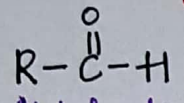


ALDEHYDE, KETONE, CARBOXYLIC ACID :-

(ORGANIC CHAPTER-3)

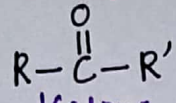
The functional group >C=O is called carbonyl group. Organic compounds containing carbonyl groups are aldehydes, ketones, carboxylic acids and their derivatives. The general formulae of these compounds are given below:-



Aldehyde

IUPAC:- Alkanal

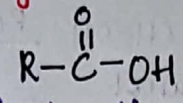
(Where R may be H or any alkyl, aryl or aalkyl group)



Ketone

IUPAC:- Alkanone

(Where R and R' may be same or different alkyl, aryl or aalkyl group)

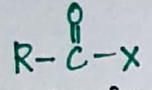


Carboxylic acid

IUPAC:- Alkanoic acid

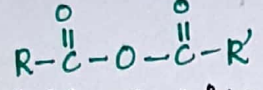
(Where R may be H or any alkyl, aryl or aalkyl group)

Derivatives of Carboxylic acids :-



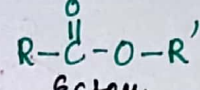
Acyl halide

(X=halogen)



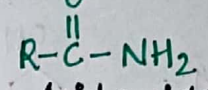
Acid anhydride

(Where R & R' may be same or different groups)



Ester

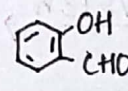
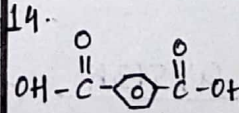
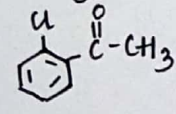
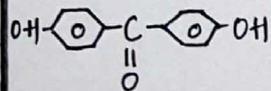
(Where R & R' may be same or different groups)



Acid amide

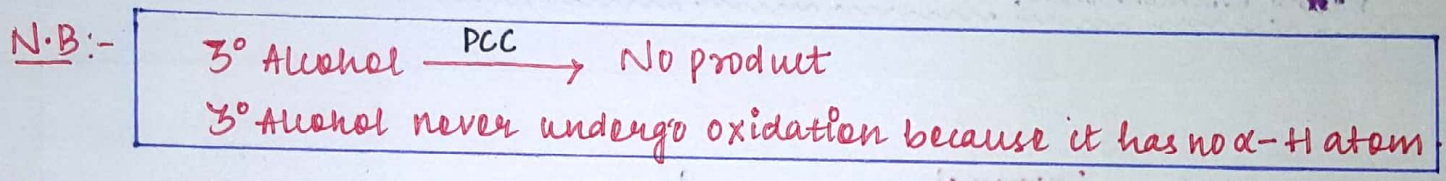
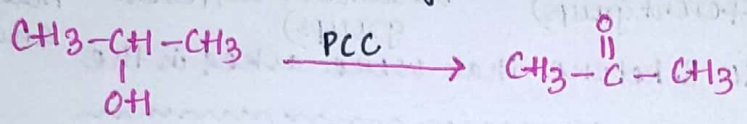
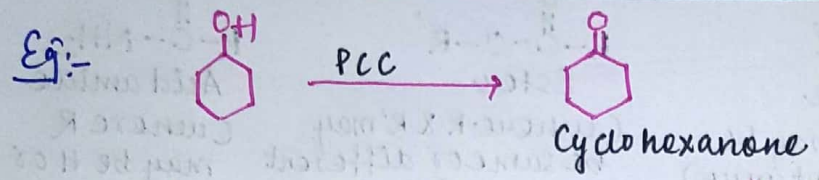
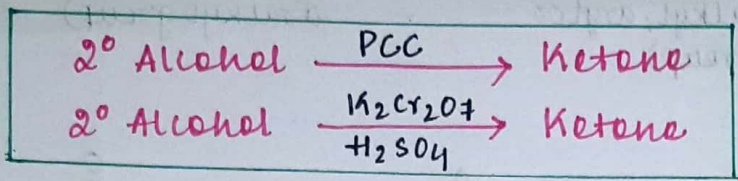
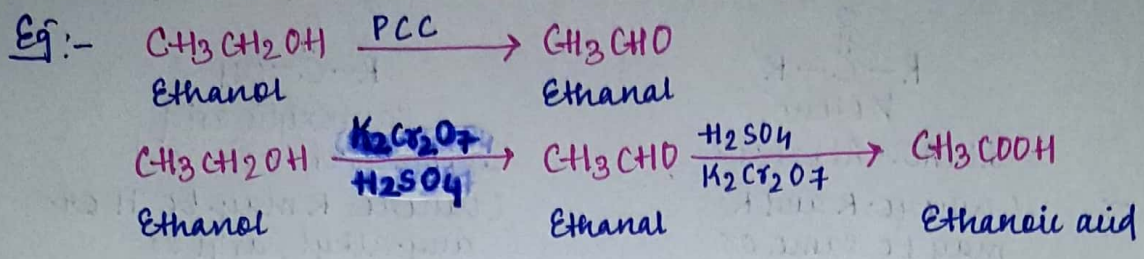
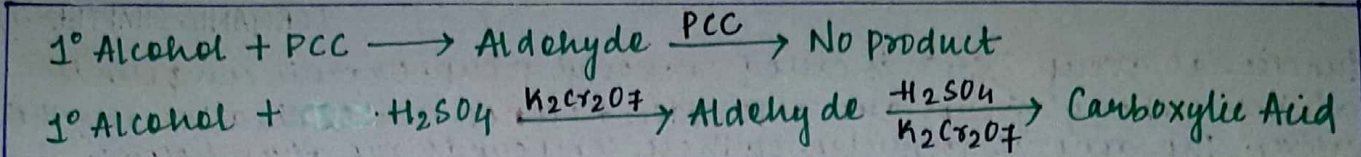
(Where R may be H or any group)

IUPAC names of some aldehyde & ketone that were asked in the board examination:-

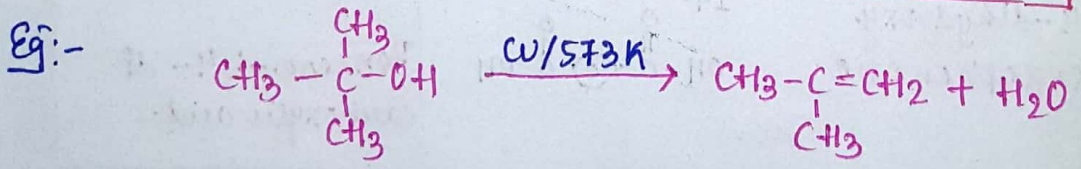
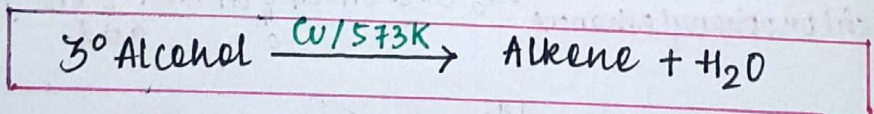
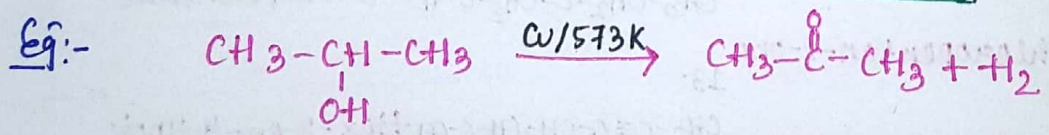
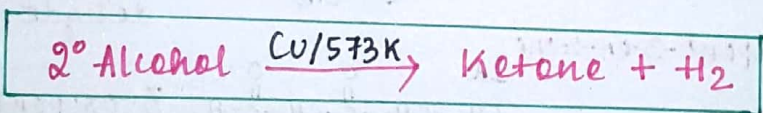
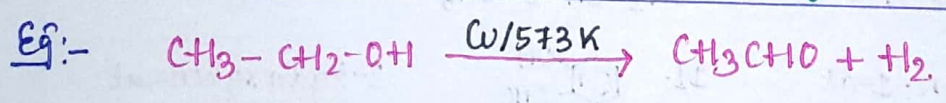
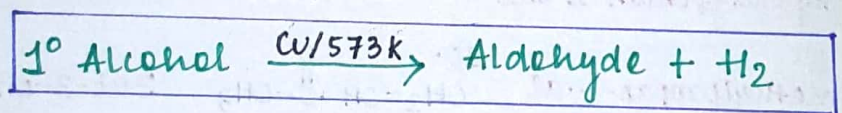
STRUCTURE	IUPAC name	STRUCTURE	IUPAC name
1. $\text{CH}_3-\text{CH}_2-\text{CHO}$	Propanal	9. $\text{CH}_3\text{COCH}_2\text{COCH}_3$	Pentane-2,4 dione
2. $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	4-hydroxypentan-2-one	10. $\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	But-3-en-2-one
3. $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CHO}$	2-methylpropan-1-al	11. 	2-hydroxybenzaldehyde
4. $\text{CH}_3-\text{CH}_2-\text{CH}=\underset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Pent-2-en-1-al	12. $\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-oxopentanal
5. $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CH}_3$	4-methylpent-3-en-2-one	13. $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}=\underset{\text{O}}{\parallel}{\text{C}}-\text{H}$	Hex-2-en-4-ynoic acid
6. $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$	4-chloropentan-2-one	14. 	Benzene-1,4-di carboxylic acid
7. 	2-chlorophenylethanone		
8. 	4,4'-dihydroxy benzophenone		

PREPARATION OF ALDEHYDE AND KETONE:-

① Oxidation of alcohol

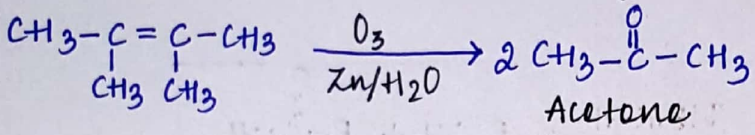
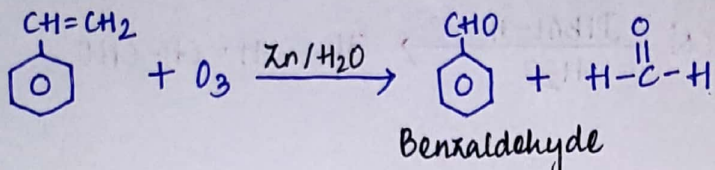
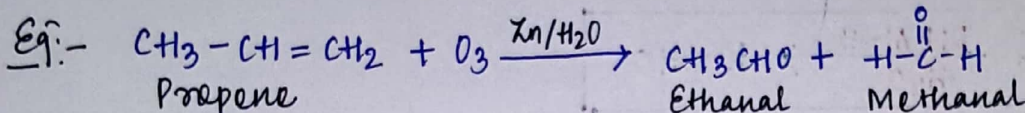
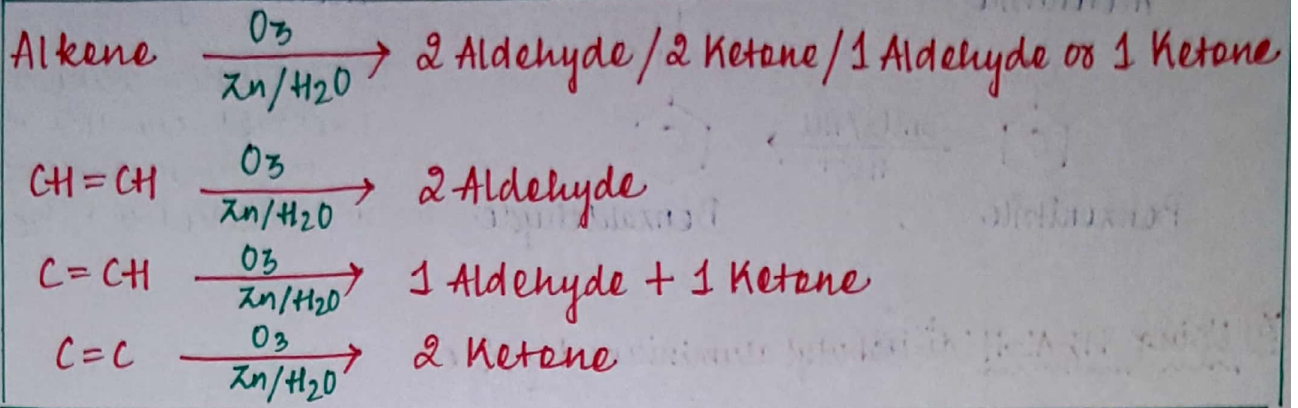


