

CHAPTER No. 12ALDEHYDES AND KETONES.INTRODUCTION.

Organic compound containing  $-\overset{\overset{O}{\parallel}}{C}-$  (carbonyl group) are called carbonyl compounds. The carbonyl compounds include ALDEHYDES and KETONES.

ALDEHYDES. When carbonyl group is bonded to atleast one hydrogen, the compound is an ALDEHYDE. It occurs at the end of chain.

General formula of an aldehyde is  $R-\overset{\overset{O}{\parallel}}{C}-H$  where  $-R$  may be "H" or alkyl group.

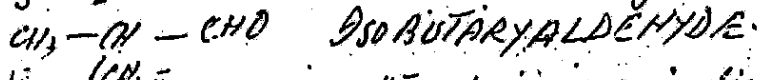
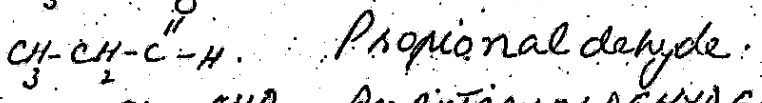
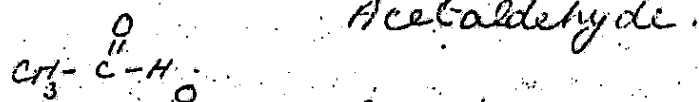
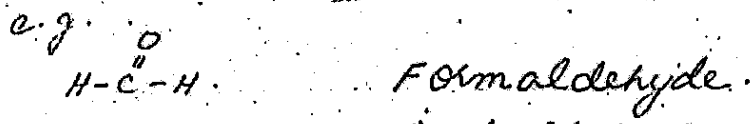
KETONES. When carbonyl group is bonded to two carbon atoms, the compound is called KETONE. It occurs within the chain.

General formula of ketones is  $R-\overset{\overset{O}{\parallel}}{C}-R$ .

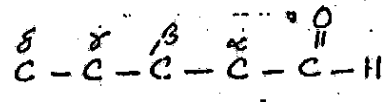
Homologous series of both aldehyde and ketone have same general formula  $C_nH_{2n}O$ . These compounds are present in naturally occurring compounds. Aldehyde group is present in most sugars. Ketone group is present in menthone and campher.

NOMENCLATURE.a. Nomenclature of ALDEHYDES.COMMON NAMES:-

Aldehydes are commonly named from the common names of carboxylic acid. The ending  $-ic$  acid is replaced by the word aldehyde. Position of other groups are indicated by Greek letters. Lettering starts on carbon next to  $-\overset{\overset{O}{\parallel}}{C}-$ .



Position of other groups on the chain are indicated by Greek letters ( $\alpha, \beta, \gamma, \delta$ ).

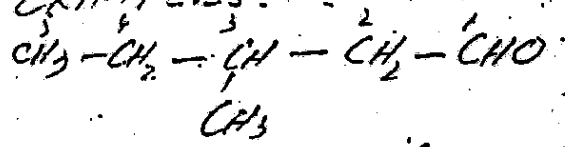


IUPAC NAMES.

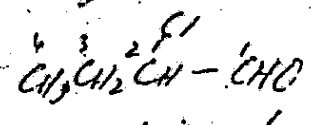
RULES OF NOMENCLATURE OF ALDEHYDES:-

- 1- Select longest carbon chain including aldehyde group -CHO
- 2- Write name of parent hydrocarbon.
- 3- Replace "e" of parent hydrocarbon by "al".
- 4- If there are some substituents, then number the longest c-chain starting from carbonyl carbon. mention position of each substituent.
- 5- Aromatic Aldehydes are not given IUPAC names.

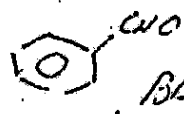
EXAMPLES:-



3-methyl pentanal



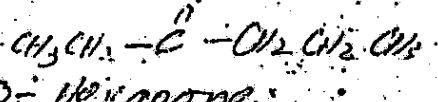
2-chloro butanal.



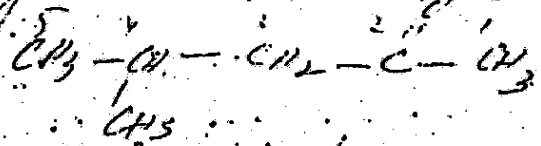
BENZALDEHYDE.

RULES OF NAMING KETONES

- 1- Select longest carbon chain including carbonyl group.
- 2- Write name of parent hydrocarbon.
- 3- Replace -e by -one.
- 4- Number carbon chain such that carbonyl group gets minimum possible number.
- 5- Aromatic ketones are not given IUPAC names.



3-hexanone



4-methyl-2-pentanone.



ACETOPHENONE.

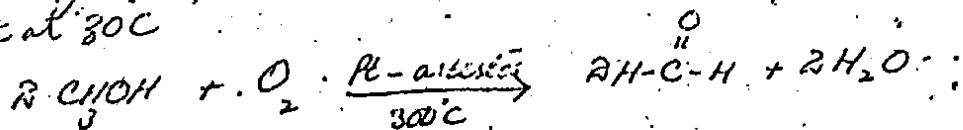
## PREPARATION OF ALDEHYDES.

Aldehydes are prepared by the oxidation of primary alcohols as:

### a. PREPARATION OF FORMALDEHYDE.

#### (i) - LABORATORY METHOD.

Formaldehyde is prepared in laboratory by passing a mixture of methyl alcohol (vap.) and air over platinised asbestos. Copper or silver may also be used as catalyst. Temperature is kept at 30°C.



