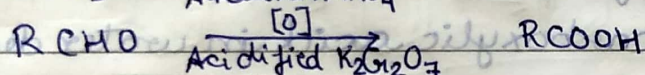
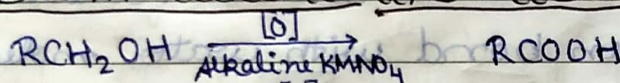
General formula:- $C_nH_{2n}O \rightarrow$ Aldehyde or Ketone

In case of benzene ring $\rightarrow [C_6H_5 + C_nH_{2n-1}]$

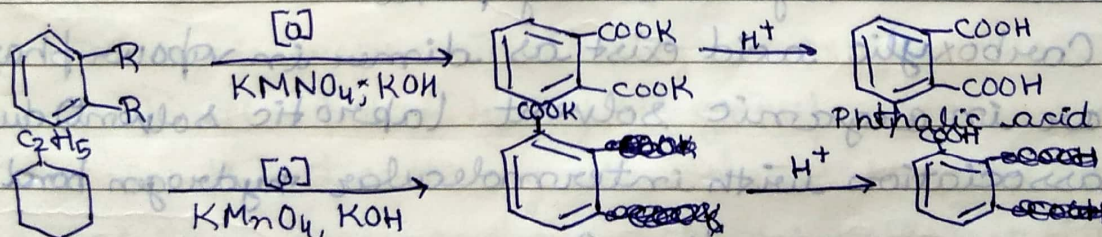
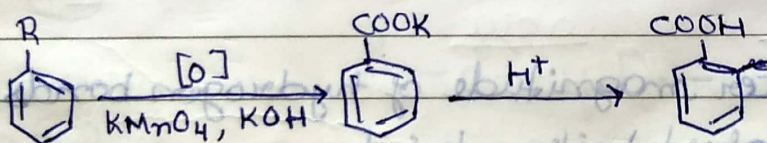
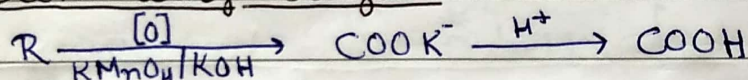
* Metamers (only ketone)

Preparation of carboxylic acid

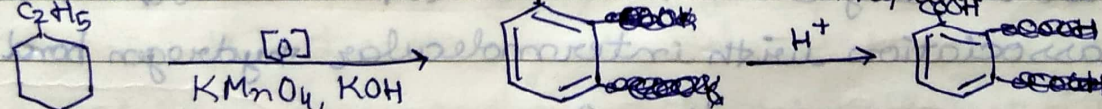
1. From alcohol and aldehydes



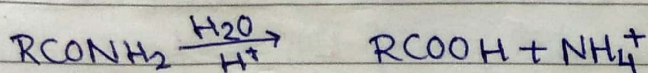
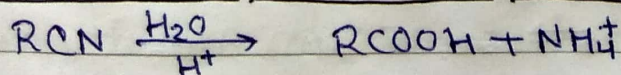
2. From alkyl benzene

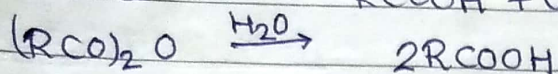
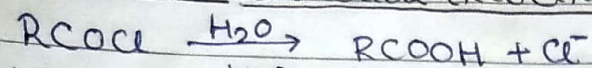
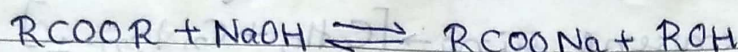
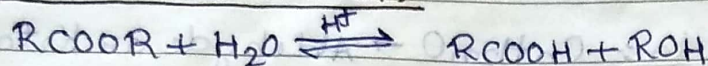
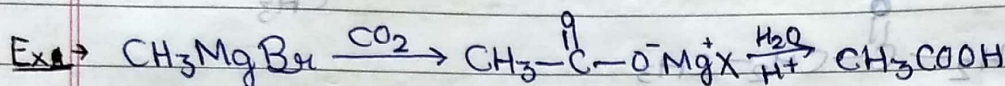
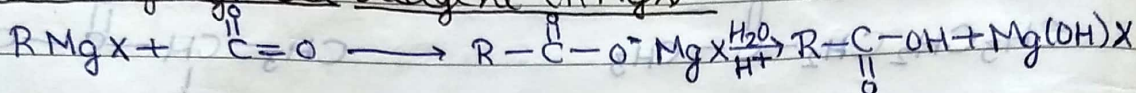


Ex $\rightarrow$



3. From Amide ($RCONH_2$) and nitrile (RCN):-



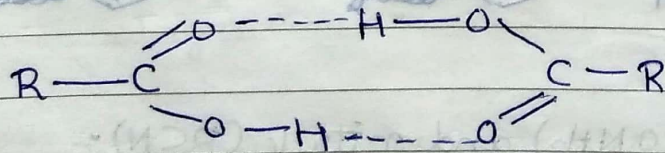
4. From acid chloride (RCOCl) and acid anhydride5. From ester (RCOOR)6. From grignard reagent (RMgX):-Physical properties of carboxylic acid

1. Solubility:- Carboxylic acid are soluble in water due to formation of hydrogen bond with water molecule. The solubility of carboxylic acid in water decreases with increase in size of alkyl group which is hydrophobic.

2. Boiling point

Due to greater magnitude of hydrogen bonds, carboxylic acid have highest boiling point.

Carboxylic acid exist as dimer in vapour phase or in organic solvent (aprotic solvent) due to association with intermolecular hydrogen bond.

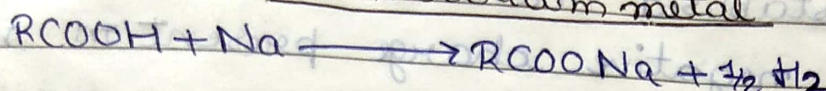


Chemical properties of carboxylic acid

(A) Reaction involving cleavage of O-H bond

These reaction explain the acidic nature of carboxylic acid. Some important reactions:-

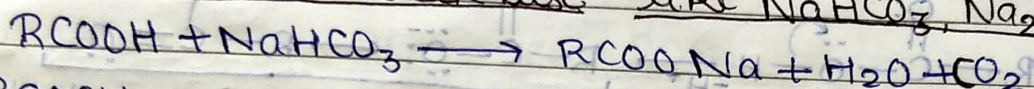
(i) Reaction with sodium metal



(ii) Reaction with ^{strong} base like NaOH, KOH etc

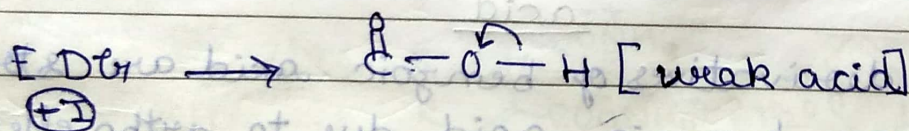
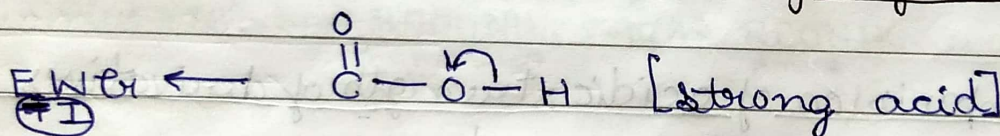


(iv) Reaction with weak base like NaHCO₃, Na₂CO₃ etc.



RCOOH react with weak base due to release CO₂ gas. This reaction is used to detect the presence of carboxylic group with organic compounds.

Comparison of acidic strength of RCOOH



EDG increase e^- density on oxygen atom. As a result the polarity of OH group decrease and hence the tendency to release H^+ ion decrease. Therefore, the compound becomes weak acid.

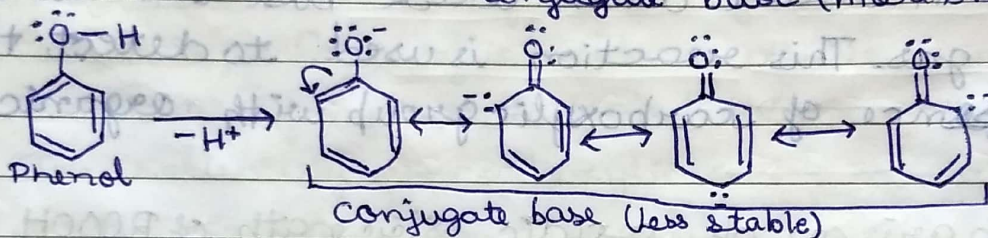
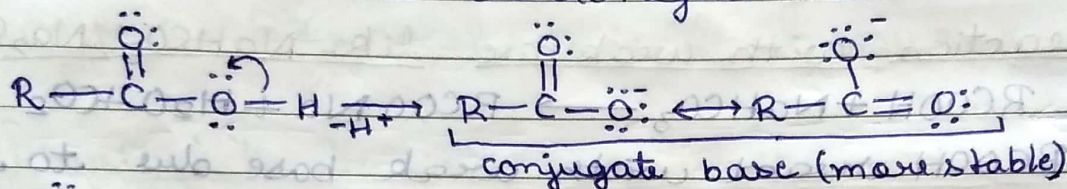
EWG decrease e^- density on oxygen atom. As a result the OH bond becomes more polar and hence the tendency to donate H^+ ion increase. Therefore, the compounds become

1. strong acid.

NC.E.R.T Q. 22

Carboxylic acid are stronger acid than phenols. This is because the conjugate base of carboxylic acid are stabilised more due to resonance. In which negative charge present on more electronegative oxygen.

Whereas the conjugate base of phenols are less stable due to resonance in which negative charge present on less electronegative carbon atom.



Comparison of acidic strength of derivatives of benzoic acid

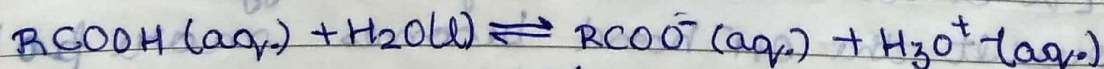
Ortho derivatives of benzoic acid are stronger acid than benzoic acid due to ortho effect.

In case of other derivatives of benzoic acid, acidic nature depends upon nature of group.

-I or -R $\Rightarrow$ stronger acid than benzoic acid.

+I or +R $\Rightarrow$ Weak acid than benzoic acid.

Hints:- Consider a weak acid.

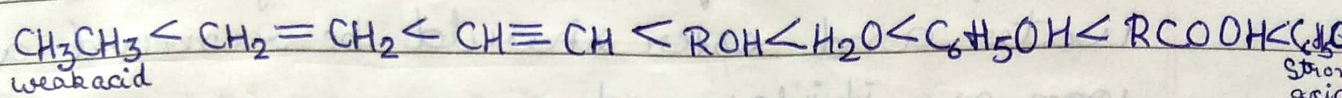


$$\text{Dissociation constant (K}_a\text{)} = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

$$* \quad pK_a = -\log K_a$$

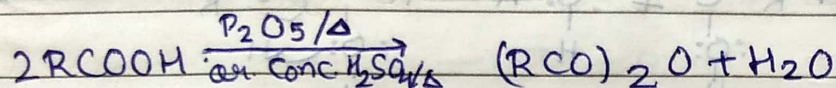
* Low value of pK_a means strong acid.