② Dehydrogenation of alcohols:-



③ FROM HYDROCARBONS:-

(a) Oxonolysis of alkenes:-

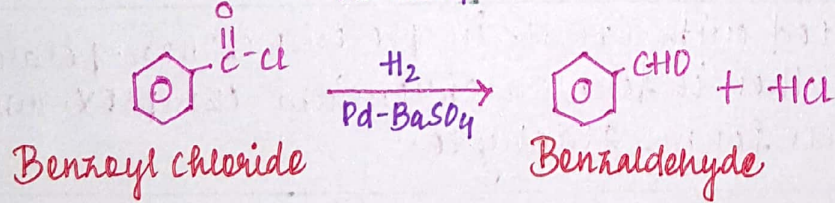
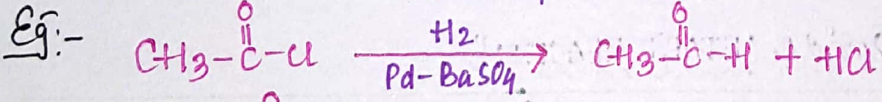
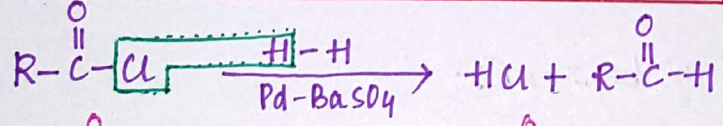
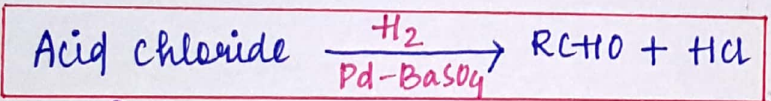


TRICK:- Remove the double bond and provide it to each C-atom.

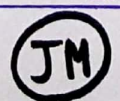
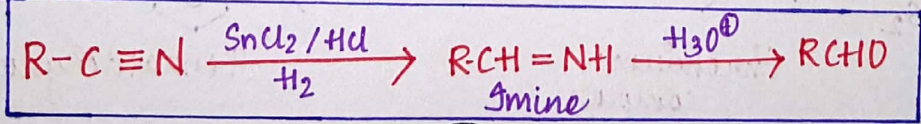
PREPARATION OF ALDEHYDE:-

① FROM ACID CHLORIDE (ROSENMOND REDUCTION REACTION)

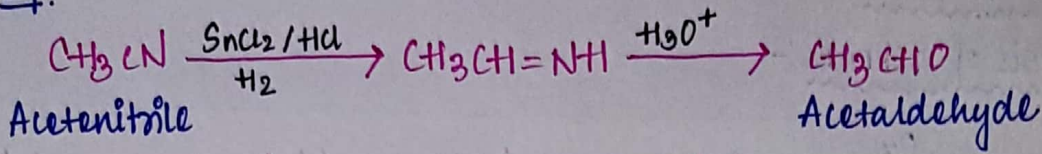
When H₂ gas is passed over acid chloride in presence of Pd supported with BaSO₄ then partially poisoned by sulphur or quinoline forms aldehyde.



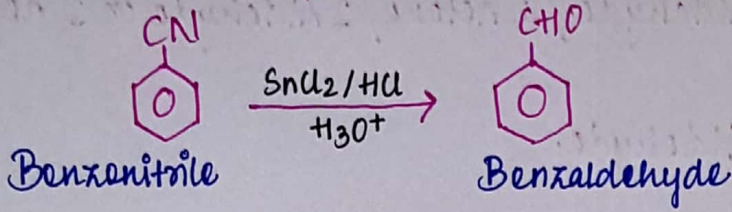
② FROM NITRILES (STEPHEN REACTION)



Eg:-

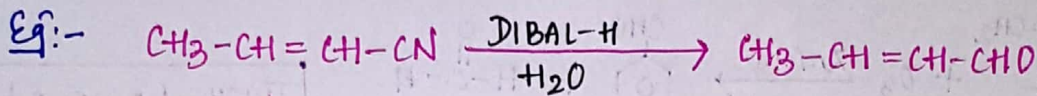
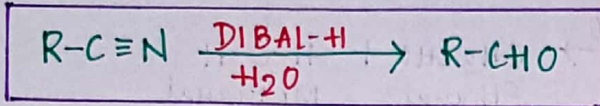


(4)

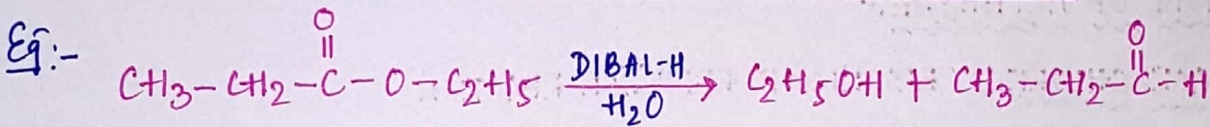
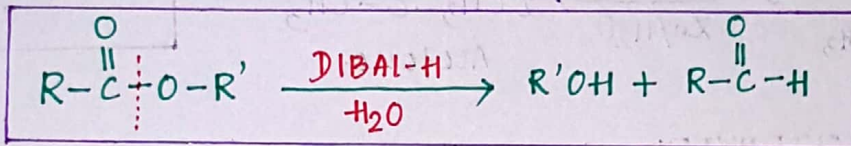


TRICK:- When imine is prepared, one H is attached to carbon and another H is attached to Nitrogen.

③ Using DIBAL-H (di-isobutyl aluminium hydride)



④ From ester:-



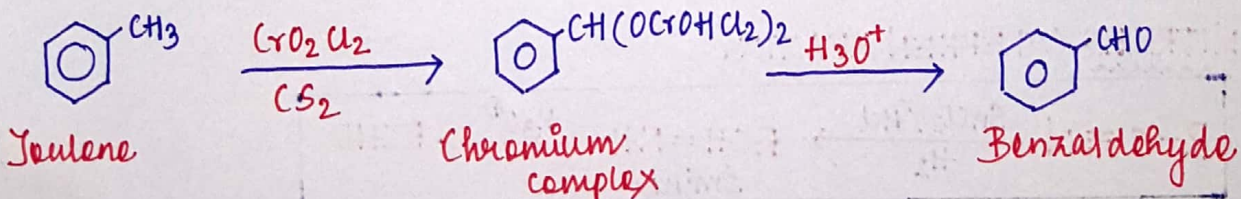
TRICK:- the bond adjacent to C=O breaks and H is attached to each 1 of the group.

⑤ FROM HYDROCARBONS:-

(i) By oxidation of methyl benzene:-

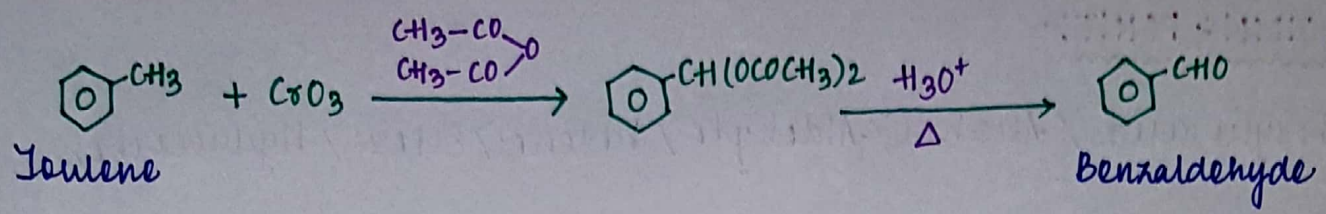
(a) Use of chromyl chloride (ETARD REACTION)

When Toluene is treated with CrO_2Cl_2 in presence of non-polar solvent like CS_2 then it forms a chromium complex, which on further hydrolysis forms aldehyde.

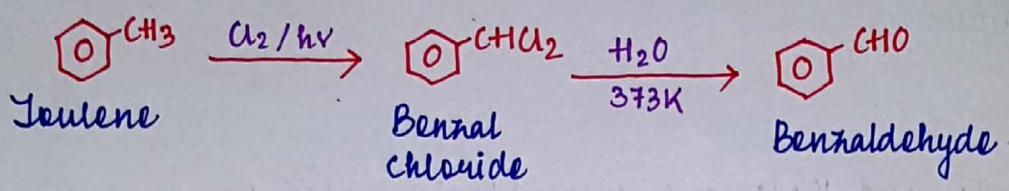


(JM)

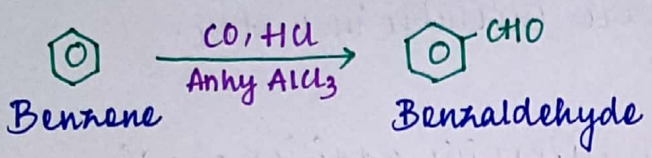
(b) USE OF CHROMIC OXIDE:-



(ii) Side chain chlorination followed by hydrolysis:-

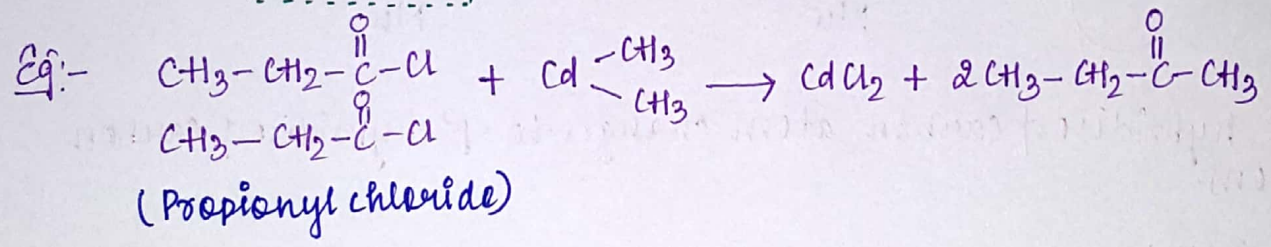
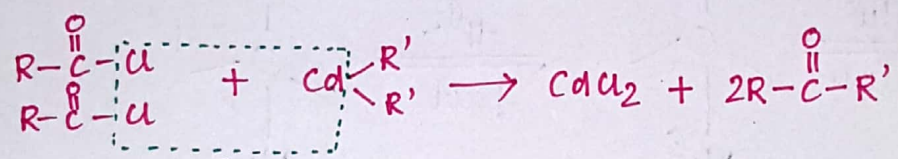