Mix is drawn through methyl alcohol with the help of suction pump. Methyl alcohol is oxidized to formaldehyde. It is absorbed in water. This mixture is called FORMALIN.

FORMALIN is a mixture of 40%  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ , 8%  $\text{CH}_3\text{OH}$  and 52%  $\text{H}_2\text{O}$ .

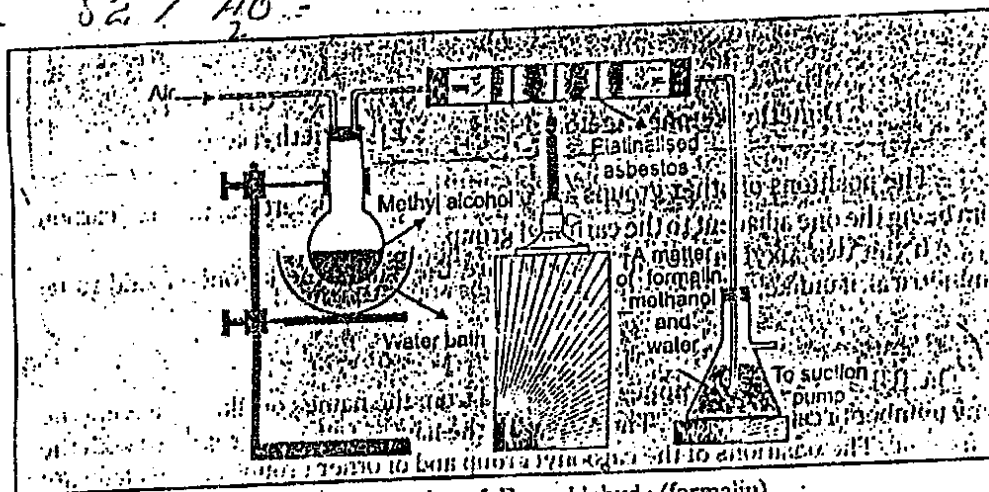
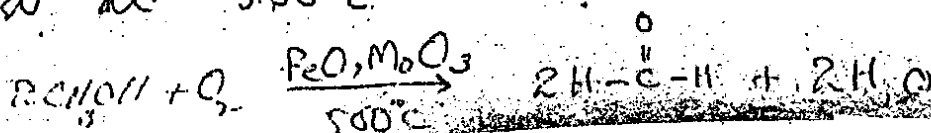


Fig. 12.1 Preparation of Formaldehyde (formalin)

#### ii - INDUSTRIAL METHOD.

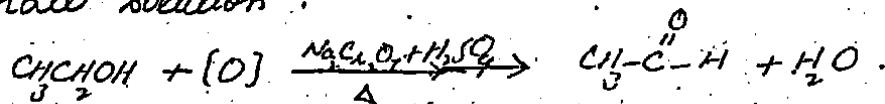
On industrial scale it is prepared by passing vapours of methanol and water air over iron oxide - Molybdenum oxide or silver catalyst at 500°C.



## b. PREPARATION OF ACETALDEHYDE.

### - LABORATORY METHOD.

Acetaldehyde is prepared in laboratory by oxidation of ethyl alcohol with acidified sodium dichromate solution.



Mixture of ethyl alcohol and sodium dichromate solution is added into boiling  $\text{H}_2\text{SO}_4$ . Vigorous reaction takes place and liquid acetaldehyde is produced. Liquid acetaldehyde is immediately distilled off to avoid the oxidation of acetaldehyde to acetic acid. Pure acetaldehyde is produced by redistillation.

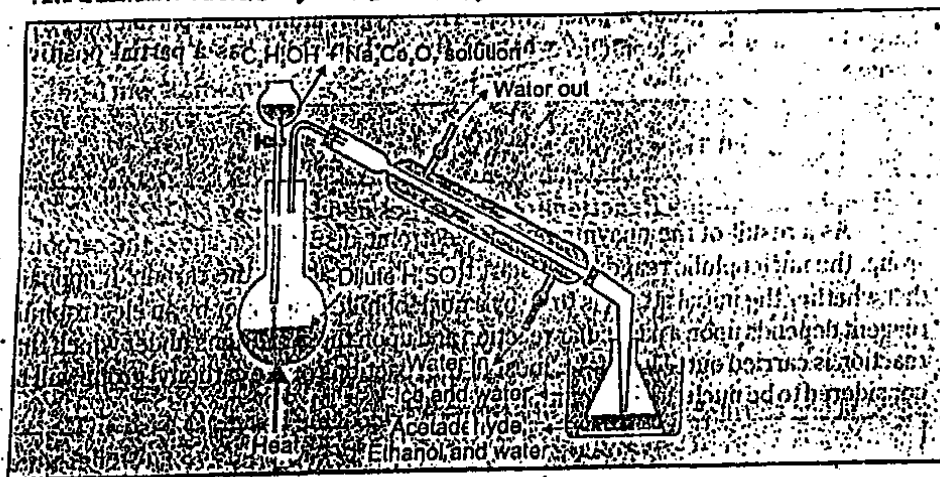
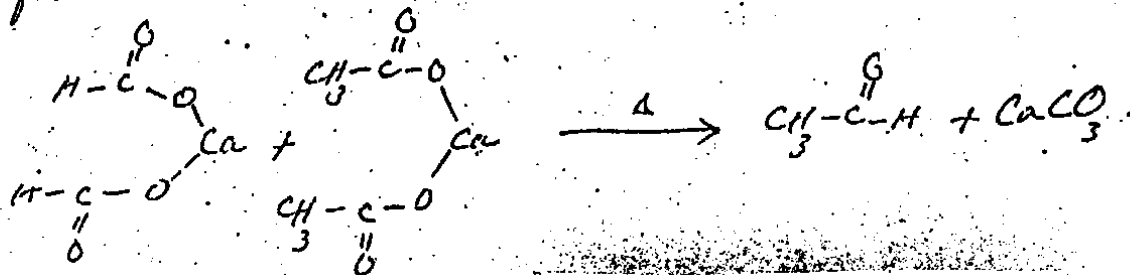