Comparison of acidic strength of different types of Acid

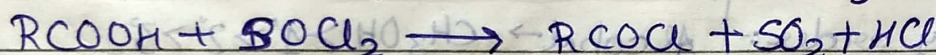
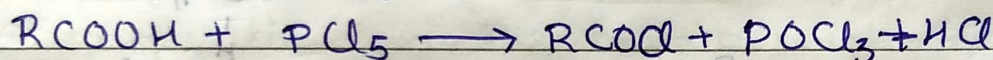
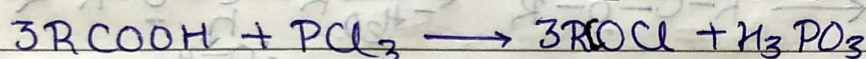


(B) Reaction involving cleavage of C-OH bond

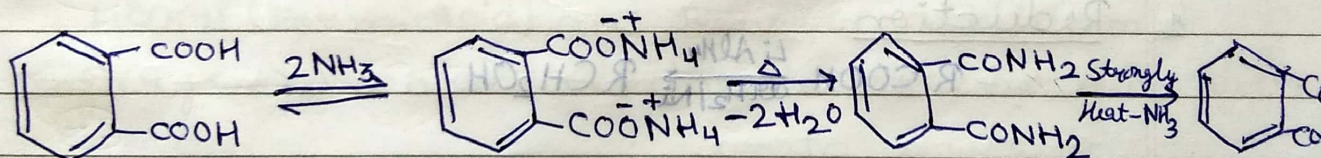
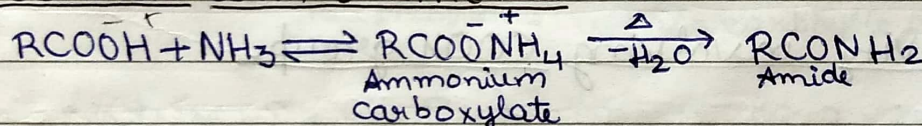
1. Formation of Anhydride



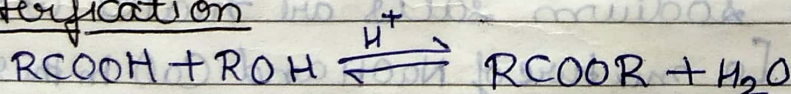
2. Reaction with PCl_3 , PCl_5 , SOCl_2



3. Reaction with Ammonia

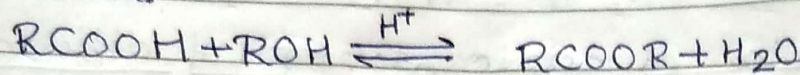


4. Esterification



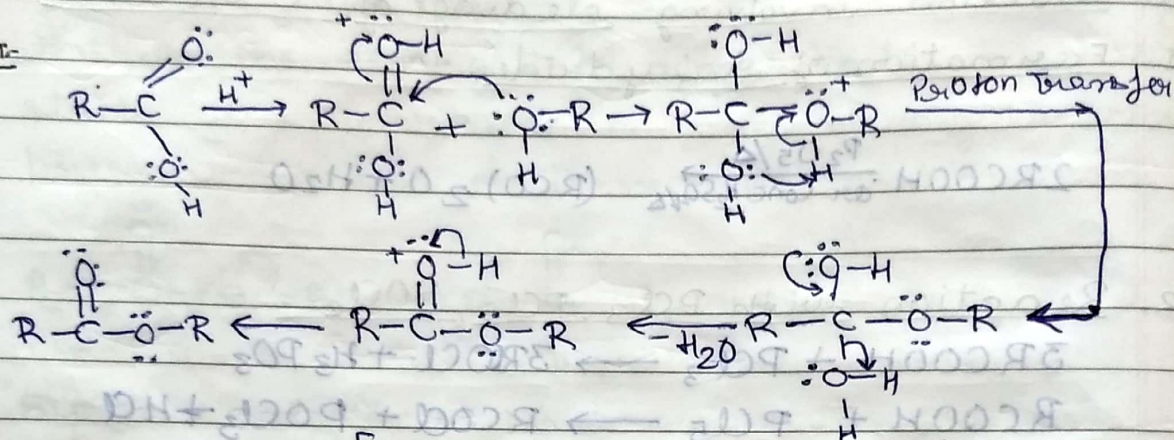
Q1 During the preparation of ester from carboxylic acid and alcohol in the presence of acid catalyst the water or the ester should be removed as soon as it is formed.

Formation of ester from acid and alcohol in the presence of acid catalyst is a reversible reaction.



To shift the equilibrium in forward direction water and ester should be removed as soon as it is formed.

Mechanism:-

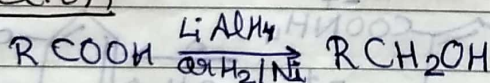


Activity order:-

- Alcohol $\rightarrow \text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ$
- Acid $\rightarrow \text{HCOOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{COOH}$

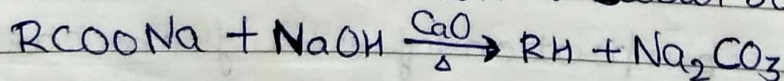
(C) Reactivity involving COOH group.

1. Reduction



**** 2. Decarboxylation

Carboxylic acid lose CO_2 to form hydrocarbon when their sodium salts are heated with soda lime [a mixture of NaOH and CaO in the ratio of 3:1]. This reaction is known as **Decarboxylation**.



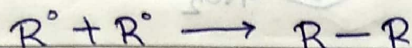
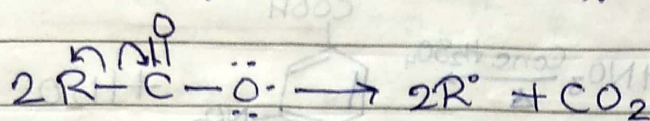
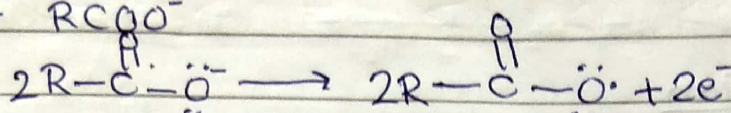
** 3. Kolbe electrolysis

Sodium or potassium salts of carboxylic acid

undergo decarboxylation on electrolysis of their aqueous solution and form hydrocarbon having twice the no. of carbon atom in alkyl group of the acid. This reaction is known as Kolbe's electrolysis.

$$2\text{RCOOK} + 2\text{H}_2\text{O} \xrightarrow{\text{Electrolysis}} \text{R-R} + 2\text{KOH} + \text{H}_2 + 2\text{CO}_2$$

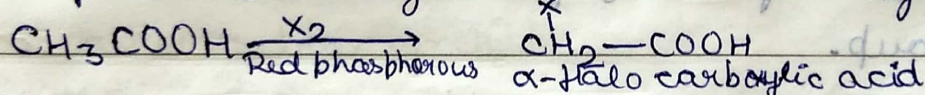
At anode:- RCOO^-



At cathode:- $2\text{H}_2\text{O} \longrightarrow \text{H}_2 + 2\text{OH}^-$

4. HVZ (Hell-Volhard Zelin sky) reaction

Carboxylic acids having α hydrogen are halogenated at α position on treatment with chlorine or bromine in the presence of small amount of red phosphorous to give α -halo carboxylic acid.



(where $\text{X} = \text{Cl}, \text{Br}$)

* HCOOH (Formic acid) and Benzoic acid do not undergo HVZ reaction due to absence of α -hydrogen.

* Convert Propanoic acid ^{into} lactic acid

$$\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{Red P}]{\text{Cl}_2} \text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{COOH} \xrightarrow[\text{KCl}]{\text{KOH (alc.)}} \text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{COOH}$$

lactic acid

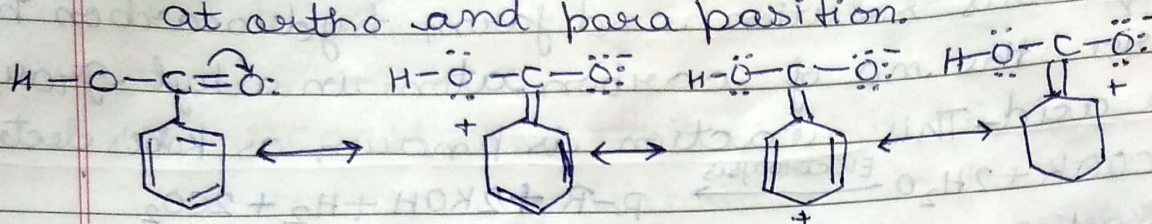
2. SE (Substitution electrophilic reaction)

Benzoic acid is less reactive towards SE reaction.

This is because carboxyl group is a deactivating group due to its $-R$ effect.

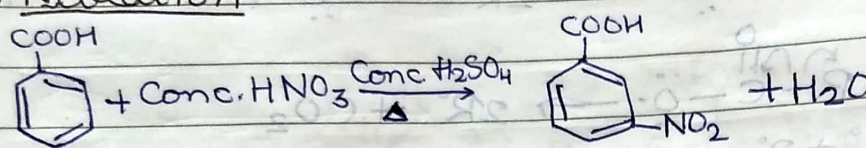
In benzoic acid, substitution nucleophilic reaction occurs at meta position due to $(+R)$ effect of carboxylate.

group which decrease electron density more at ortho and para position.

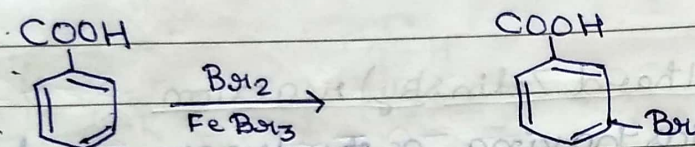


Example →

(i) Nitration



(ii) Bromination



* Benzoic acid does not undergo Friedel-Crafts alkylation because the carboxyl group is deactivating and the catalyst $AlCl_3$ gets bonded to the carboxyl group.

• Which acid of each pair is stronger acid?

1. CH_3COOH or CH_2FCOOH

CH_2FCOOH is a strong acid due to $-I$ effect of fluorine atom.

2. CH_2FCOOH or $CH_2ClCOOH$

CH_2FCOOH is a strong acid due to more $-I$ effect of fluorine atom.

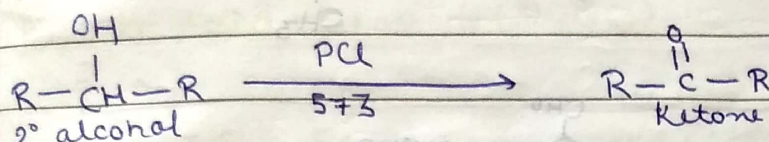
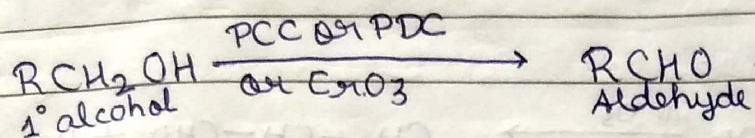
3. $CH_2FCH_2CH_2CO_2H$ or $CH_2CH_2FCH_2CO_2H$

$CH_2CH_2FCH_2CO_2H$ is a strong acid, because the magnitude of $-I$ effect of 'F' is more due to near position of 'F' atoms.