(iii) By Gatterman-Moeh reaction:-

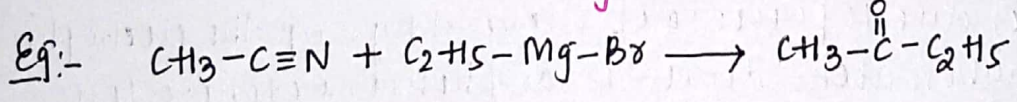
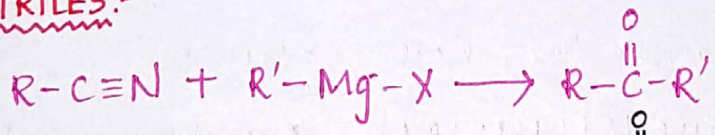


PREPARATION OF KETONES:-

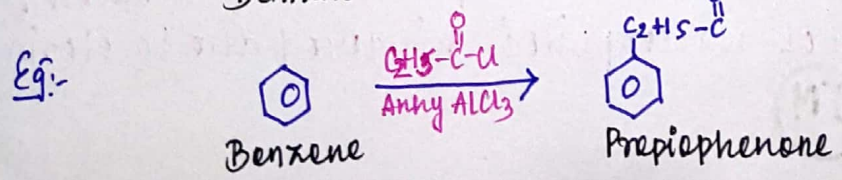
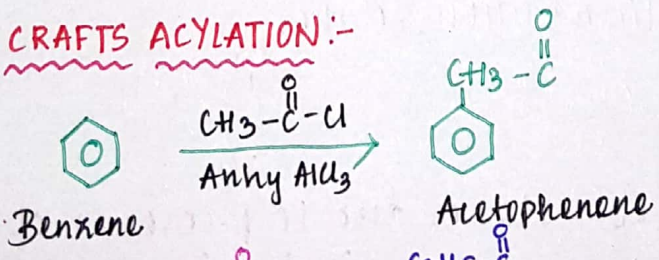
① FROM ACID CHLORIDES:-



② FROM NITRILES:-



③ FRIEDEL-CRAFTS ACYLATION:-



PHYSICAL PROPERTIES:-

① BOILING POINT:-

Carboxylic acid > Alcohol > Aldehyde > Ketone > Ester > Hydrocarbon

The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

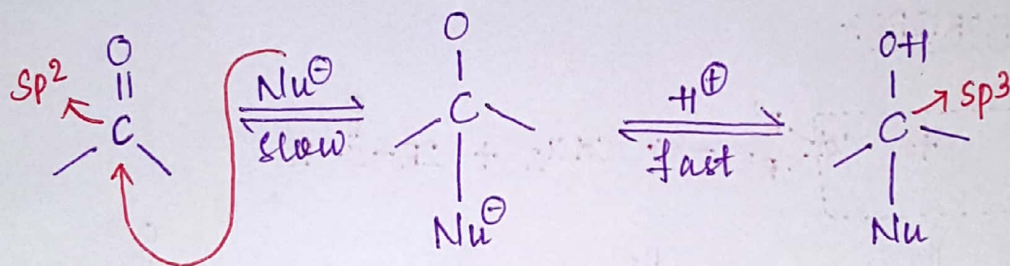
② SOLUBILITY:-

- * Lower aldehyde and ketone are soluble in water because of intermolecular hydrogen bonding.
- * Higher aldehyde and ketone are insoluble in water.

CHEMICAL PROPERTIES:-

1. Aldehyde and ketone undergo nucleophilic addition reaction.

(i) Mechanism of nucleophilic addition reaction:-

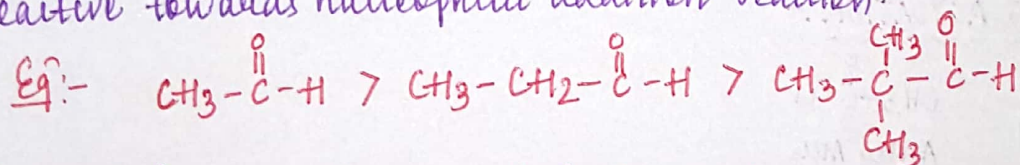


The sp² hybridised carbon atom changes to sp³ hybridised carbon atom.

(ii) Reactivity:-

Aldehyde are more reactive than ketone because:-

① In case of ketone, due to presence of more +I group, the electrophilicity of carbonyl carbon atom decreases and hence, ketone is less reactive towards nucleophilic addition reaction.



② Steric factor:- In case of ketone, due to presence of 2 bulkier alkyl group, the approach of nucleophile is hindered due to steric repulsion.

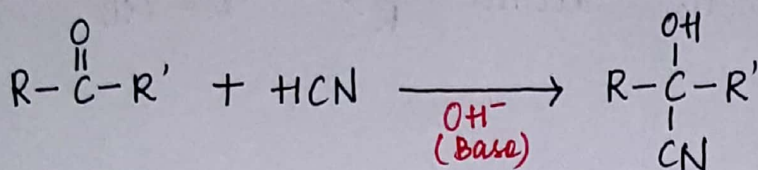
JM

(ii) Some important examples of nucleophilic addition and nucleophilic addition-elimination reactions:-

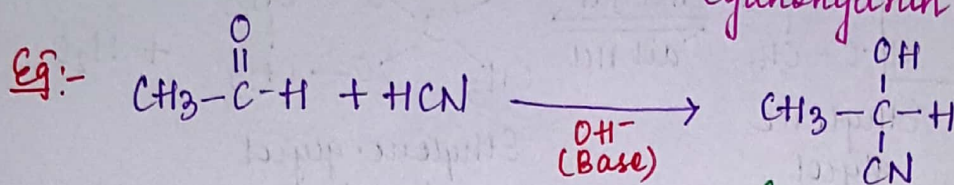
(7)

(a) Addition of HCN:-

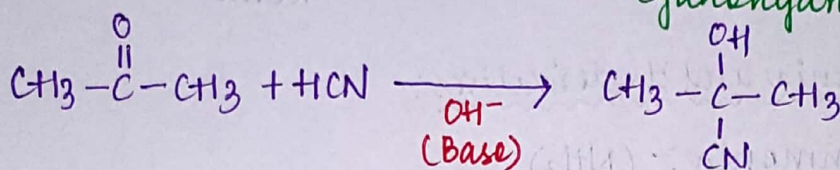
Since, HCN is a weak acid, it generates nucleophile in basic medium



Cyanohydrin complex

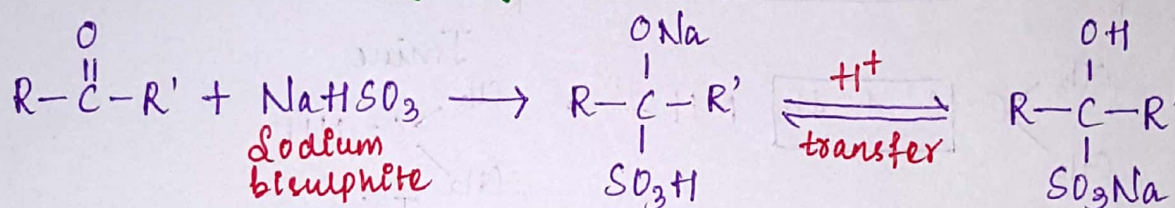


Cyanohydrin complex



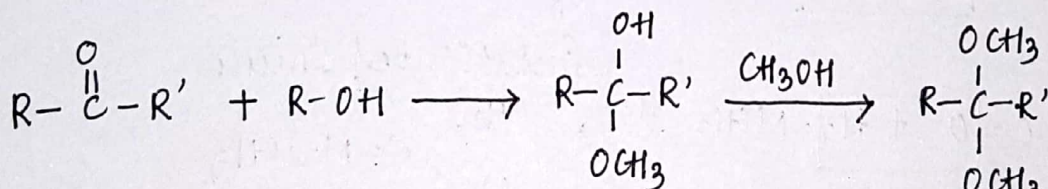
Cyanohydrin complex

(b) Addition of sodium hydrogen sulphite:-



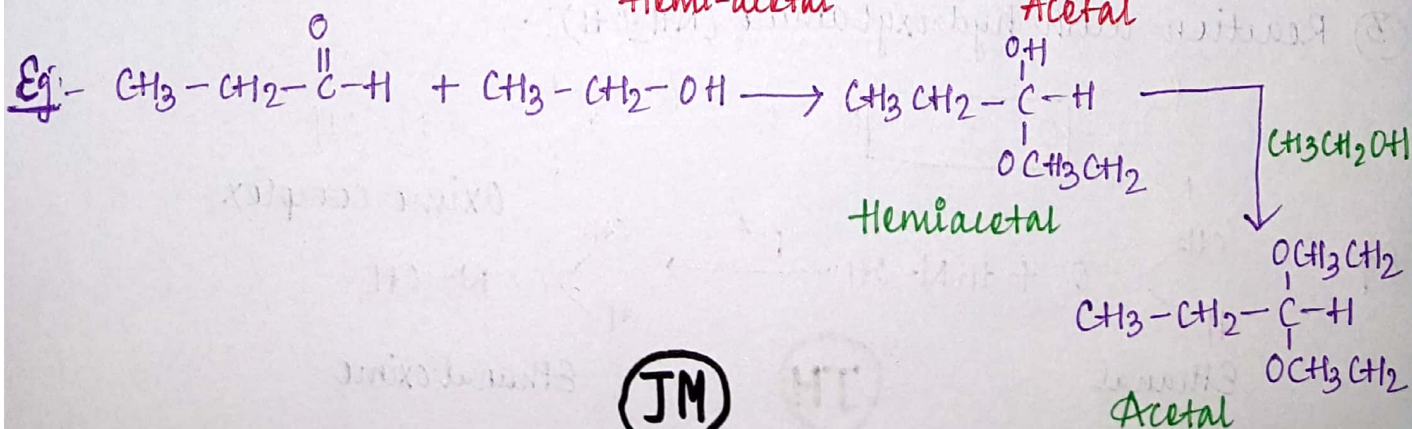
(c) Addition of alcohol:-

Aldehyde react with monohydric alcohol to form hemiacetal and acetal.



Hemi-acetal

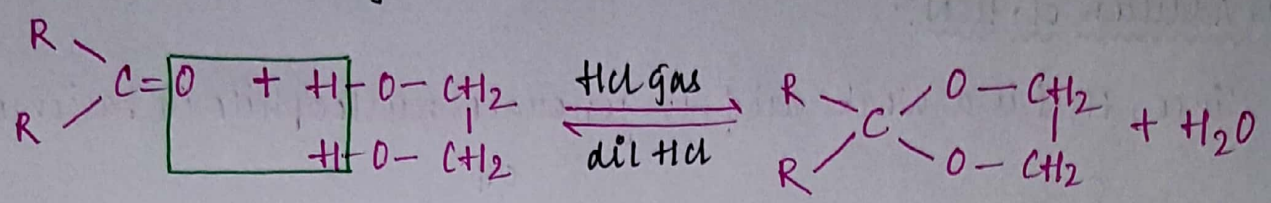
Acetal



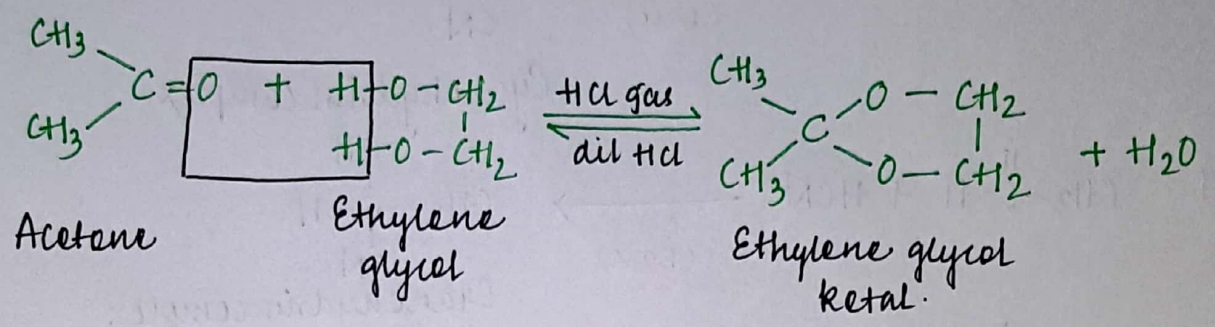
JM

* Reaction with ethylene glycol -

Ketone react with dihydric alcohol to form ketals.