Fig. 12.2 Preparation of Acetaldehyde

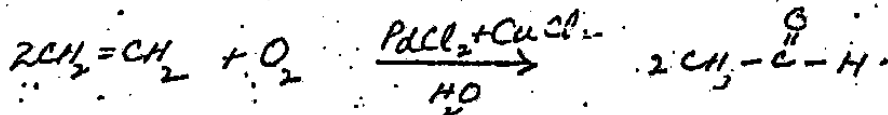
### FROM CALCIUM ACETATE.

Acetaldehyde can also be prepared by the dry distillation of mixture of calcium salts of formic acid and acetic acid.



## INDUSTRIAL PREPARATION

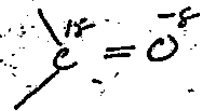
Acetaldehyde is prepared industrially by air oxidation of ethylene using palladium chloride catalysts with a cupric or chloride promoter.



## REACTIVITY OF CARBONYL GROUP

Carbonyl group has a  $\sigma$  and  $\pi$ -bonds. Thus it can undergo addition reactions.

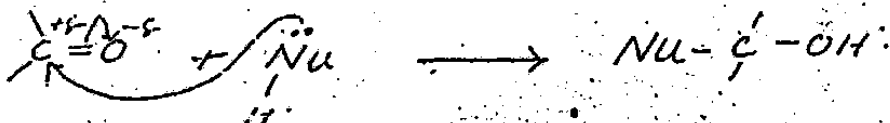
Oxygen atom is more electronegative. It has a partial negative charge on it as it tends to attract the  $\pi$  electrons to itself. This attraction makes carbonyl more polar group. Oxygen has partial -ve charge and is NUCLEOPHILIC. Whereas Carbon atom has a partial +ve charge and is electrophilic.



## NUCLEOPHILIC ADDITION REACTIONS OF ALDEHYDES AND KETONES.

Carbon has partial +ve charge and nucleophile can attack on carbon atom of carbonyl group.

Most of the reactions of carbonyl group will be considered to be nucleophilic addition reaction.



In these reactions -ve part of reagent combines with carbon of carbonyl group and +ve part goes to oxygen atom.

Nucleophilic addition reactions are catalysed by both acids and bases. Product is same in both cases.

A base catalyst increases the nucleophilic character of the reagent, while an acid catalyst promotes the nucleophilic attack by increasing the character of the carbonyl carbon.

## REACTIONS OF CARBONYL COMPOUNDS:

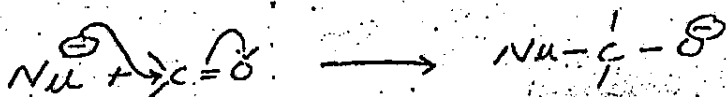
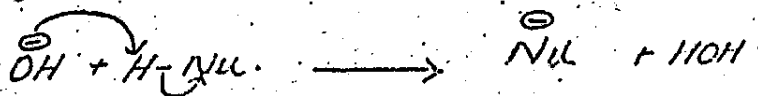
### NUCLEOPHILIC ADDITION REACTIONS:

The characteristic reactions of carbonyl compounds are nucleophilic addition reactions. These may be base or acid catalysed.

#### (i) - BASE CATALYSED ADDITION REACTION

Reaction of carbonyl compound with strong nucleophilic reagent - takes place in presence of base.

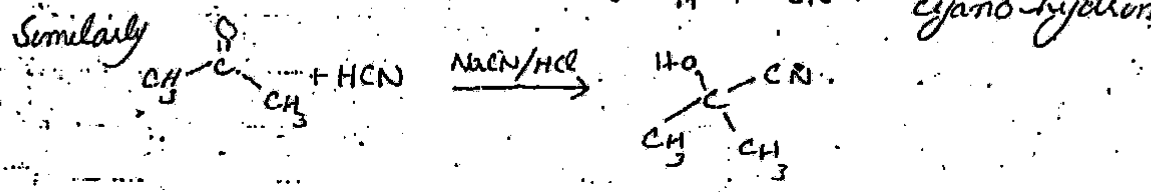
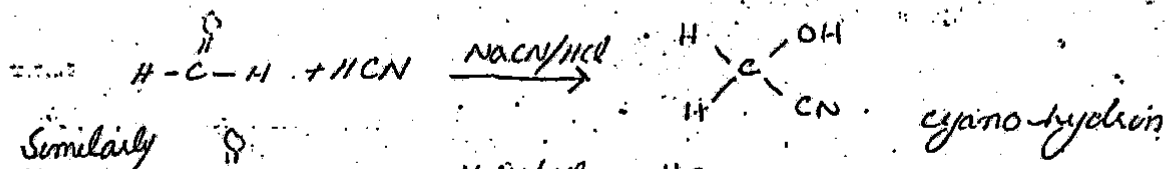
Base reacts with the reagent and generates the nucleophile. Addition takes place by the attack of nucleophile on the electrophilic carbon of carbonyl compound group. General mechanism is as