Preparation of aldehyde and ketone

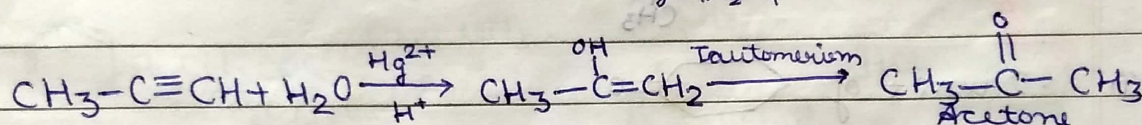
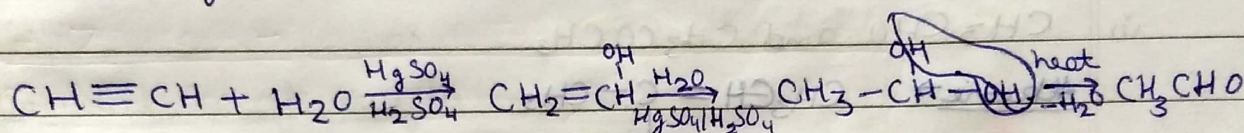
* Both

1. From alcohols

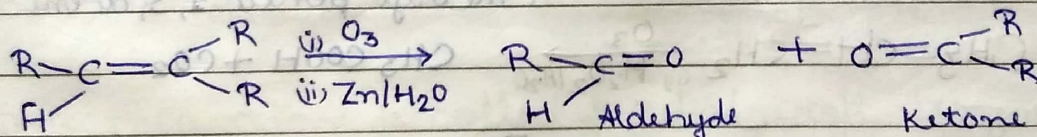
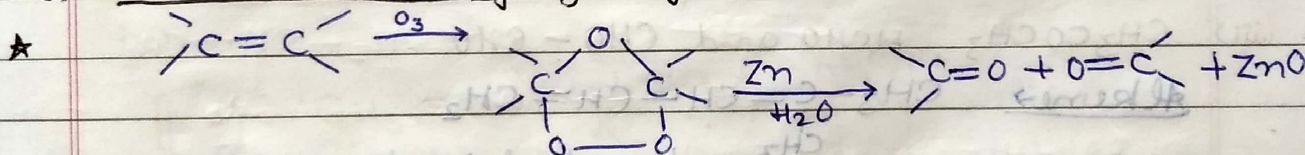


2. By hydration of alkynes ($\equiv$):-

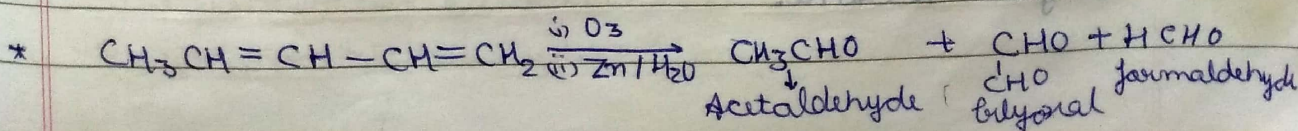
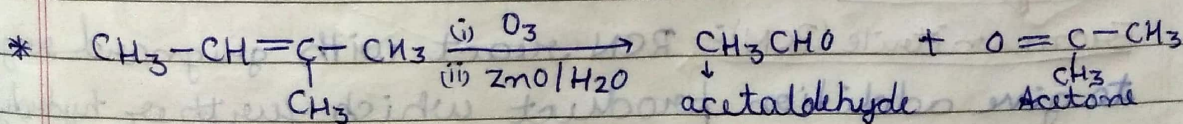
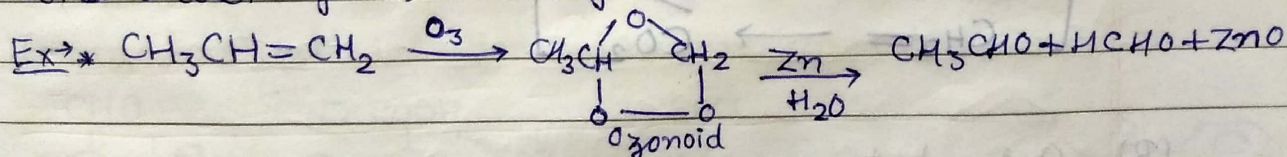
According to Markovnikov's rule only one water molecule,

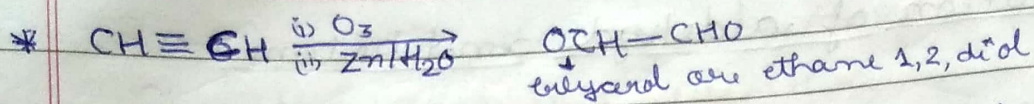


3. From alkenes by ozonolysis

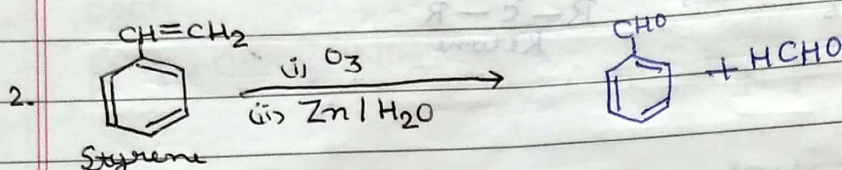
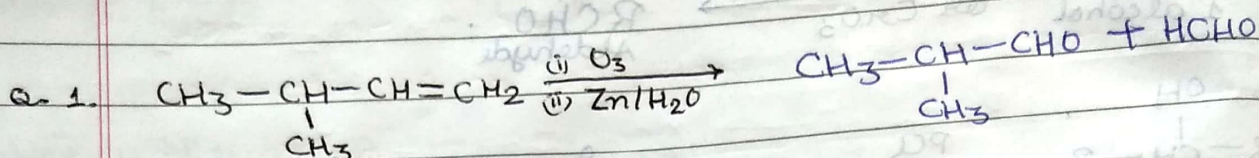


ozonolysis of alkene followed by reaction with Zn dust and water gives aldehyde or ketone or both.

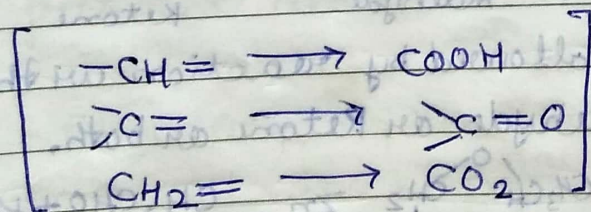
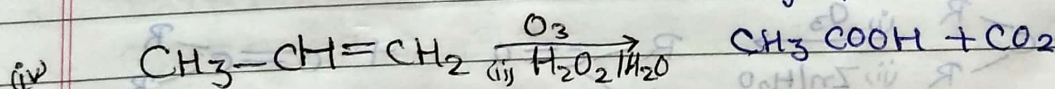
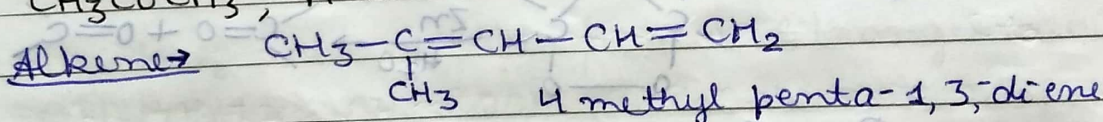
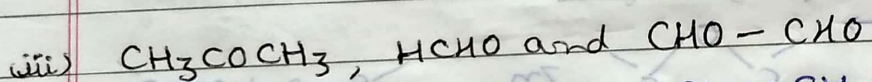
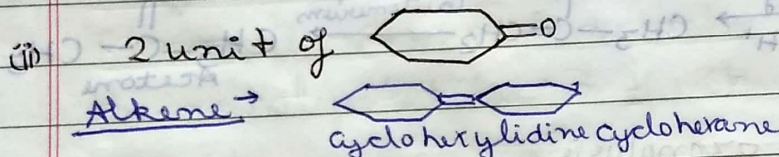
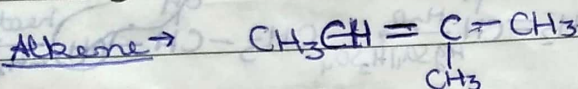
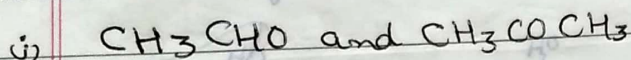




This reaction detect the position of double bond in alkene.

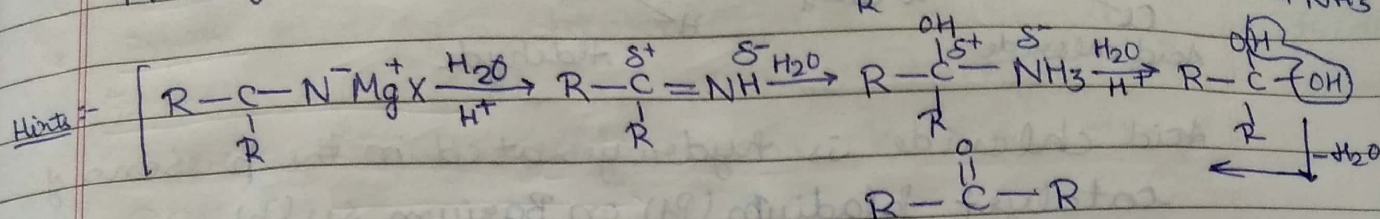
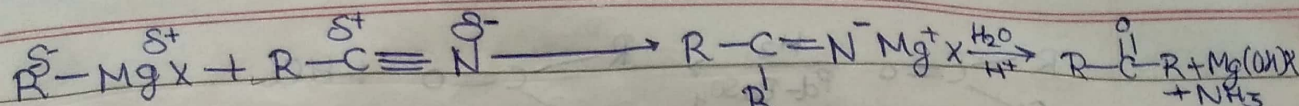


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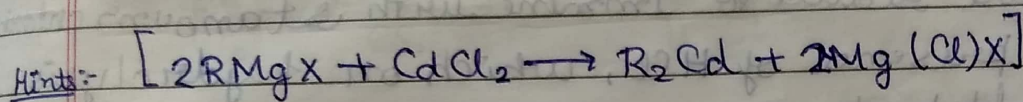
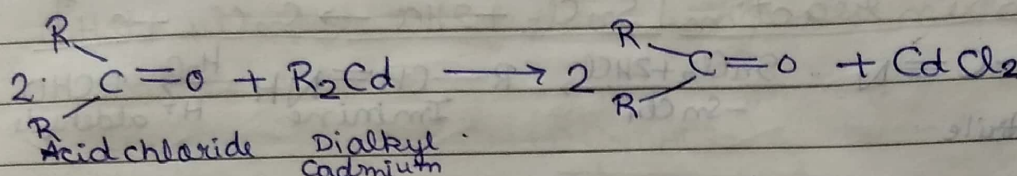


(B) Only ketone

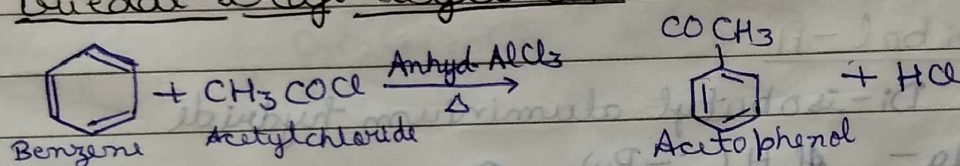
1. From nitrile (RCN): RCN react with grignard reagent to give addition product which further hydrolyse to give ketone.