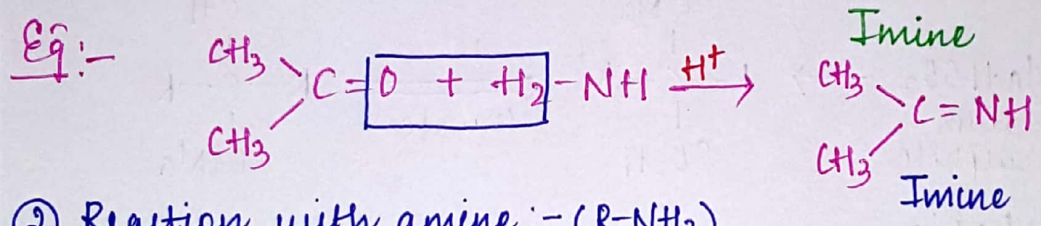
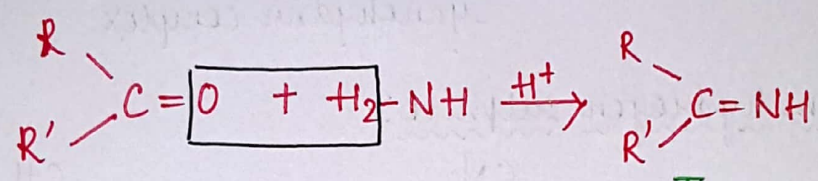


Eq:-

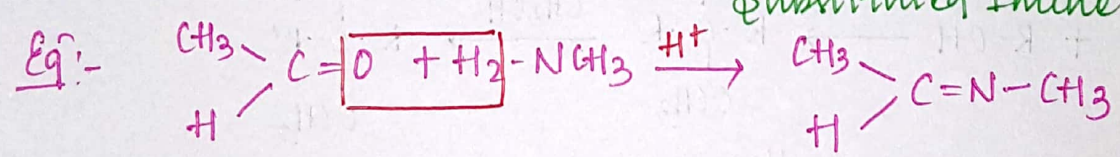
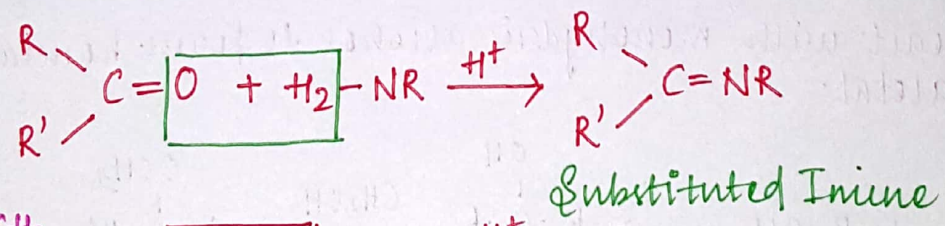


(d) Addition of ammonia and its derivatives:-

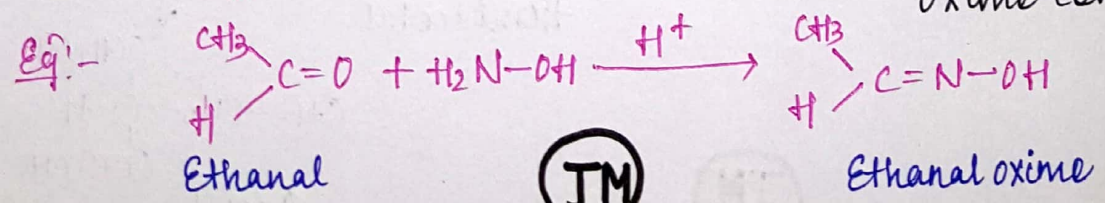
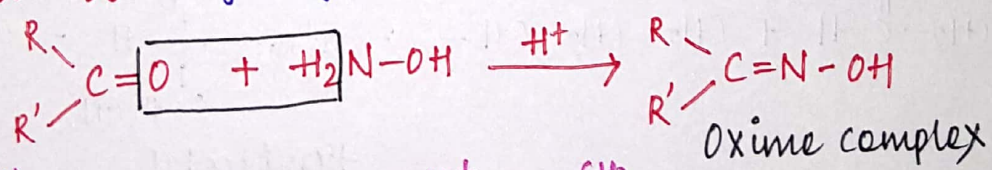
① Reaction with ammonia:- (NH₃)



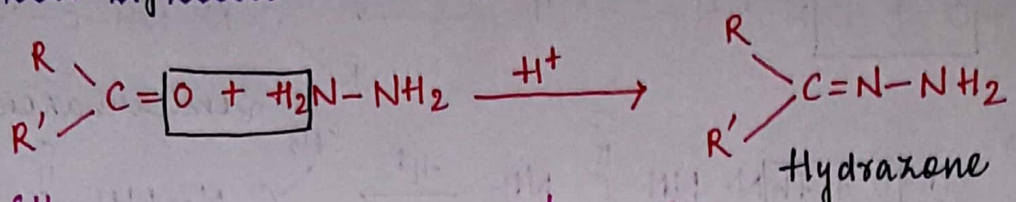
② Reaction with amine:- (R-NH₂)



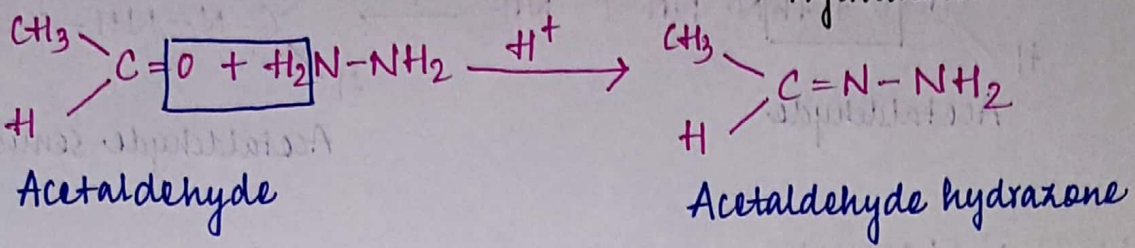
③ Reaction with hydroxylamine (NH₂OH):-



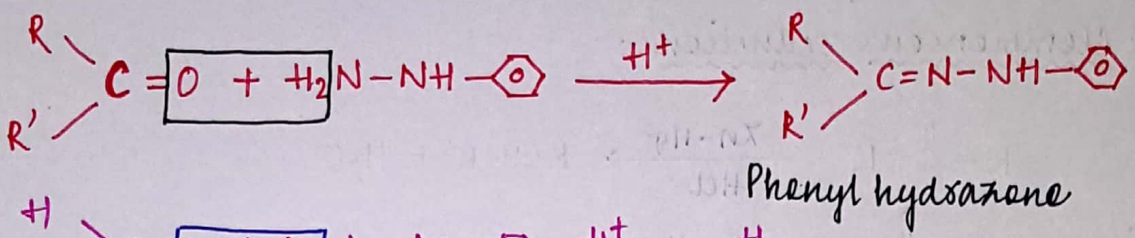
④ Reaction with hydrazine (NH₂-NH₂):-



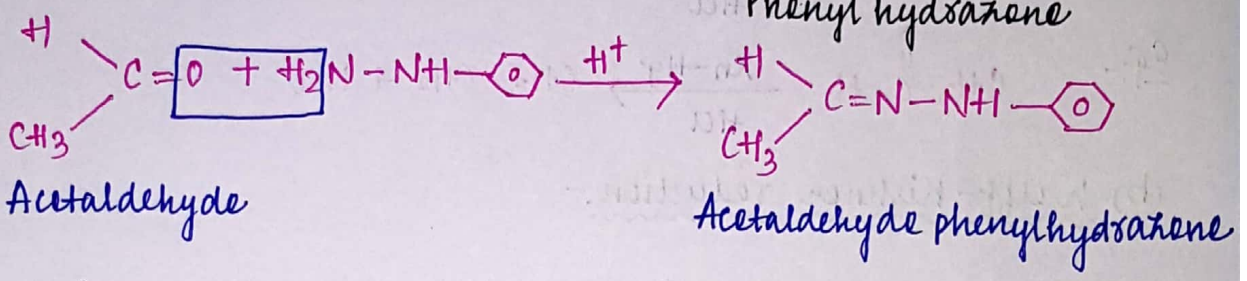
Eg:-



⑤ Reaction with phenylhydrazine (C₆H₅-NH-NH₂):-

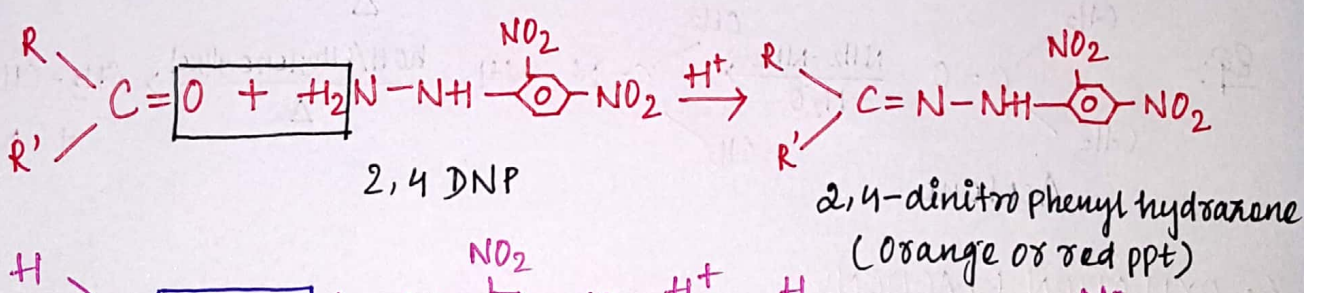


Eg:-

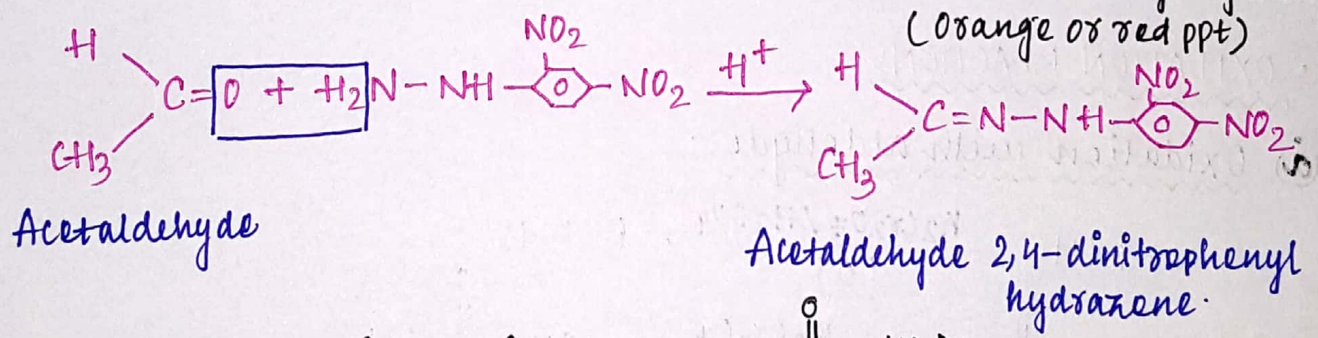


⑥ Reaction with 2,4 DNP (2,4-dinitro phenyl hydrazine):-

* It is used to test the presence of carbonyl group. It gives a orange/red precipitate.