Base catalysed reactions of aldehyde and ketone are as

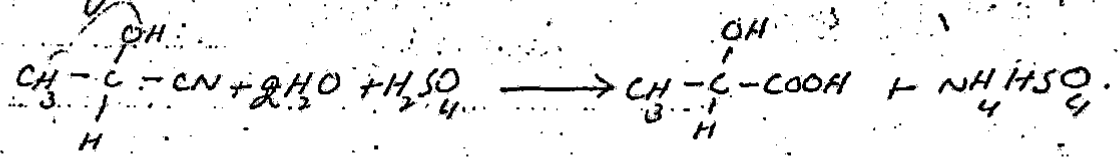
# 1. ADDITION OF HYDROGEN CYANIDE.

Addition of hydrogen cyanide to aldehydes or ketones form cyanohydrins. Reaction is carried out by adding mineral acid to aqueous solution of sodium cyanide. Acid generates HCN from NaCN.

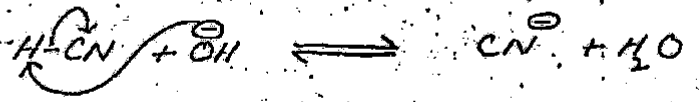


acetone cyanohydrin

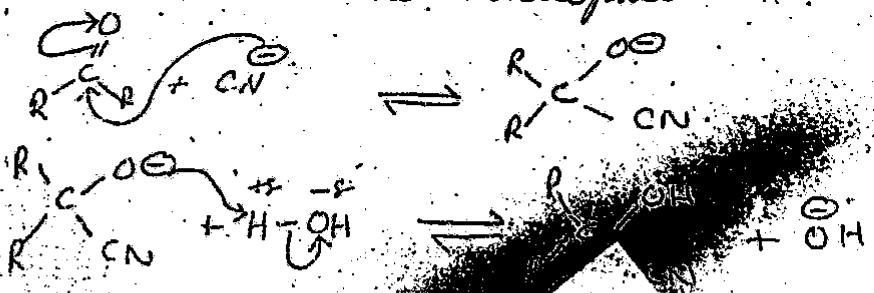
The cyano group,  $-C \equiv N$  on hydrolysis produce carboxylic acid.



Reaction is used in the synthesis of  $\alpha$ -hydroxy acids.  
**MECHANISM.**



Reaction is base catalysed because HCN has no lone pair on its carbon. Base generate  $CN^{\ominus}$  as above. This  $-CN^{\ominus}$  act as nucleophile.

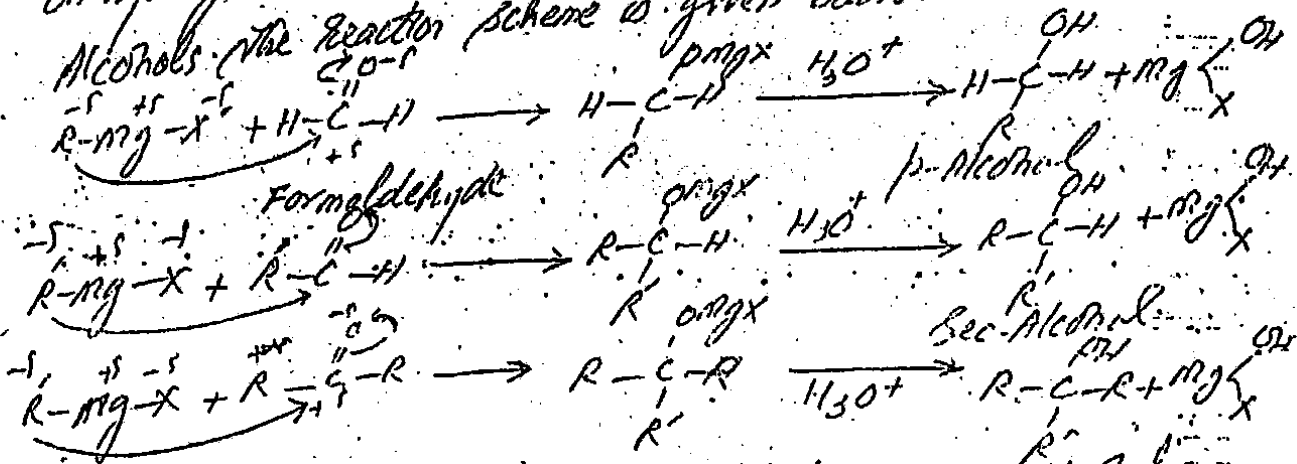


$OH^{\ominus}$  produced  
molecules

will react other HCN.