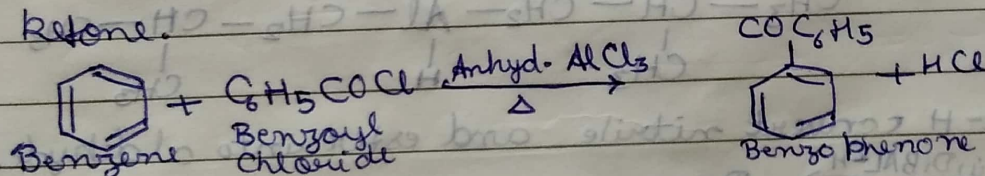
2. Emm Acid chloride (RCOCl)



3. Friedal craft acylation



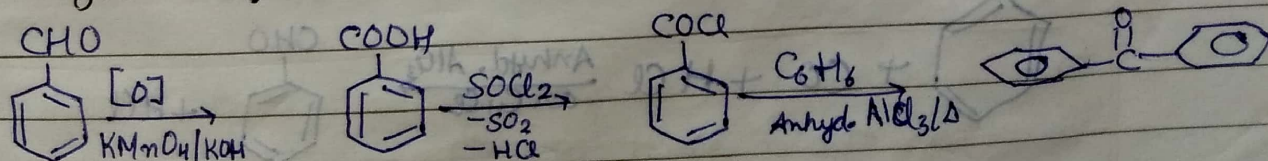
This reaction is used for the preparation of aromatic ketone.



This reaction is called friedal craft benzoylation.

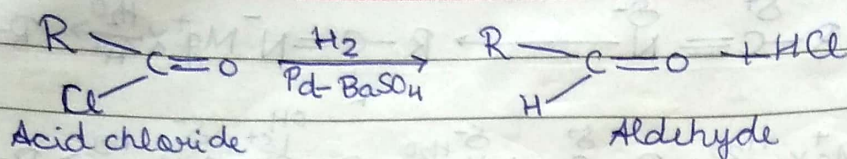
1. Convert:-

(a) Benzaldehyde into Benzophenone

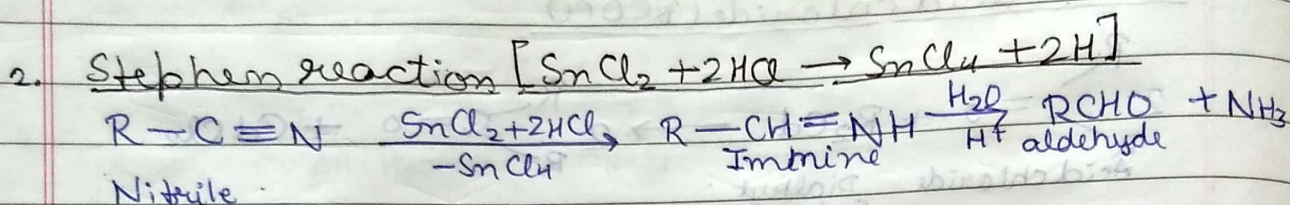


(c) Only Aldehyde

1. Rosenmund reduction



Acid chloride is hydrogenated in the presence of catalyst platinum (Pd) on Barium sulphate. This reaction is called Rosenmund reaction.



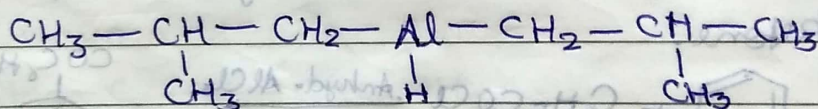
Nitrile are reduced to Imine with stannous chloride in the presence of HCl, which on hydrolysis give aldehyde.

3. By Dibal-H

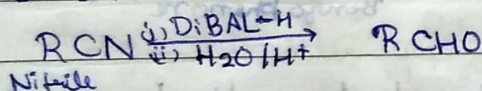
Name- Di-isobutyl aluminium hydride

Formula- $\text{AlH}(\text{i-Bu})_2$

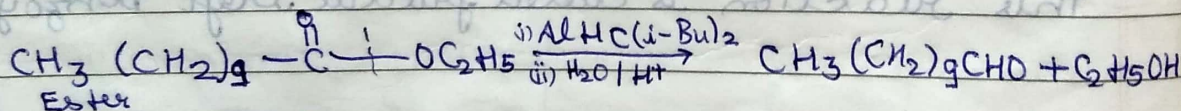
OR



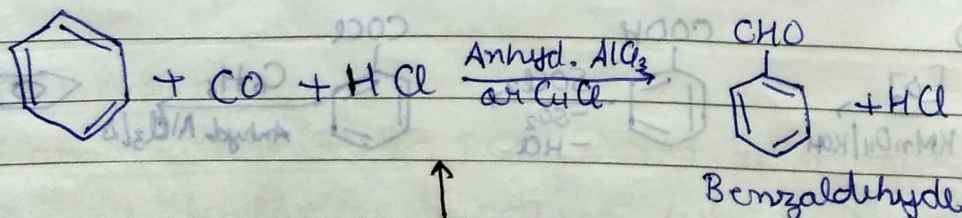
DiBAL-H convert nitrile and ester into aldehyde.



Nitrile



4. From Benzene and its derivatives

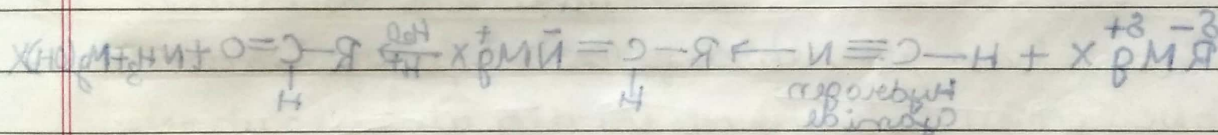
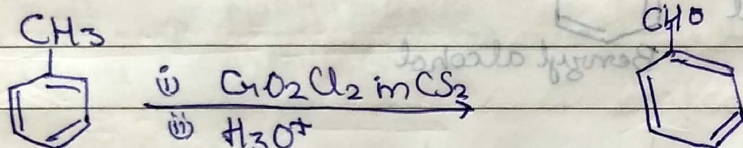
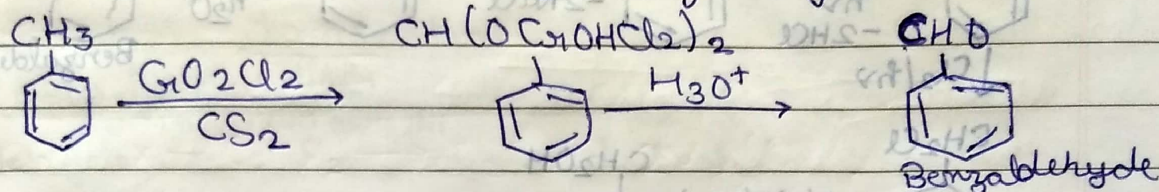


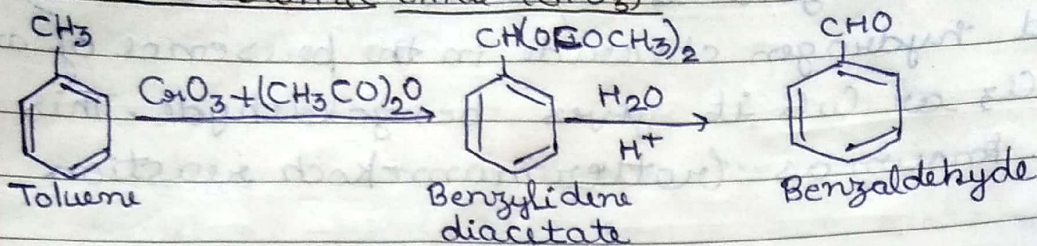
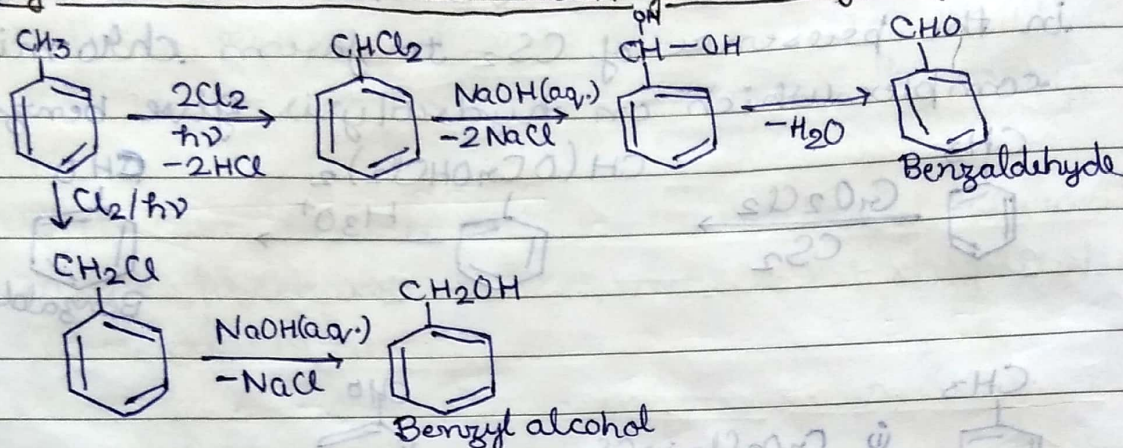
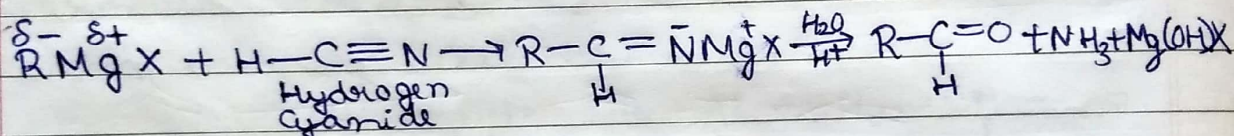
(a) Catterman-Koch Reaction → (or Formylation)

When Benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydride $AlCl_3$ or $CuCl$ it gives benzaldehyde. This reaction is known as Gattermann-Koch reaction.

(b) Etard reaction

Toluene reacts with chromic chloride (CrO_2Cl_2) in the presence of CS_2 to form chromium complex which on hydrolysis give benzaldehyde.



C. From chromic oxide (CrO_3)D. By side chain chlorination followed by hydrolysisE. From grignard reagentPhysical properties of aldehyde and ketone

1. Solubility:- Aldehyde and ketone are soluble in water due to formation of H-bond with molecule. The solubility of compound in water decrease with increase in size of alkyl group which is hydrophobic.

2. Boiling point

The boiling points of aldehyde and ketone are higher than that of alkane. This is because aldehyde and ketone are polar group and hence dipole-dipole interaction are present in them whereas alkanes are non-polar and

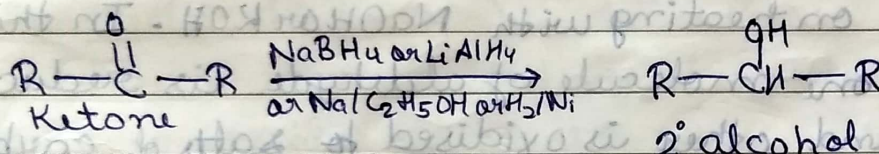
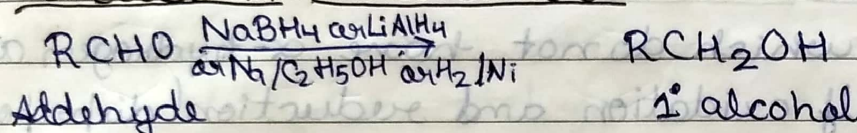
weak vander wall force (dispersion force) are present in them.