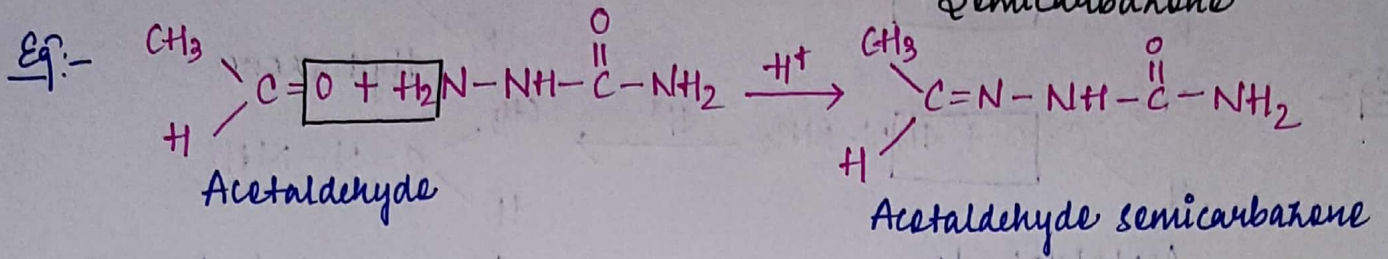
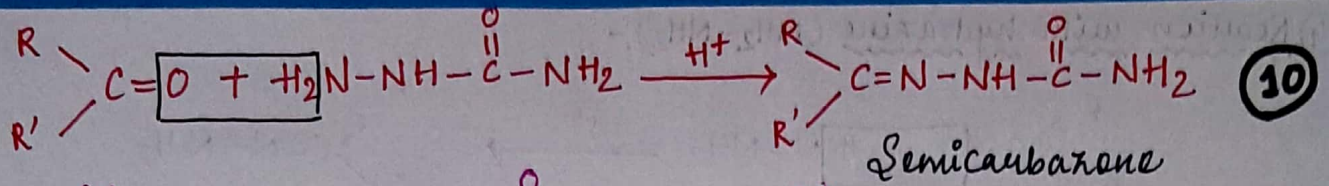


Eg:-



⑦ Reaction with semicarbazide (NH₂-NH-C(=O)-NH₂):-

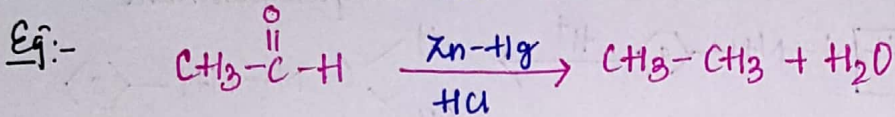
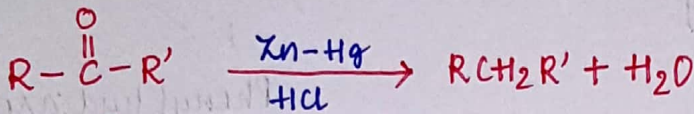
* Out of the two NH₂ groups present in semicarbazide, the one which is away from -C(=O)- is involved in the reaction.



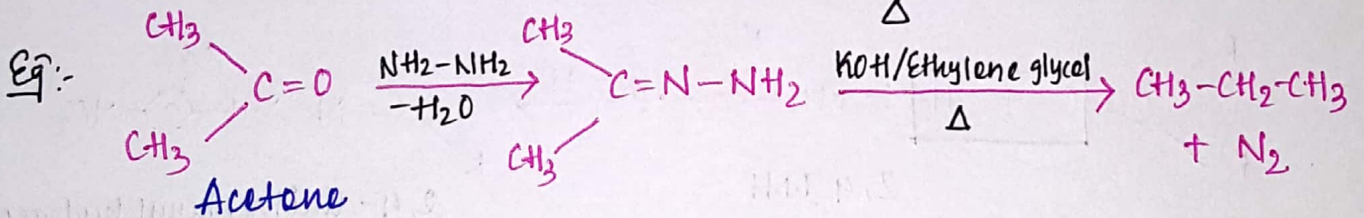
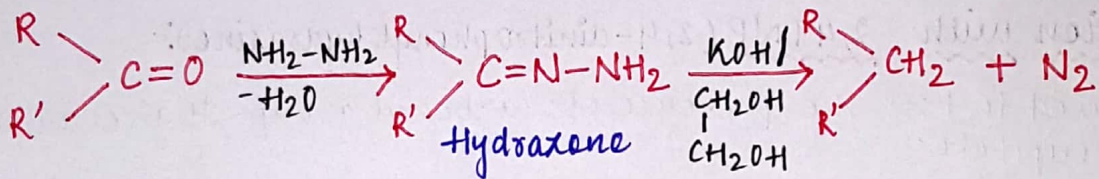
2. REDUCTION REACTIONS:-

(i) Reduction to hydrocarbons:-

(a) Clemmensen's reduction:-

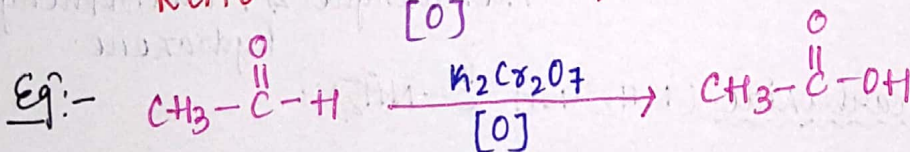
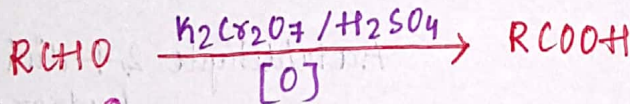


(b) Wolff-Kishner reduction:-

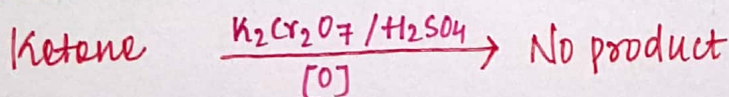


3. OXIDATION REACTIONS:-

(a) Oxidation with aldehyde:-

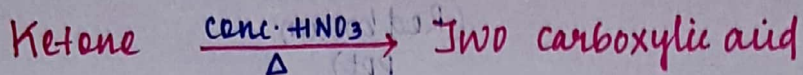


(a) Oxidation with ketone:-



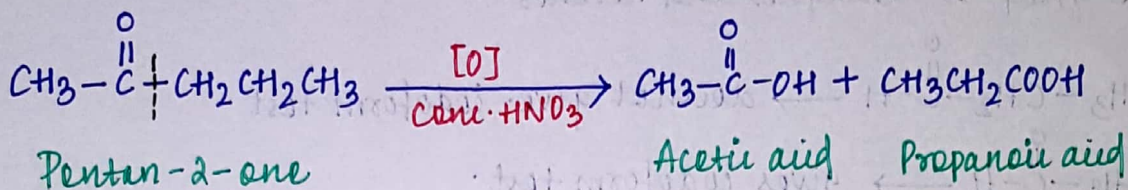
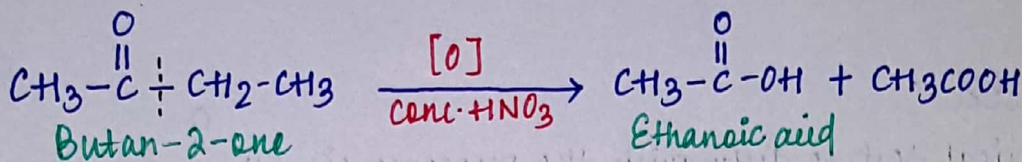
JM

Ketones in presence of conc. HNO_3 (drastic condition) oxidises.



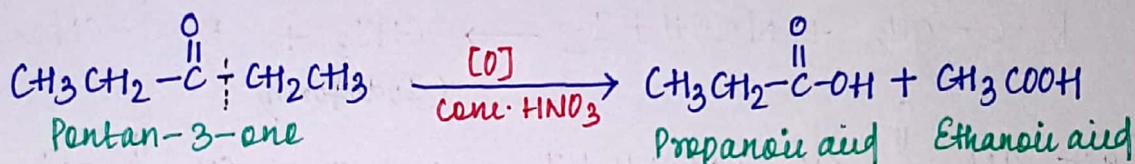
In case of unsymmetrical ketones such as Butan-2-one or Pentan-2-one etc, the point of cleavage is such that the keto group stays with smaller alkyl group preferentially. (Popoff's rule)

Eg:-



However, in case of symmetrical ketones, only one type of cleavage occurs.

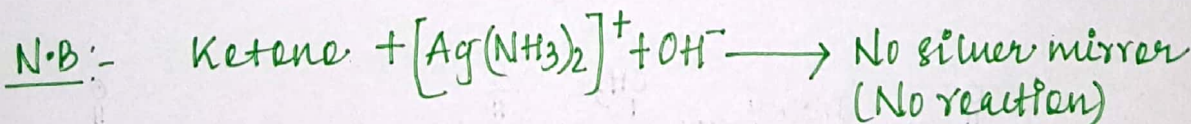
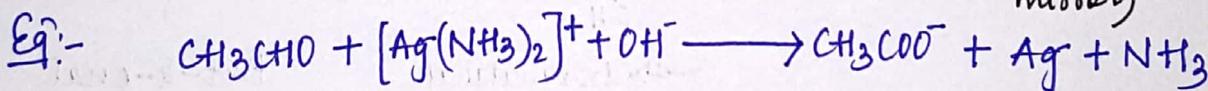
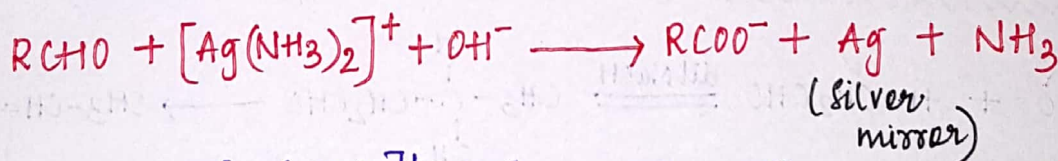
Eg:-



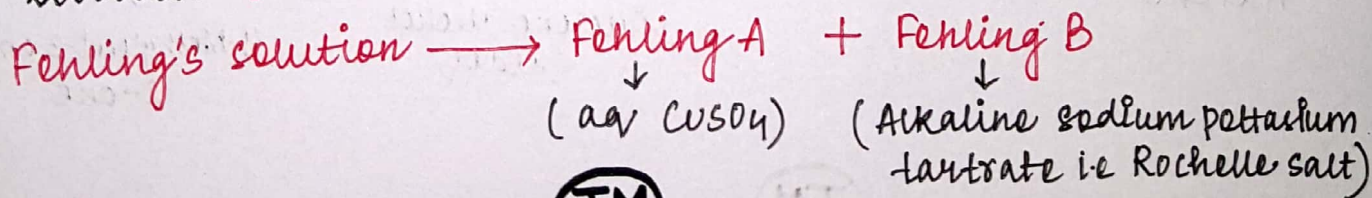
The mild oxidising agents given below are used to distinguish aldehydes from ketones:-

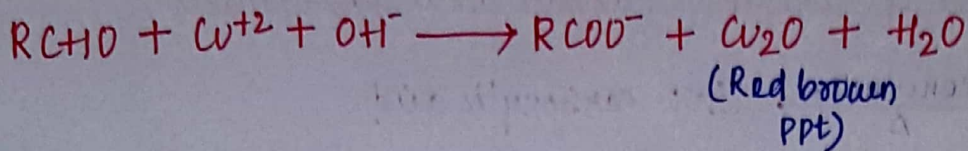
(i) Oxidation by Tollens' reagent:-

- * Tollens' reagent is ammoniacal silver nitrate solution. $[\text{Ag}(\text{NH}_3)_2]^+ + \text{OH}^-$
- * It is the confirmatory test of aldehyde.