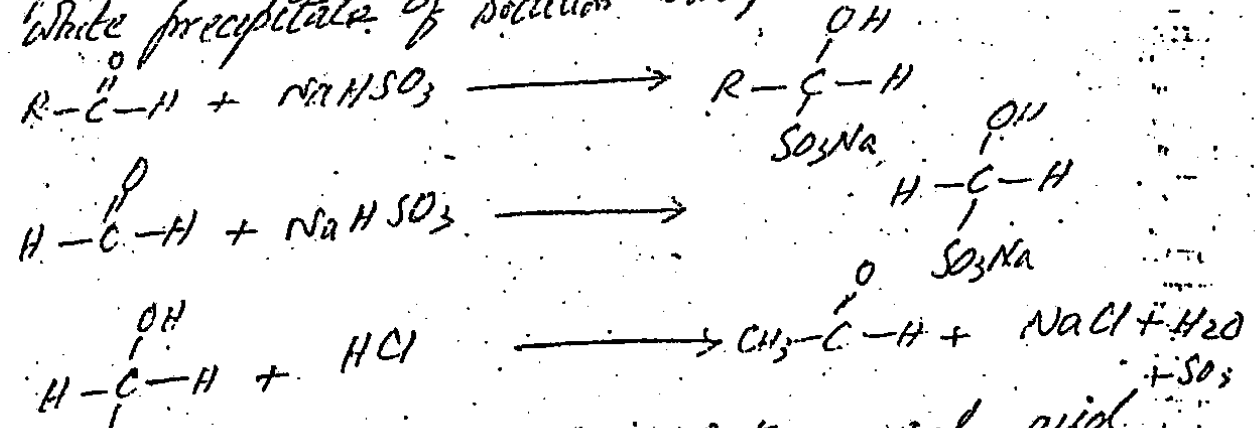
## ADDITION OF GRIGNARD REAGENT

Grignard reagent adds to aldehydes and ketones to form an adduct which on hydrolysis with dil mineral acid ( $\text{HCl}$ ,  $+ \text{H}_2\text{O}$ ) gives Alcohols. The reaction scheme is given below.



## ADDITION OF SODIUM BISULPHITE

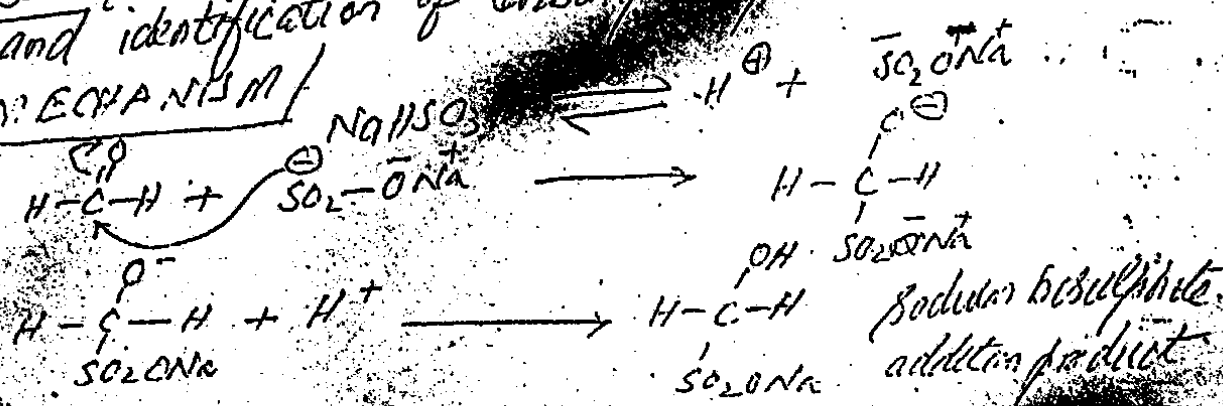
Aldehydes and small methyl ketones react with a saturated aqueous soln of sodium bisulphite to form a crystalline white precipitate of sodium bisulphite adduct.



Bisulphite on heating with dilute mineral acid ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ) regenerates parent aldehyde or ketone.

USE:- This reaction is used for separation, purification and identification of carbonyl compound.

### MECHANISM





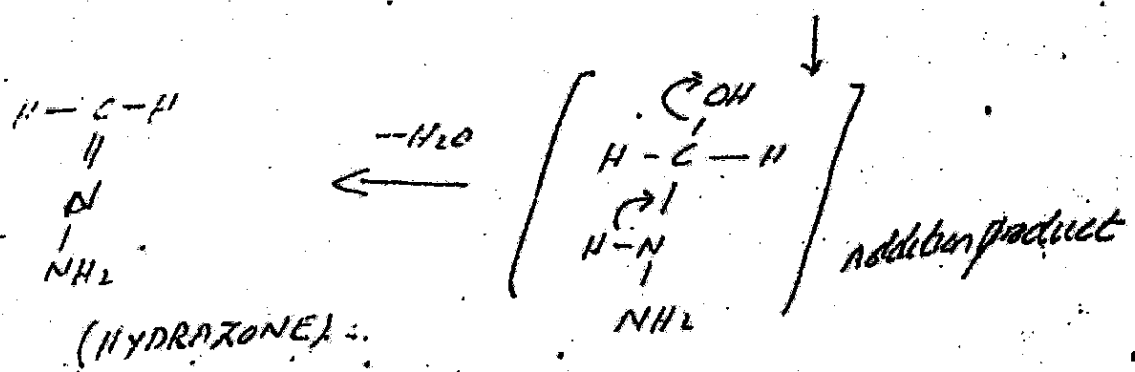
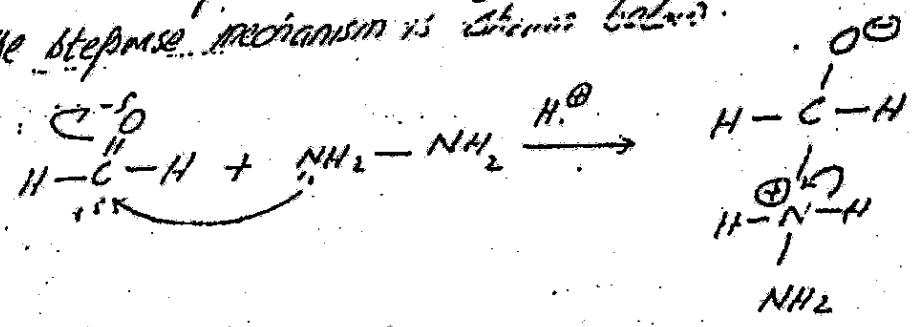
CONDENSATION REACTIONS:-