The boiling point of ketones are slightly higher than that of aldehydes. This is because ketones are more polar and hence the magnitude of dipole-dipole interaction is higher in them.

Chemical properties of aldehyde or ketone

(A) Reduction

1. Reduction to alcohols

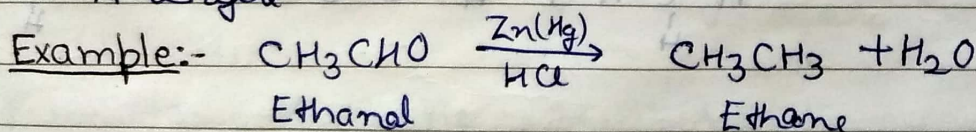
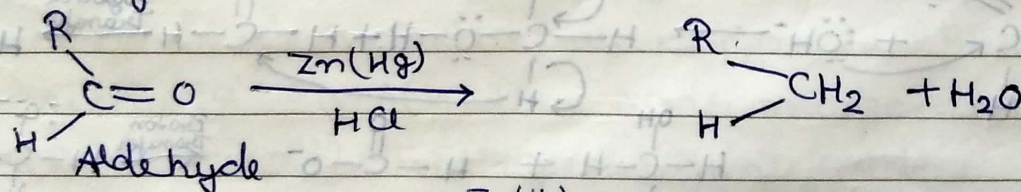


2. Reduction to alkane

Carbonyl group ($\text{C}=\text{O}$) of aldehyde and ketone are reduced to alkane in the following reaction:-

** Clemmensen Reduction

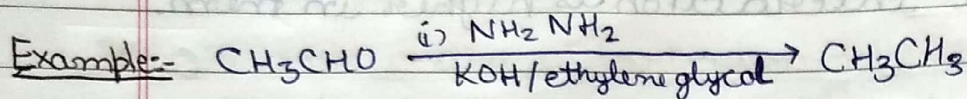
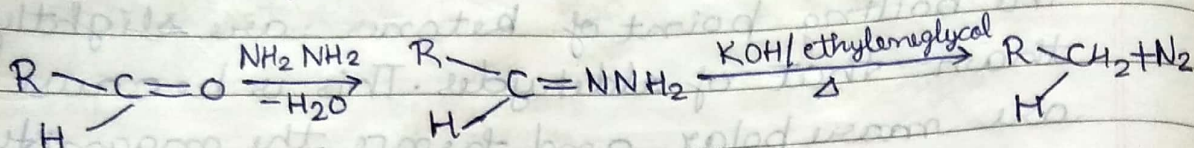
Carbonyl group of aldehyde and ketone are reduced to methylene (CH_2) group on treatment with Zinc Amalgam and conc. HCl.



** Wolff Kishner reduction

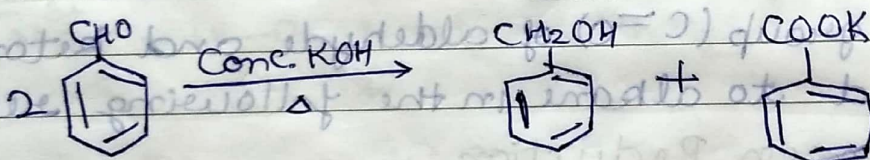
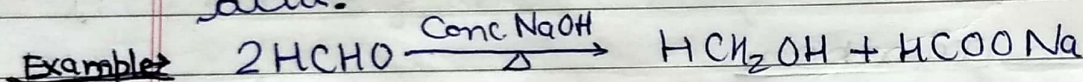
Carbonyl group of aldehyde or ketone is reduced to CH_2 group on treatment with hydrazine

followed by heating with KOH in the presence of ethylene glycol.

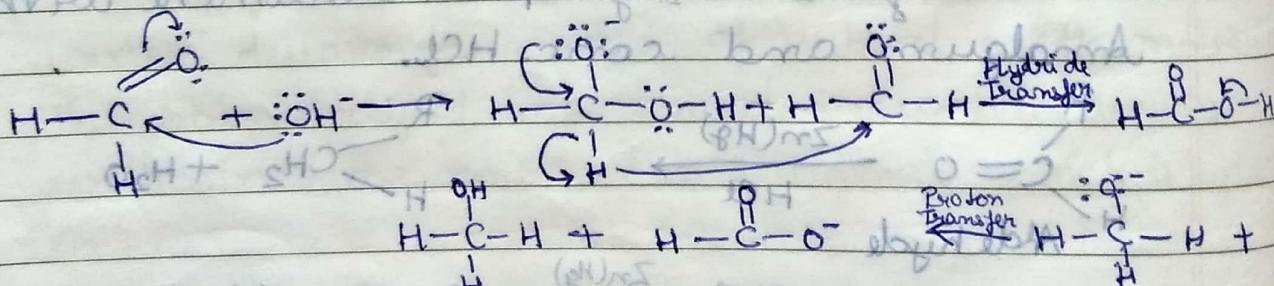


* * (B) Cannizzaro's reaction

Aldehydes which do not have α -hydrogen atom undergo self oxidation and reduction (disproportionation) reaction on heating with NaOH or KOH. In this reaction one molecule of aldehyde is reduced to alcohol and other is oxidised to salts of carboxylic acid.



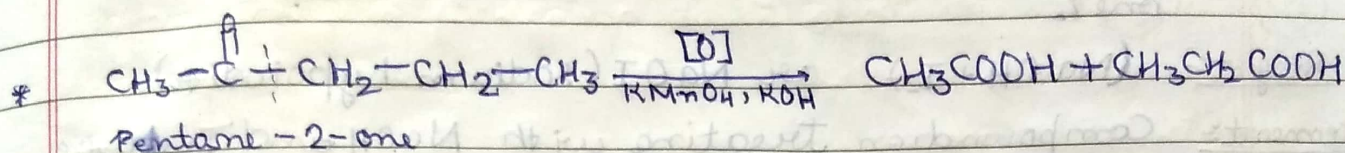
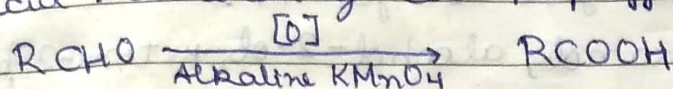
Mechanism of Cannizzaro's reaction



(C) Oxidation

- (i) oxidation by strong oxidising agent (Alkali KMnO_4 , Acidified $\text{K}_2\text{Cr}_2\text{O}_7$, H_2CrO_4 (chromic acid) or Conc. HNO_3)
- Aldehyde and ketones are oxidised by strong

oxidising agent. Aldehyde give only one carboxylic acid but ketone gives a mixture of carboxylic acid according to popoff's rule. Ex $\Rightarrow$

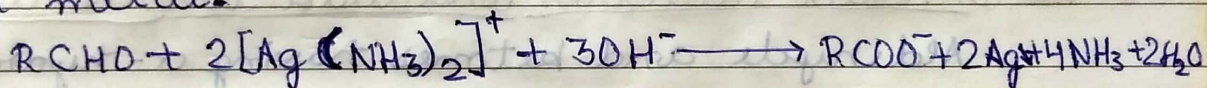


2. Oxidation by mild oxidising agent (Tollen's reagent, Fehling's reagent)

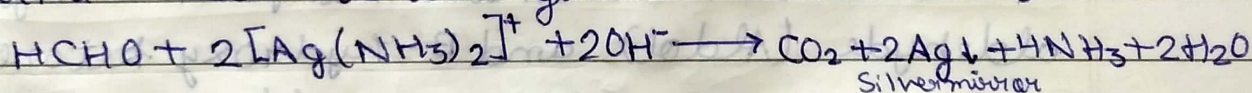
(i) Tollen's reagent:- Ammonia silver nitrate solution is known as Tollen's reagent. It is used to oxidise all aldehydes and formic acid.

Formula:- $[Ag(NH_3)_2]^+ + 3OH^-$ or Ag_2O

Silver mirror test:- Aldehyde reacts with Tollen's reagent to give a bright silver mirror or to produce a silver mirror due to formation of silver metal.



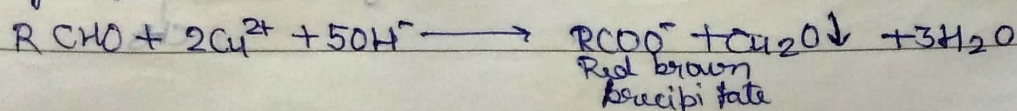
Formic acid is also give silver mirror test.



(ii) Fehling's reagent:- It is a mixture of 2 solution, Fehling solution 'A' and Fehling solution 'B'. Fehling solution 'A' is aqueous copper sulphate. Fehling solution 'B' is Alkaline sodium potassium Tartarate (Rochelle salt). Fehling reagent oxidise aliphatic aldehydes.

Formula:- ~~Aliphatic~~ $2Cu^{2+} + 5OH^-$

Fehling test:- Aliphatic aldehydes reacts with Fehling reagent to produce brown precipitate of Cu_2O .



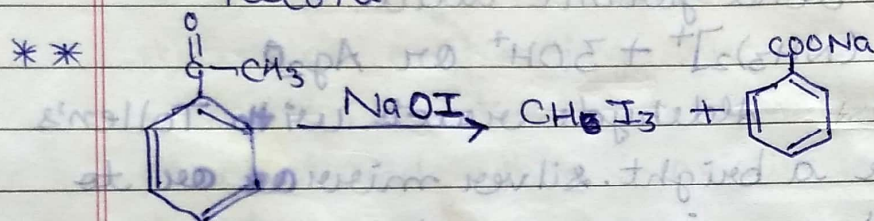
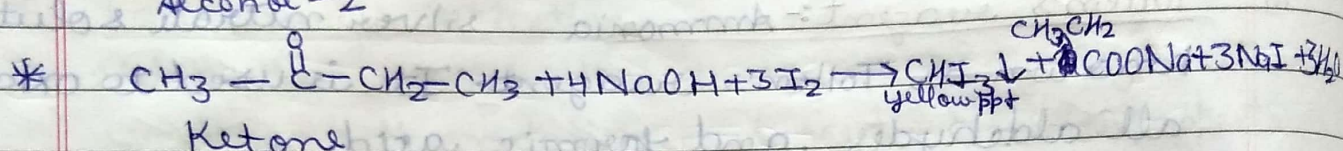
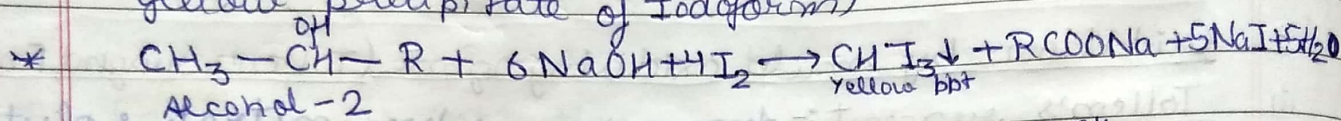
Iodoform test:-

Condition:- Compounds containing $(\text{CH}_3-\overset{\text{OH}}{\text{C}}-)$ part or (CH_3-CH) part give Iodoform test.