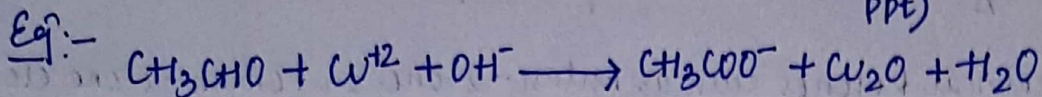


(ii) Oxidation by Fehling's solution:-





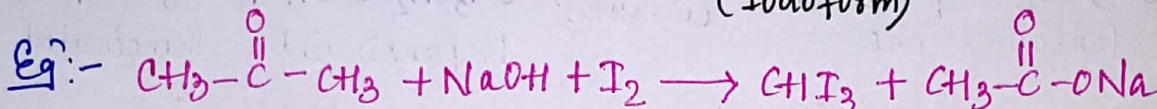
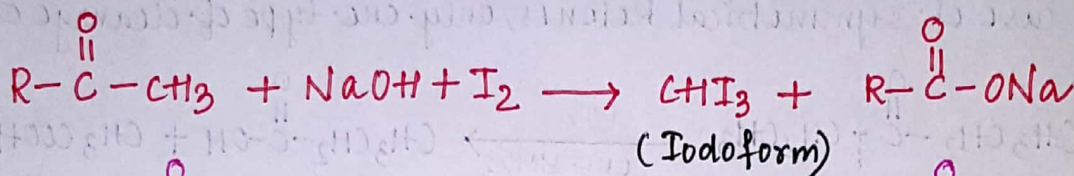
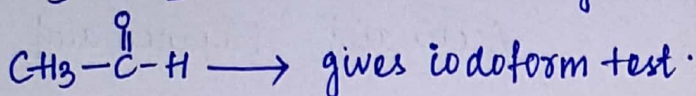
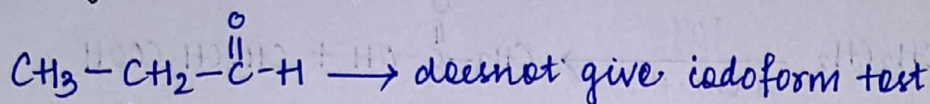
(12)



N.B:- Aromatic aldehyde, (benzaldehyde) however does not reduce Fehling's solution.

(iii) Iodoform test:-

* It is a chemical test to distinguish the presence of $CH_3-C(=O)$ group or methyl ketone group in aldehydes and ketones.

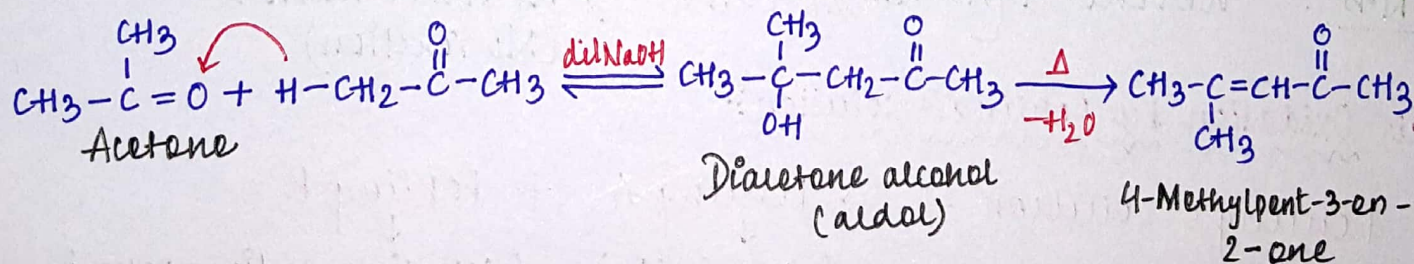
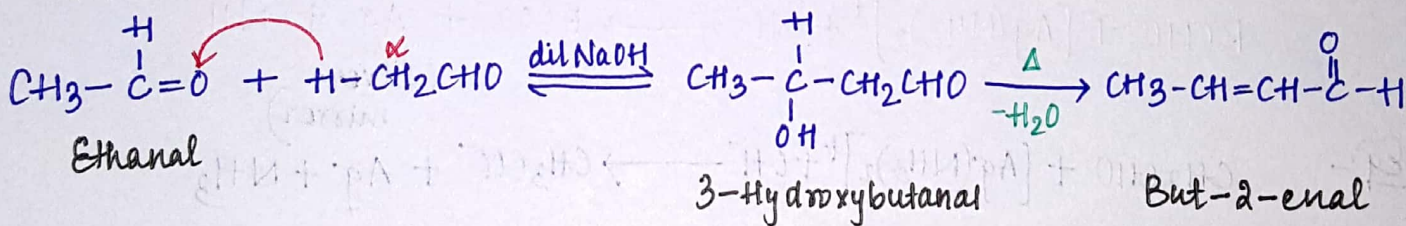


4. Reactions due to α -hydrogen:- (ALDOL CONDENSATION)

Aldol is defined as the combination of both alcohol and aldehyde group in two consecutive carbon atoms.

* The aldehyde or ketone must have one α -H atom

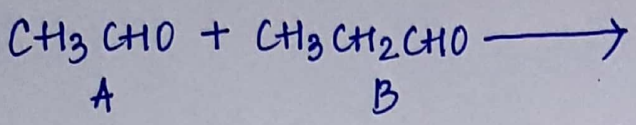
(i) Self aldol condensation (If both are same type of reactant):-



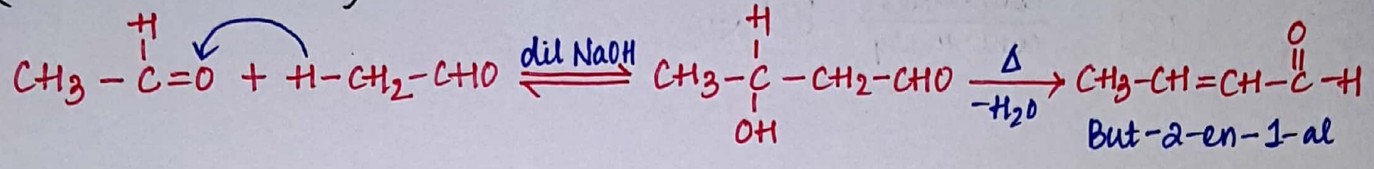
JM

(ii) Cross aldol condensation:-

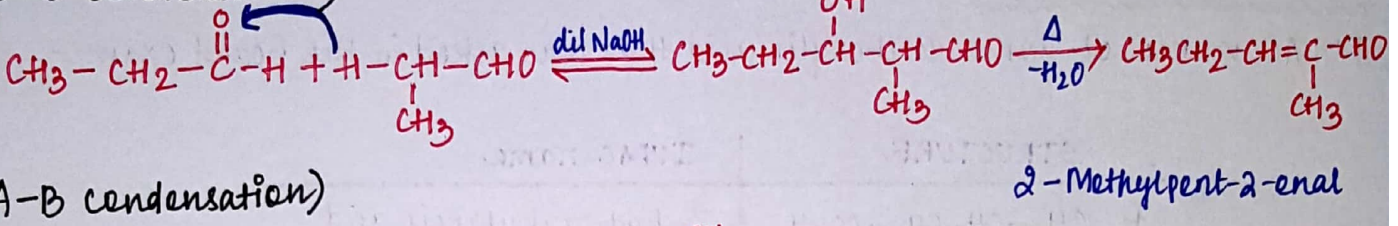
When 2 different aldehyde both having α -H atom reacts with dil NaOH we get 4 Aldol i.e (A+A, B+B, A+B, B+A)



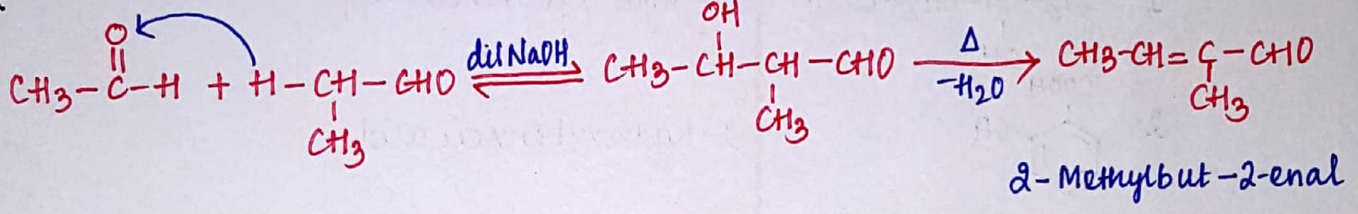
(A-A condensation)



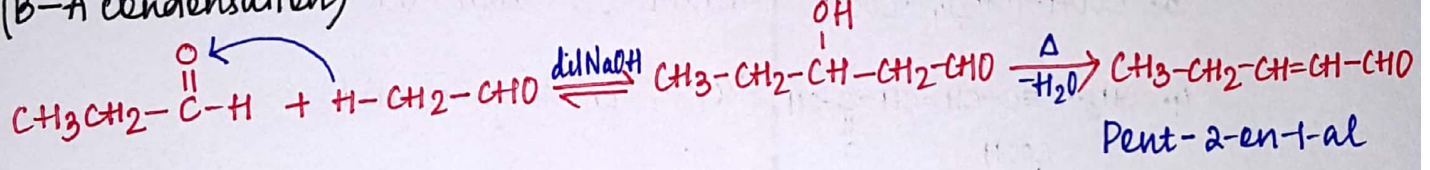
(B-B condensation)



(A-B condensation)



(B-A condensation)

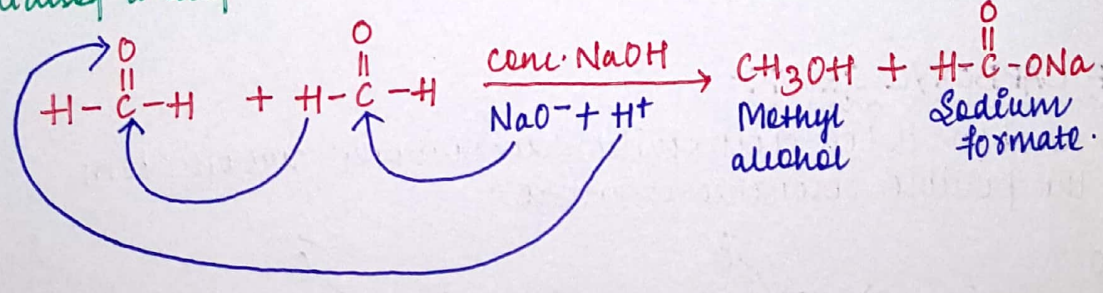


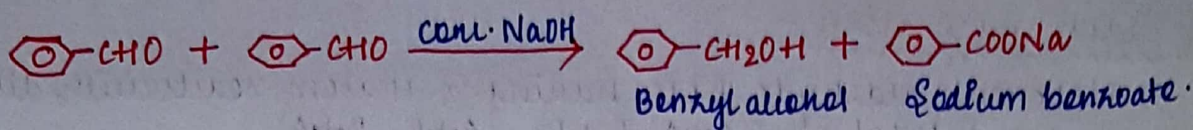
* In this, we get 2 self aldol products and 2 cross aldol products.