(1) REACTION WITH HYDRAZINE  $\text{NH}_2-\text{NH}_2$

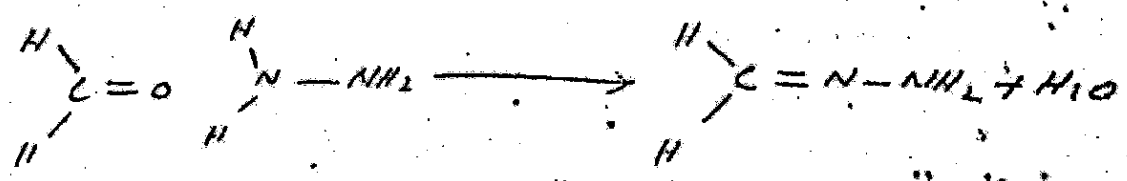
These are reactions which involve addition of two molecules with spontaneous loss of a small molecule (such as water) are

The reaction of hydrazine with formaldehyde involve nucleophilic attack of  $\text{NH}_2-\text{NH}_2$  on carbonyl carbon.

The stepwise mechanism is shown below.

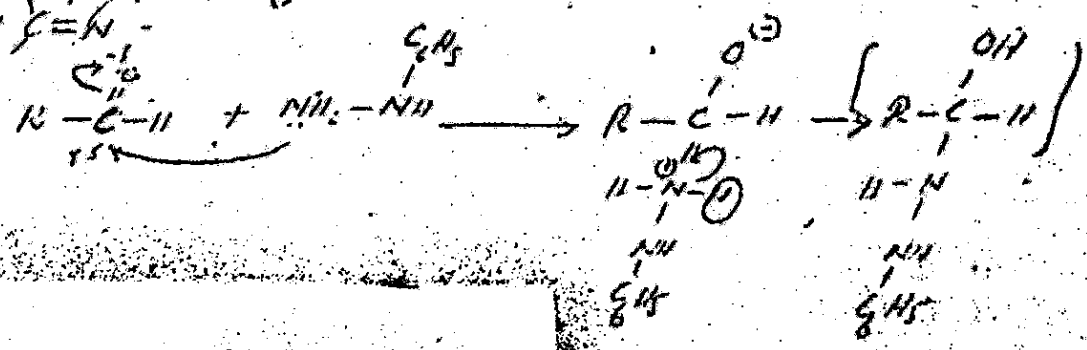


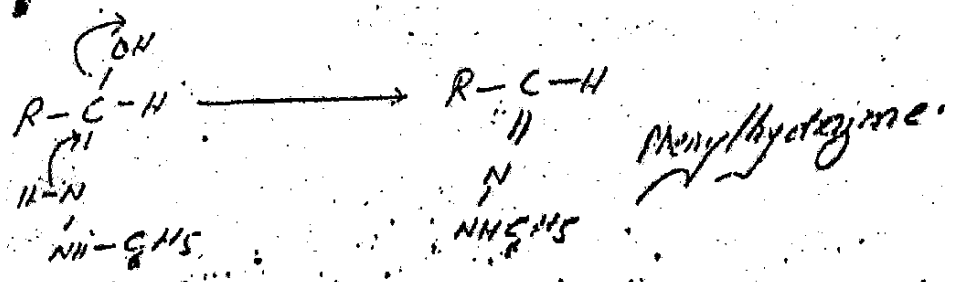
The net result is replacement of  $\text{C}=\text{O}$  by  $\text{C}=\text{NH}$



REACTION WITH PHENYL HYDRAZINE  $\text{C}_6\text{H}_5-\text{NH}-\text{NH}_2$

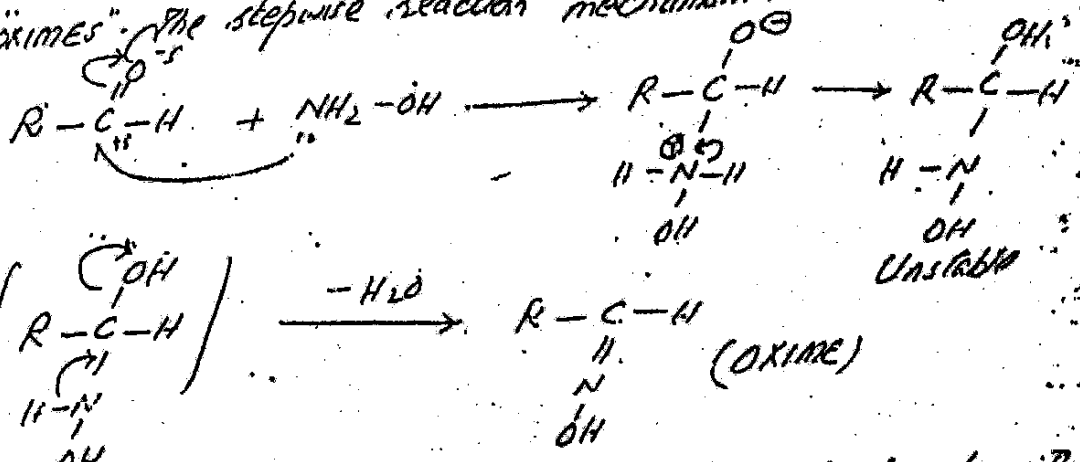
Aldehydes react with phenylhydrazine to produce products called phenylhydrazones. The net result is replacement of  $\text{C}=\text{O}$  by  $\text{C}=\text{N}$ .