Ex Ethanal, Ethanol, alcohol-2-ol, ketone-2, propane-2-one.

Reagent:- $(\text{NaOH} + \text{I}_2)$ or NaOI (sodium hypoiodite)

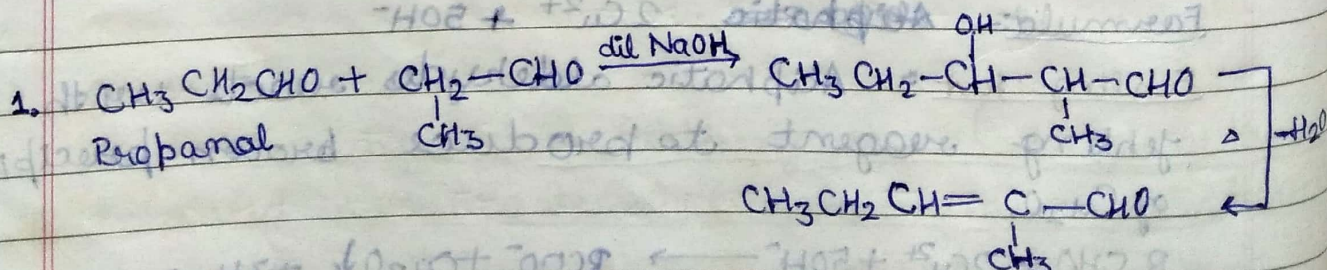
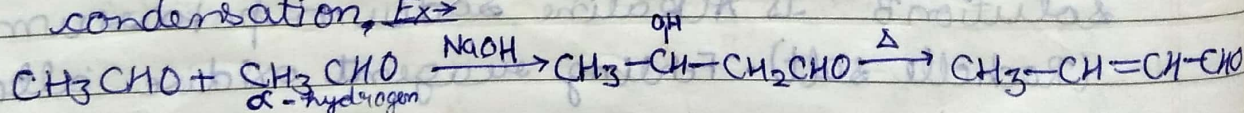
Statement:- Compound on treating with NaOH and I_2 to give yellow precipitate of Iodoform

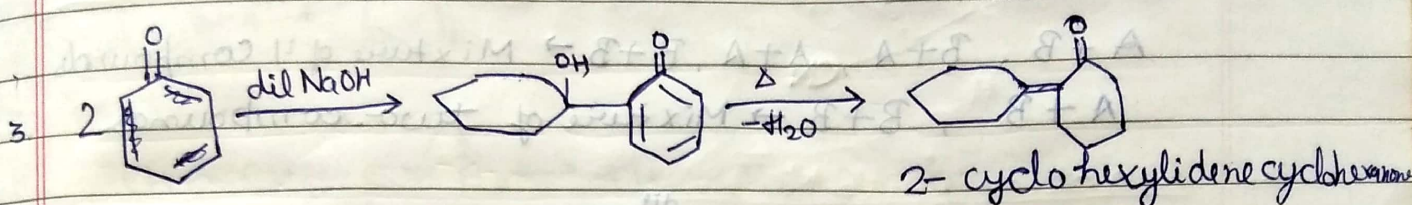
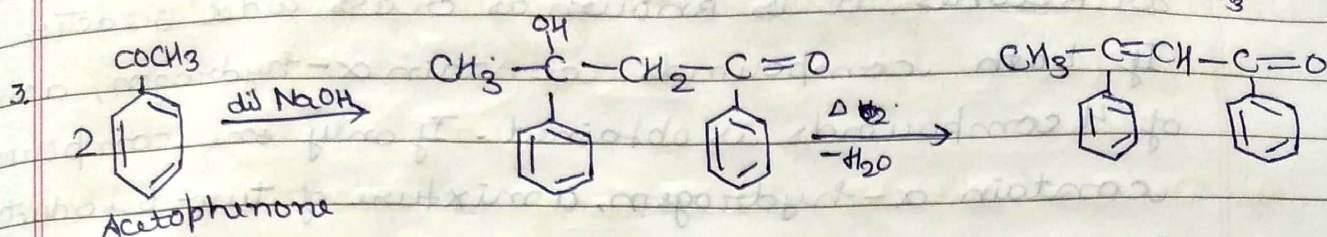
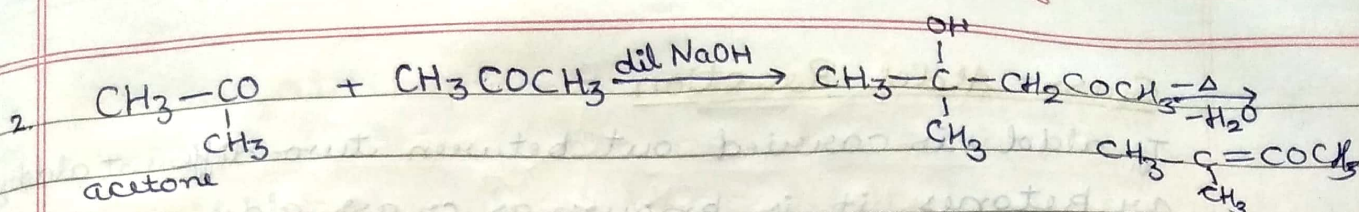


** ** (D) Aldol reaction and aldol condensation

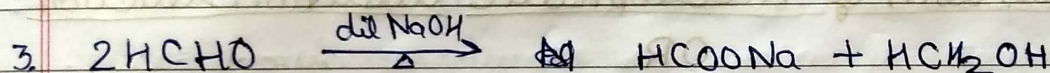
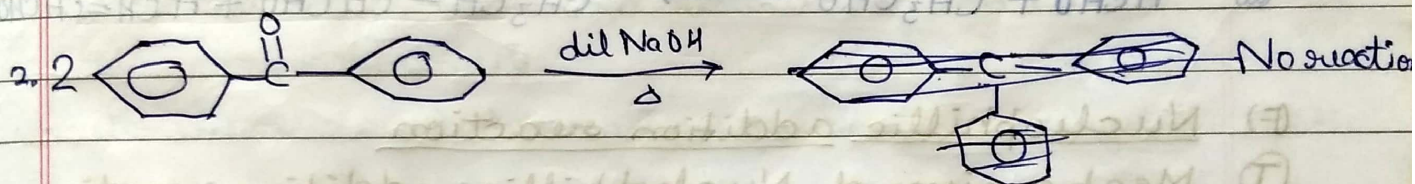
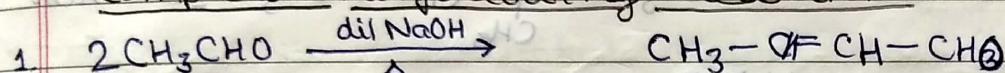
Aldehyde and ketones having α -hydrogen reacts with dilute NaOH and KOH to form β -hydroxy aldehyde (Aldol) and β -hydroxy ketone (ketol) respectively. This is known as aldol reaction.

Aldol and ketol lose water molecule to form α, β unsaturated aldehyde and ketone respectively. This reaction is known as aldol condensation, Ex



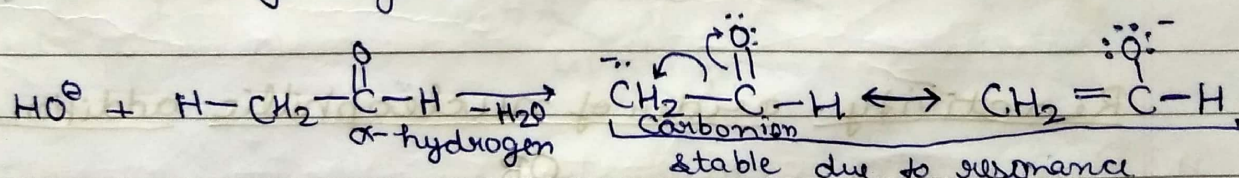


Complete the following reaction:-

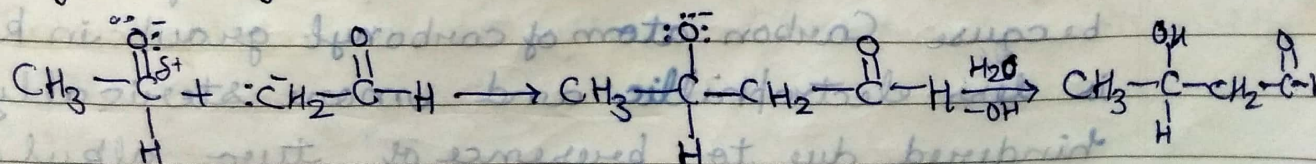


Mechanism of Aldol reaction

Step 1:- Formation of carbon ion which stabilise by resonance (α -hydrogen in aldehyde and ketone behave as acidic hydrogen)



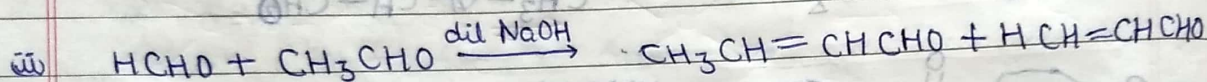
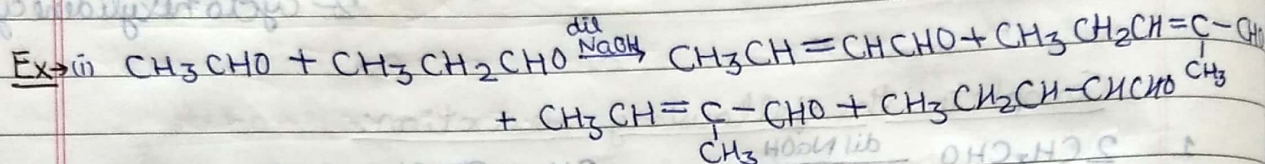
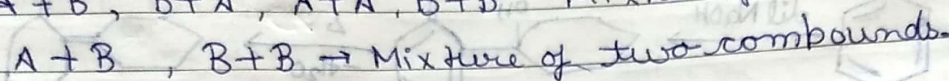
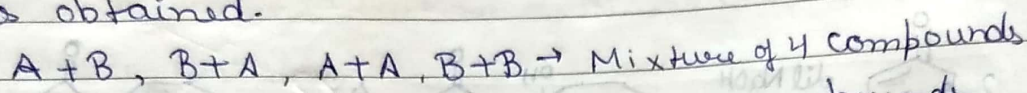
Step 2:- Nucleophilic attack of carbanion on other molecule of aldehyde or ketone.



Cross Aldol Reaction

If aldol is carried out between two different aldehydes or ketones, it is known as cross aldol reaction.

If both compounds contain α -hydrogen, a mixture of 4 compounds is obtained. If only one compound contains α -hydrogen, a mixture of two products is obtained.