5. OTHER REACTIONS:-

(i) CANNIZZARD REACTION:-

Alddehyde which donot have α -H atom, undergo self oxidation and reduction in presence of conc. NaOH which is reduced to alcohol and oxidised to acid.

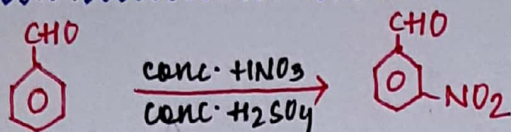




(14)

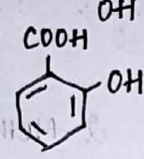
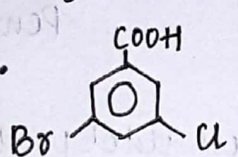
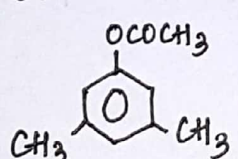

TRICK:- In Cannizzaro reaction, 1 CHO group becomes CH₂OH and another CHO group becomes COONa.

(ii) Electrophilic substitution reaction:-



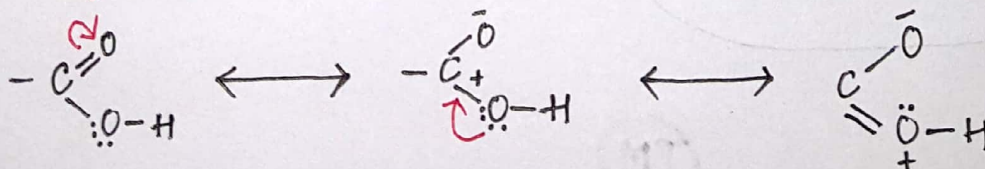
CARBOXYLIC ACIDS:-

IUPAC name of some carboxylic acid that was asked in the board exam:-

STRUCTURE	IUPAC name
1. $\text{CH}_3\text{-CH(OH)-CH}_2\text{-COOH}$	3-hydroxybutanoic acid
2. 	2-hydroxybenzoic acid
3. $\text{COOH-(CH}_2\text{)}_4\text{-COOH}$	Hexane-1,6-dioic acid
4. $\text{CH}_3\text{-C}\equiv\text{C-CH=CH-C(=O)OH}$	Hex-2-en-4-yn-oic acid
5. 	3-bromo-5-chlorobenzoic acid
6. 	3,5-dimethylphenyl ethanoate.
7. $\text{O=C-OC}_2\text{H}_5$ 	Ethyl-4-chlorobenzoate

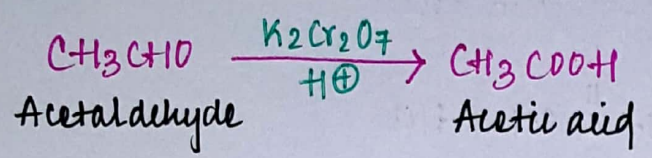
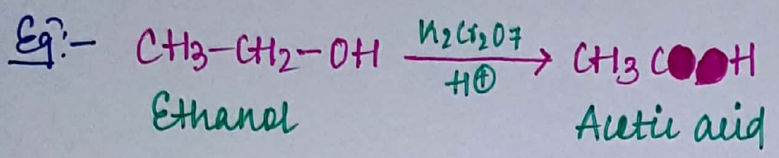
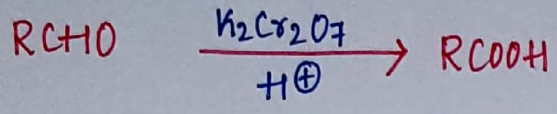
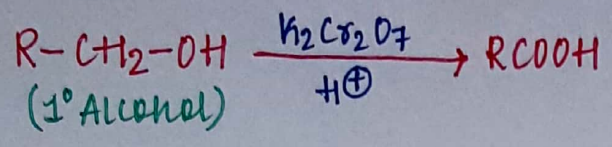
STRUCTURE OF CARBOXYL GROUP:-

The carboxylic carbon is less electrophilic than carbonyl carbon atom because of the possible resonance structure:-

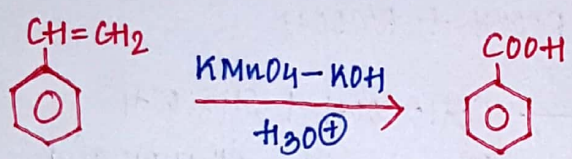
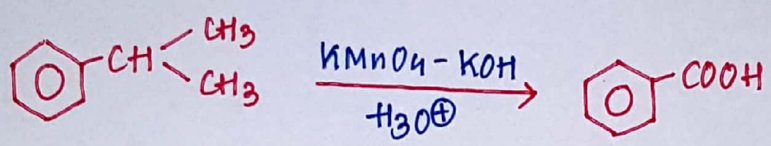


PREPARATION OF CARBOXYLIC ACID:-

1. FROM PRIMARY ALCOHOL AND ALDEHYDE:-

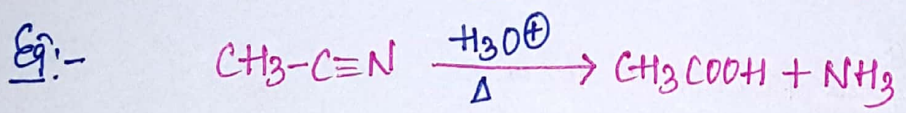
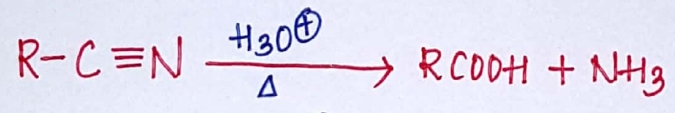


2. FROM ALKYL BENZENES:-

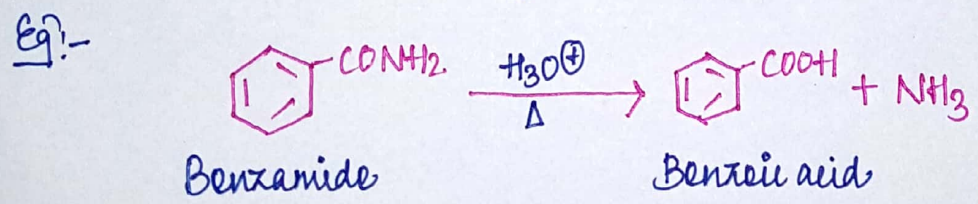
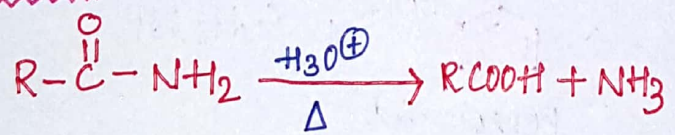


TRICK:- It will convert total side chain to COOH.

3. FROM NITRILES:-

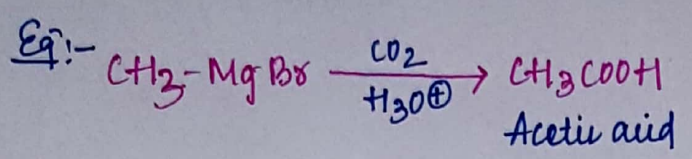
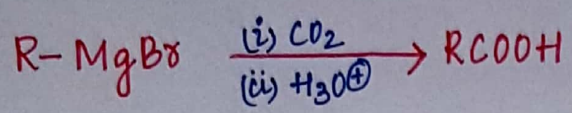


4. FROM AMIDES:-

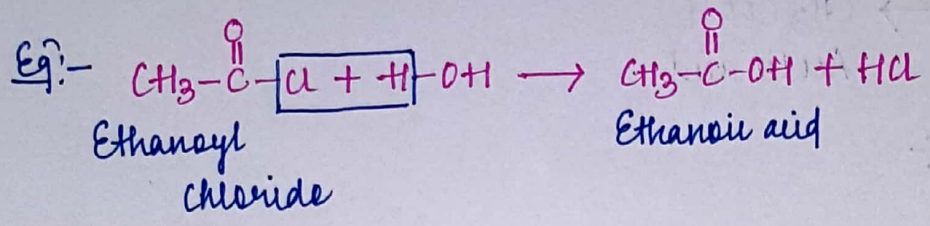
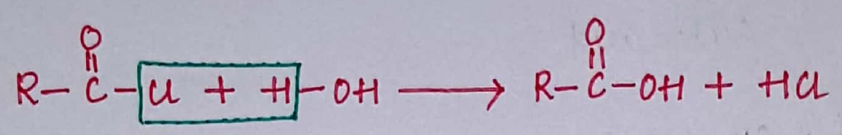


5. FROM GRIGNARD REAGENT :-

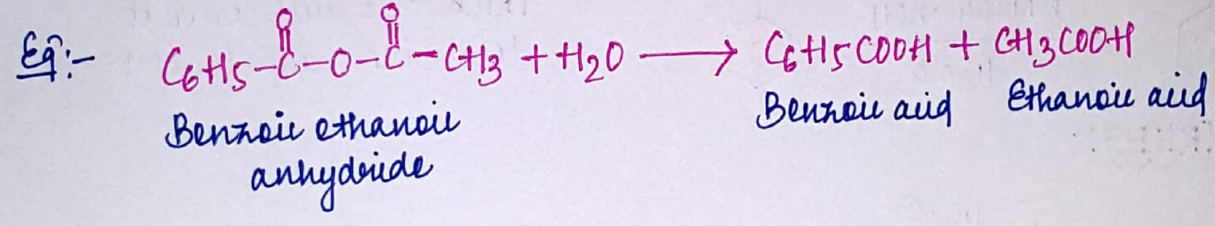
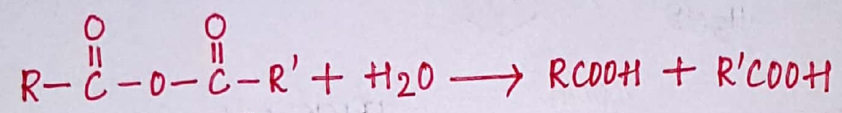
* It is the method to increase one C.



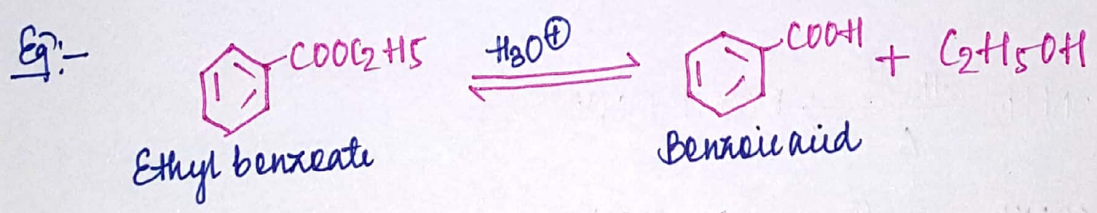
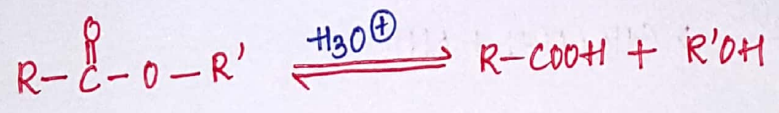
6. FROM ACYL HALIDES :-



7. FROM ANHYDRIDES :-



8. FROM ESTERS :-



PHYSICAL PROPERTIES :-

BOILING POINT :-

Carboxylic acid have higher boiling point due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

* The hydrogen bonds are not broken completely even in the vapour phase. Most carboxylic acid exist as dimer in vapour phase.