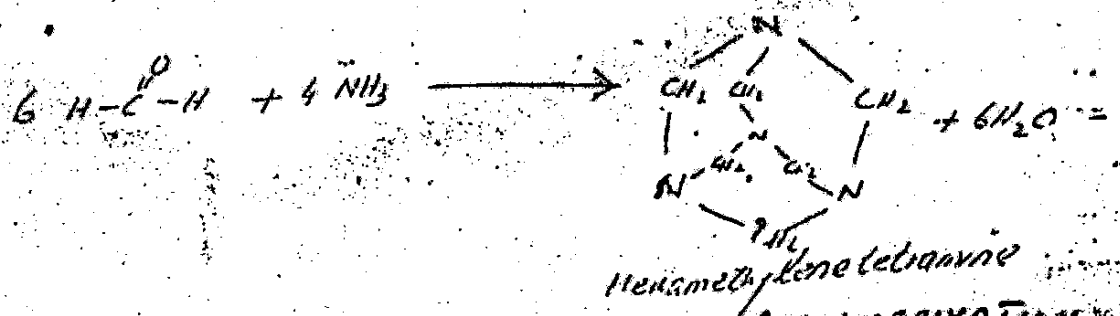


**REACTION WITH HYDROXAL AMINE:-**  $\text{NH}_2\text{OH}$

It is also a condensation reaction leading to formation of oximes. The stepwise reaction mechanism is shown below.



**REACTION WITH AMMONIA:-** Formaldehyde reacts with ammonia and produce hexamethylenetetramine (Urotropine). It is used for preparation of urinary antiseptic and also for manufacture of cyclonite (an explosive).



**IRITE OXIDATION, REDUCTION & POLYMERIZATION OF FORMALDEHYDE.**

**OXIDATION:-** Oxidation may be defined as

- (i) Addition of oxygen
- (ii) Removal of hydrogen or electron.

Formaldehydes is easily oxidized to formic acid on treatment with a mixture of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  (this mixture produce nascent oxygen).



## ALDOL CONDENSATION

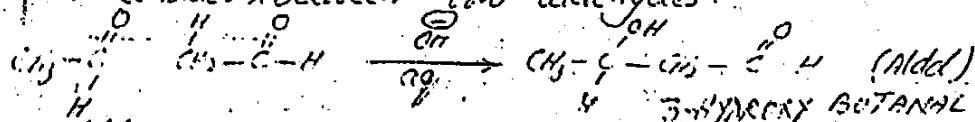
These aldehydes and ketones which possess at least one  $\alpha$ -hydrogen undergo a base catalyzed reaction called Aldol Condensation. The product of this condensation is a compound having an alcoholic and aldehydic group or ketonic group. The product is called Aldol or Keto-l. The condensation is usually followed by elimination of water molecule producing an  $\alpha,\beta$  unsaturated aldehyde or ketone.

The condensation is usually catalyzed by weak alkalies like  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ , dil.  $\text{NaOH}$  or alkoxide in low concentration.

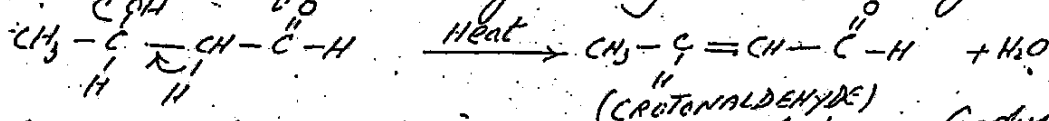
The aldol condensation can occur between two

- (i) Two same or different aldehydes or ketones
- (ii) An aldehyde and a ketone.

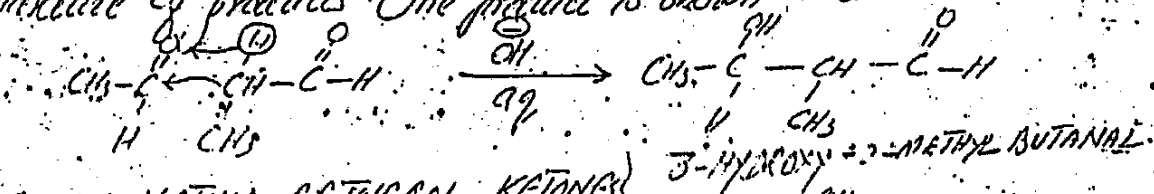
Let us consider  $\alpha$  between two aldehydes.



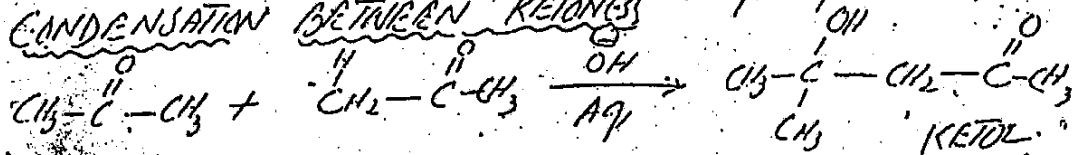
The aldol so formed undergoes dehydration on heating.