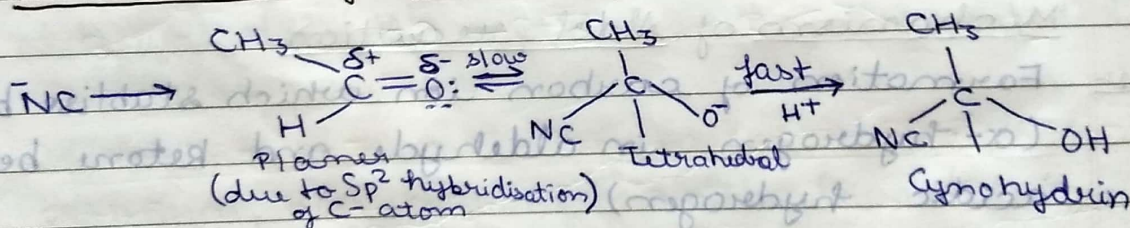


(F) Nucleophilic addition reaction

(I) Mechanism of Nucleophilic addition reaction

OR

Mechanism of addition of HCN on aldehyde or ketone



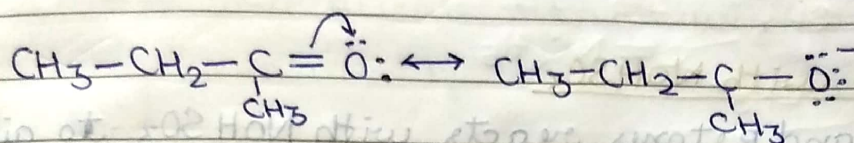
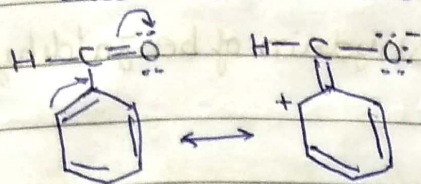
Reactivity order of nucleophilic addition reaction

OR

Reactivity order of the compounds towards addition

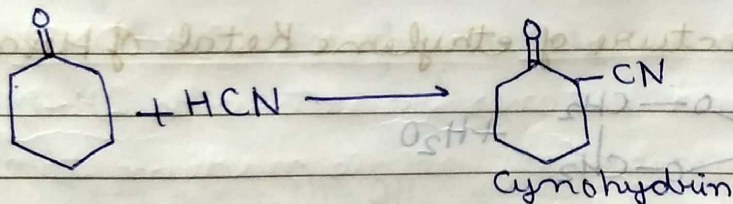
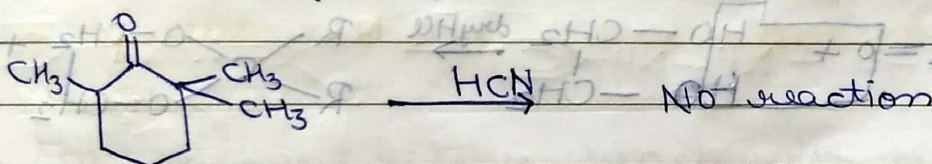
1. Ketones are less reactive than that of aldehydes because Carbon atom of carbonyl group in ketones is less electrophilic and more sterically hindered due to presence of two alkyl group.

2. Benzaldehyde is less reactive than that of propanal. This is because the carbon atom of Carbonyl group of benzaldehyde is less electrophilic than carbon atom of carbonyl group of propanal due to resonance.



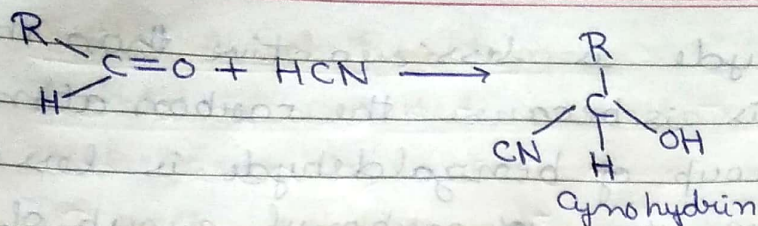
3. 2,2,6-trimethylcyclohexanone does not form cyanohydrin due to more crowding on carbon atom of carbonyl group.

Whereas cyclohexanone forms cyanohydrin with HCN due to less crowding on carbon atom of carbonyl group.

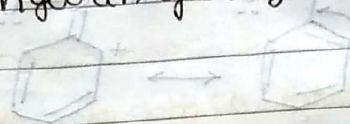
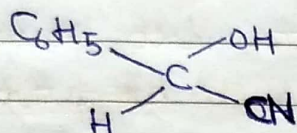


Some Important Examples of Nucleophilic addition reaction:-

1. Cyanohydrin:- Aldehyde and Ketones reacts with HCN to form addition product known as Cyanohydrin.

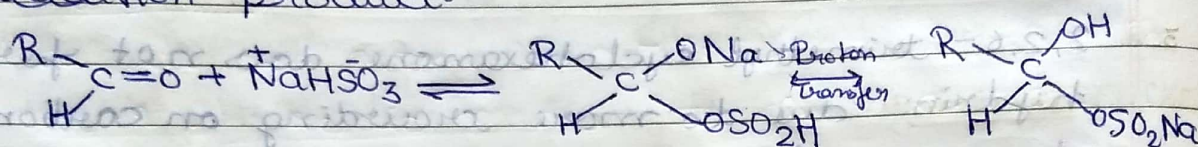


Q. Draw the structure of cyanohydrin of benzaldehyde.

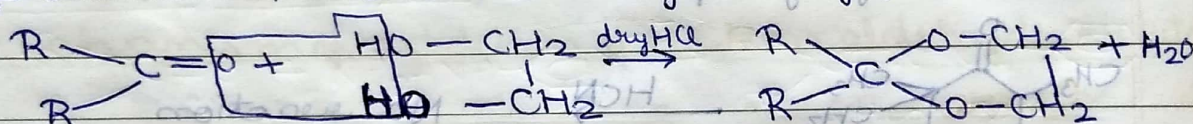


2. Reaction with NaHSO₃

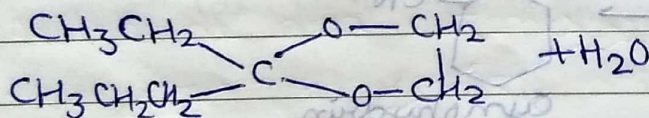
Aldehyde and ketones react with NaHSO₃ to give an addition product.



3. From Ketal → Ketone reacts with ethylene glycol in the presence of dry HCl gas to form a cyclic product known as ethylene glycol ketal.

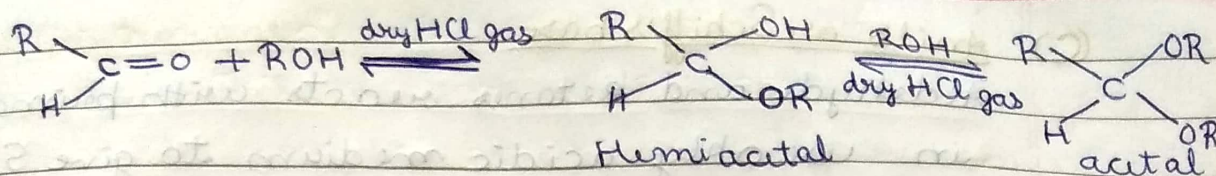


Q. Draw structure of ethylene ketal of Hexan-3-one

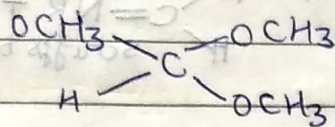


4. Hemiacetal and Acetal

Aldehyde reacts with alcohol in the presence of dry HCl gas to form alkoxy alcohol known as hemiacetal which further reacts with alcohol to form geminal-di-alkoxy compounds known as acetal.

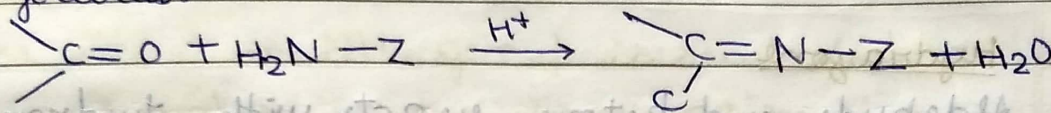


Q. Draw structure of ⁺acetaldehyde or dimethylacetal

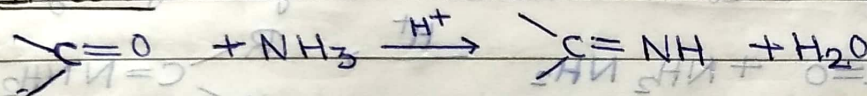


5. Addition of Ammonia and its derivatives

Aldehydes and ketones reacts with ammonia and its derivatives in weakly acidic medium to give product as follows:-



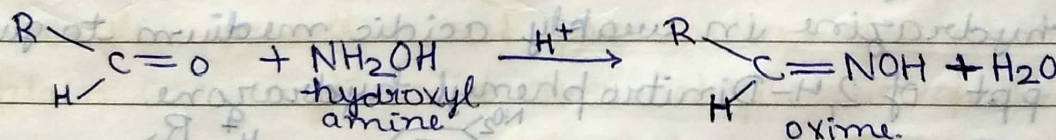
(a) Imines



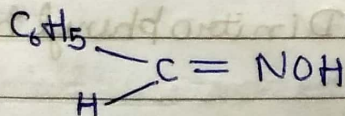
Aldehydes and ketones reacts with ammonia in weakly acidic medium to give imine.

(b) Oxime

Aldehyde and ketones reacts with hydroxyl amine in the presence of weakly acidic medium to form oxime.

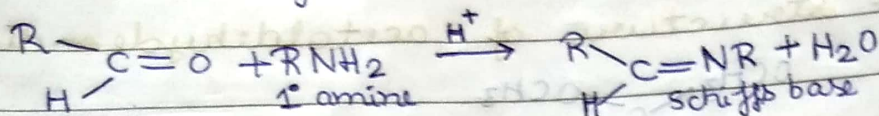


Q. Draw structure of oxime of benzaldehyde

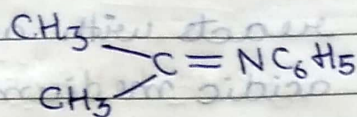


(C) Anils or Schiff's base

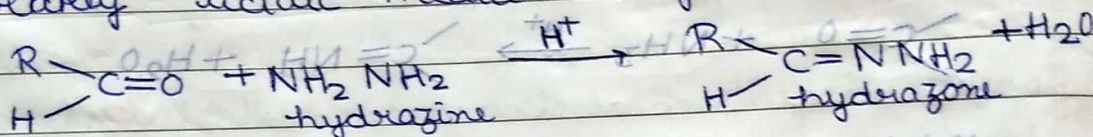
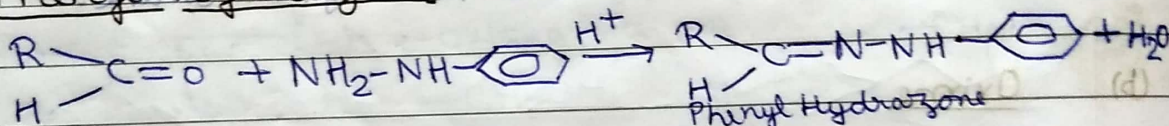
Aldehyde and ketones reacts with primary amine in weakly acidic medium to give Schiff's base.