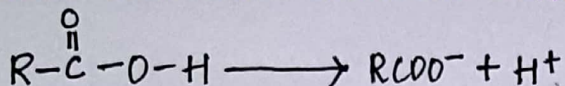
SOLUBILITY:-

* The solubility decreases with increase in number of carbon atoms.

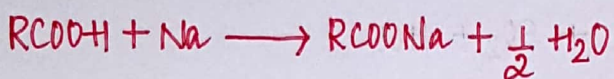
* Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part.

CHEMICAL REACTIONS:-

① REACTIONS INVOLVING CLEAVAGE OF O-H BOND:-



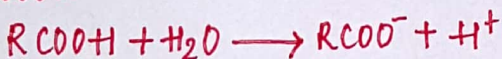
REACTION WITH Na:-



REACTION WITH H₂O:-



ACIDITY:-

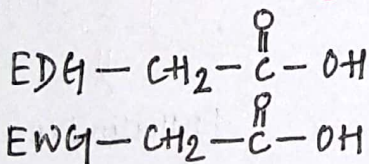


$$K_a = \frac{[RCOO^-][H^+]}{[RCOOH]}$$

$$K_a \propto [H^+] \propto \text{Acidity}$$

$$\Rightarrow pK_a \propto \frac{1}{K_a} \propto \frac{1}{\text{Acidity}}$$

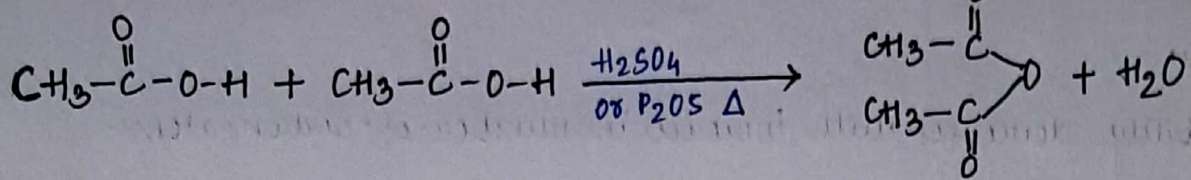
∴ Compounds which have more acidity value, their pKa is less.



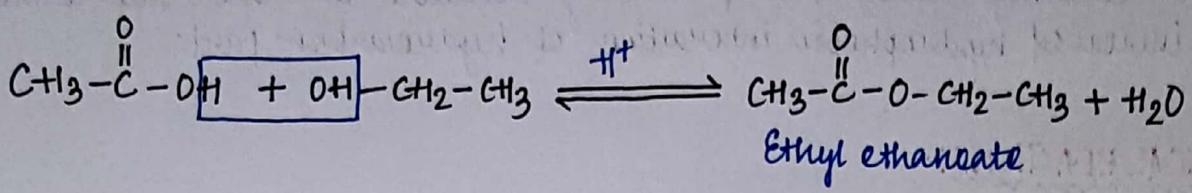
By putting EWG, O-H bond polarity ↑. Hence, H⁺ removal become easier. So EWG increases acidity.

② REACTIONS INVOLVING CLEAVAGE OF C-OH BOND:-

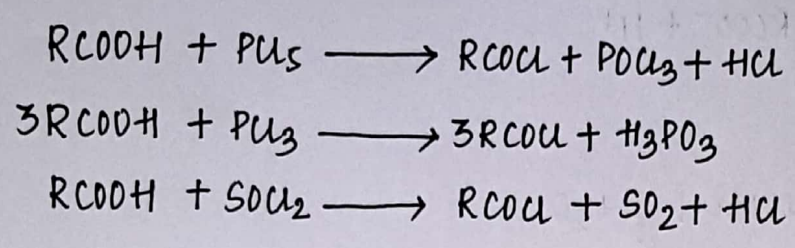
(i) FORMATION OF ANHYDRIDE:-



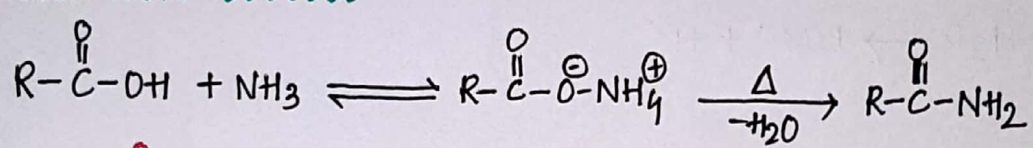
(ii) ESTERIFICATION:-



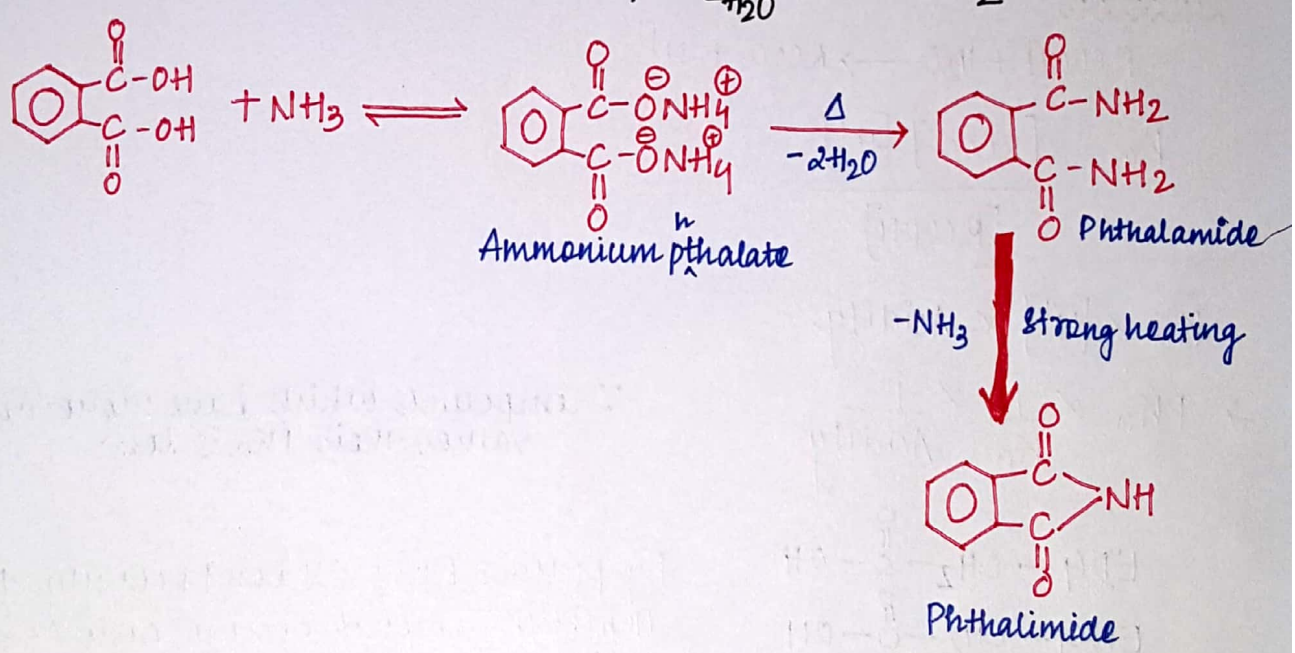
(3) REACTIONS WITH PCl_5 , PCl_3 and $SOCl_2$:-



(4) REACTION WITH AMMONIA:-

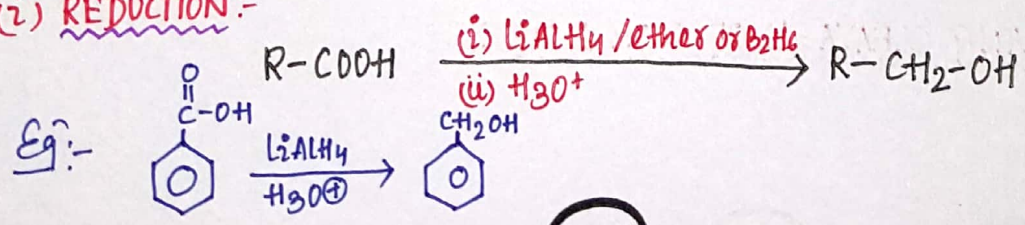


Eg:-



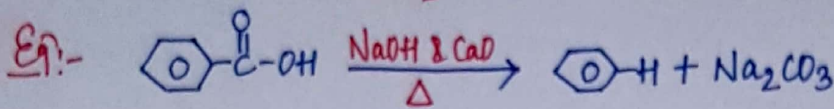
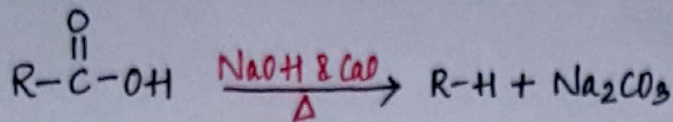
(3) REACTIONS INVOLVING $-COOH$ GROUP:-

(i) REDUCTION:-



② DECARBOXYLATION:-

In this method, one C is decreased from its parent carbon.

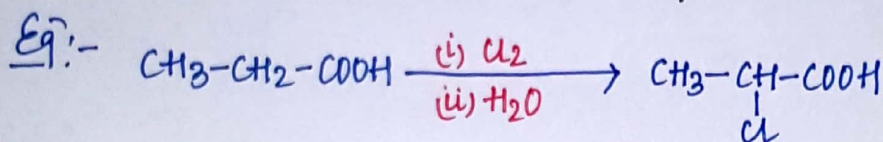
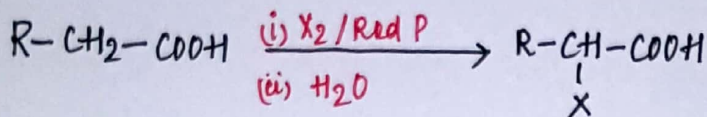


④ SUBSTITUTIONS REACTIONS IN THE HYDROCARBON PART:-

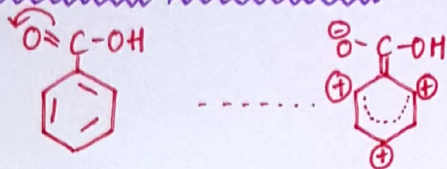
① HALOGENATION:-

HVZ REACTION:-

(Hell-Volhard-Zelinsky reaction)

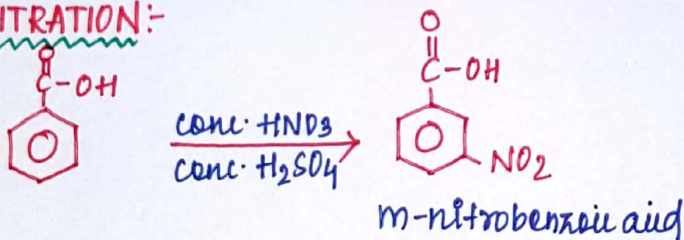


② ELECTROPHILIC SUBSTITUTION:-



COOH is an EWG. Hence it deactivates the benzene ring. Hence, next electrophile will attack at meta position.

(i) NITRATION:-



(ii) BROMINATION:-