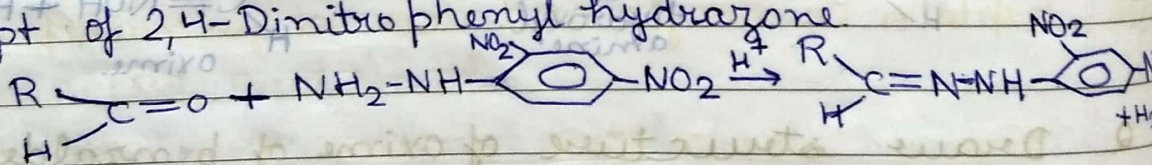
Q. Draw the structure of Schiff's base of aniline with acetone

(D) Hydrazone

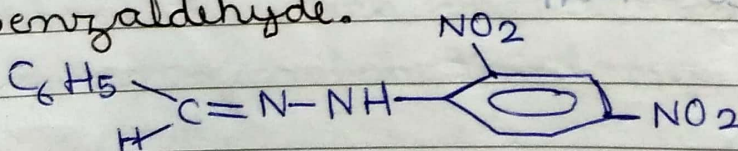
Aldehyde and ketone reacts with hydrazine in weakly acidic medium to give hydrazone.

(E) Phenyl Hydrazone(F) 2,4-Dinitrophenyl hydrazone (2,4-DNP)

Aldehyde and ketones reacts with 2,4-Dinitrophenyl hydrazine in weakly acidic medium to give orange ppt of 2,4-Dinitrophenyl hydrazone.

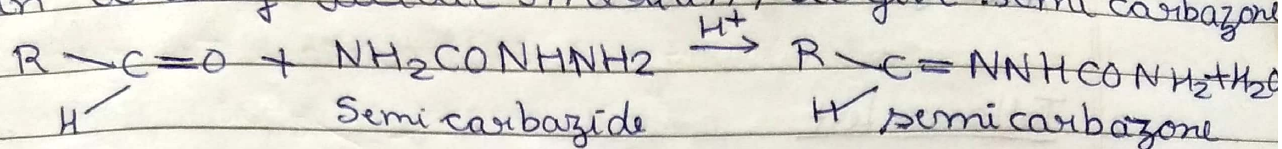


Q. Draw structure of 2,4-Dinitrophenyl hydrazone of benzaldehyde.

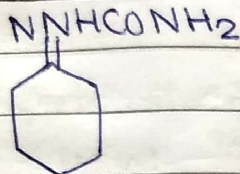


(B1) Semi Carbazone

Aldehyde and ketone reacts with Semicarbazide in weakly acidic medium to give semi carbazone



Q. Draw structure of semi carbazone of cyclohexanone

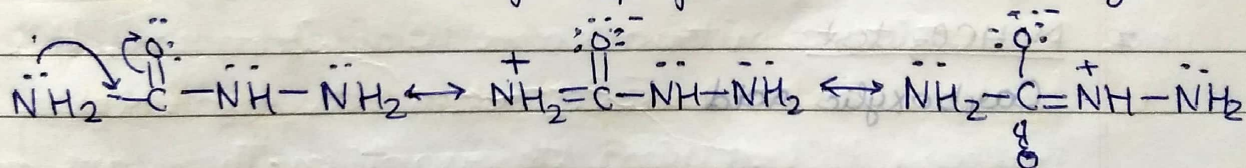


Q. Explain:-

1. There are two NH_2 group in semicarbazide but only one is involved in the formation of semicarbazone.

Ans. Lone pair of electron on nitrogen atom of NH_2 group attached with CO is involved in resonance and hence this NH_2 group does not involved in the formation of Semicarbazone.

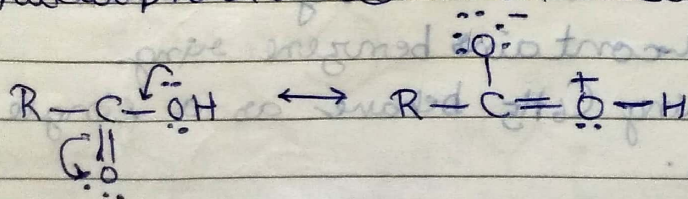
Whereas lone pair of electron of Nitrogen atom of NH_2 group attached with NH is not involved in resonance and hence this NH_2 group form semicarbazone.



2. Carboxylic acid does not give the test of carbonyl group.

OR Explain carboxylic acid does not give nucleophilic addition reaction

Ans. Carbon atom of carbonyl group of carboxylic acid is less electrophilic because carbonyl group involve in resonance with OH -group. Therefore carboxylic acid do not give nucleophilic addition reaction.



Condition for unknown compound

1. 2,4-DNP test, NaHCO_3 test, oxime test

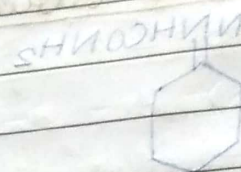
Aldehyde or ketone

2. Tollen's test

Aldehyde or formic acid

3. Fehling test

Aliphatic aldehydes



4. Aldol reaction

Aldehyde or ketones with α -hydrogen

5. Cannizzaro reaction

Aldehydes without α -hydrogen

6. Iodoform test

$\text{CH}_3-\overset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}}-\text{X}$ part or $\text{CH}_3-\overset{\text{OH}}{\text{CH}}-\text{X}$ part
 CH_3CHO and $\text{CH}_3\text{CH}_2\text{OH}$

7. NaHCO_3 test

Carboxylic acid

8. Na or K metal test

Alcohol or phenol or carboxylic acid.

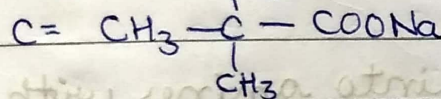
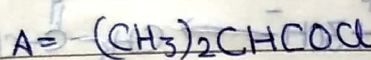
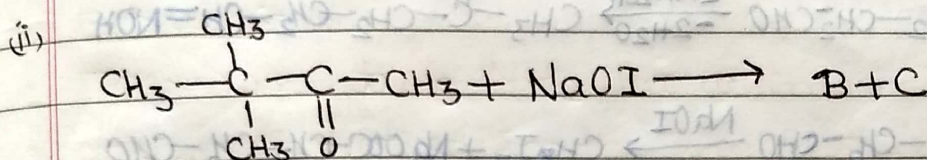
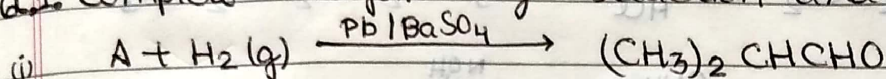
9. Condition for benzene ring

If a compound contains six or more than six carbon atom and similar no. of carbon atoms, the compound contains benzene ring.

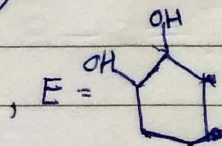
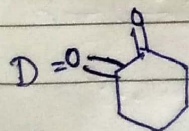
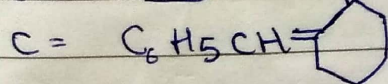
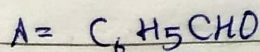
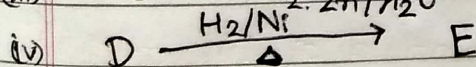
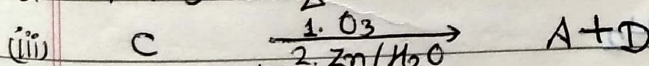
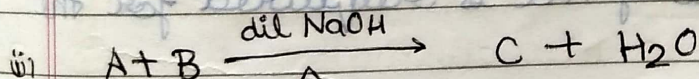
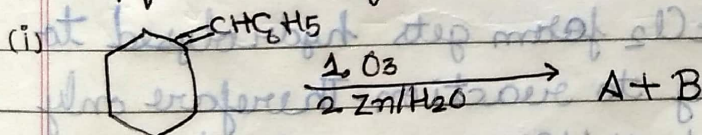
One benzene ring C_6H_5 behave as a single hydrogen atom.

10. From molecular formula* $C_nH_{2n} \Rightarrow$ alkene ($C=C$) and cycloalkane (Δ).* $C_nH_{2n-2} \Rightarrow$ Alkyne ($C \equiv C$) and cycloalkene.* $C_nH_{2n+2}O \Rightarrow$ Alcohol (ROH) or ether (ROR)* $C_nH_{2n}O \Rightarrow$ Aldehyde or ketone* $C_nH_{2n}O_2 \Rightarrow$ Carboxylic acid or ester* $C_nH_{2n+3}N \Rightarrow$ amine $\begin{matrix} \rightarrow 1^\circ \\ \rightarrow 2^\circ \\ \rightarrow 3^\circ \end{matrix}$

Q.1. Complete the following reaction and identify A, B, C.

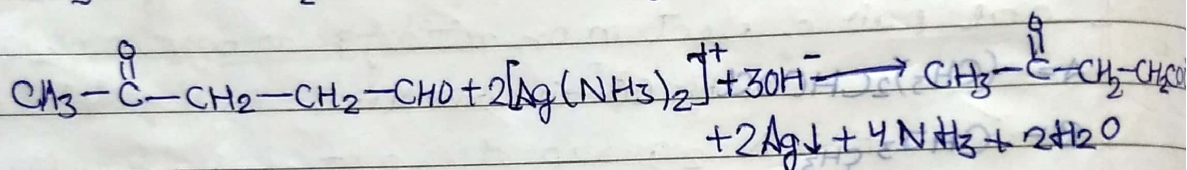
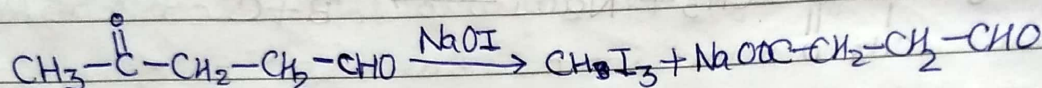
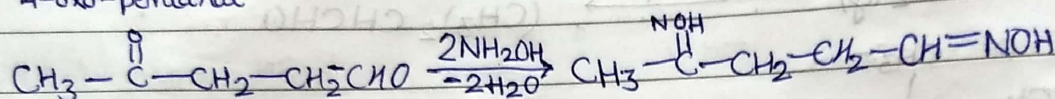
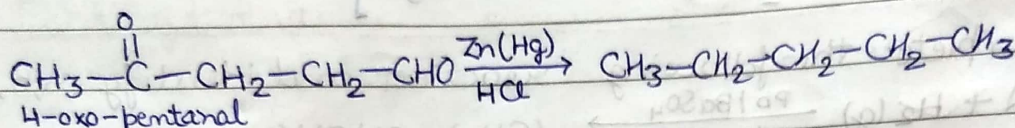
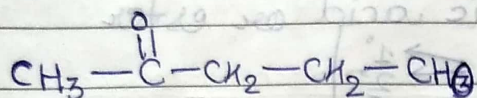


Q.2. Identify the compounds A to E in the following sequence of reaction:



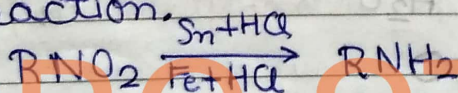
- Q. An organic compound 'A' molecular formula $C_5H_8O_2$ reduced to n-pentane on treatment with $Zn(Hg)/HCl$. Compound 'A' form di-oxime with hydroxyl amine and give positive iodoform test and tollens test. Identify the compound A and write reaction involve.

Ans →



- Q. Reduction of Nitro alkane into amines with Iron and HCl is preferred than other reducing agent. Why?

Ans. Reduction of nitroalkane with iron and HCl is preferred because $FeCl_2$ form gets hydrolysed to release HCl during to reaction. Therefore only a small amount of HCl is required for the reaction.



SBG STUDY