Two different aldehydes each having  $\alpha$ -hydrogen produce a mixture of products. One product is shown below.

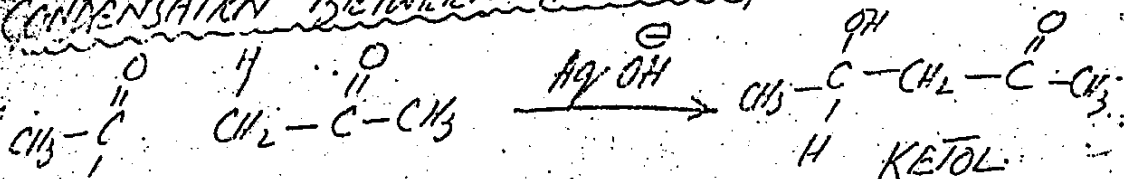


## CONDENSATION BETWEEN KETONES



Two different ketones will produce a mixture of products due to self condensation and cross condensation.

## CONDENSATION BETWEEN AN ALDEHYDE & KETONE

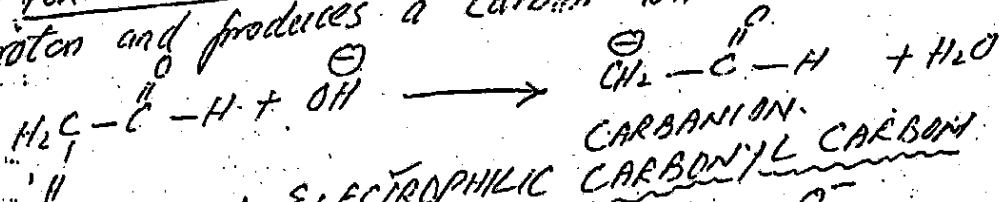


It will also produce a mixture of products due to self and cross condensation. (4-HYDROXY-2-PENTANONE)

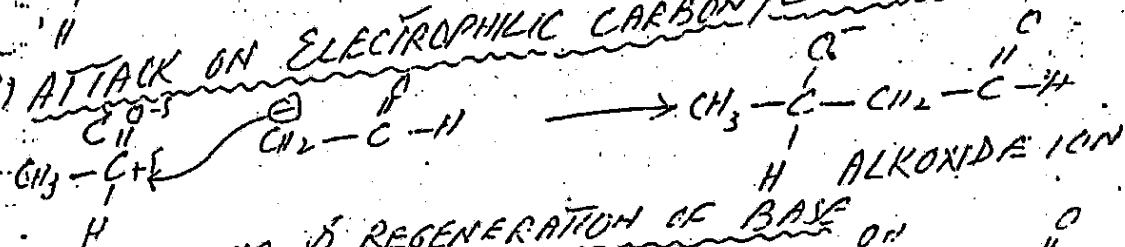
# MECHANISM OF ALDOL CONDENSATION

involves following steps:

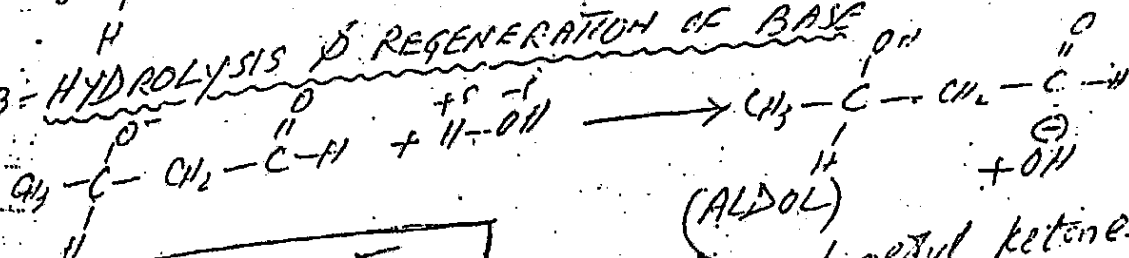
1) FORMATION OF ANION The hydroxide ion removes proton and produces a carbanion.



2) ATTACK ON ELECTROPHILIC CARBONYL CARBON

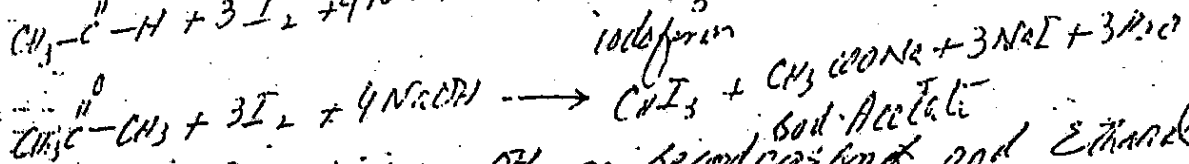
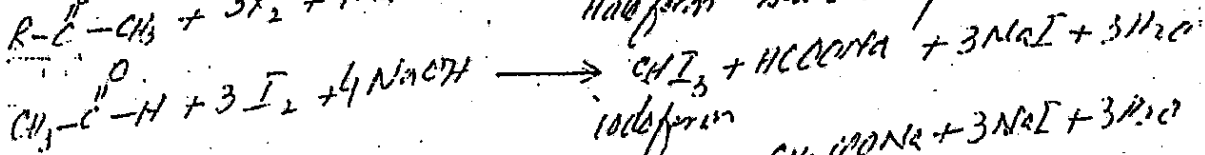
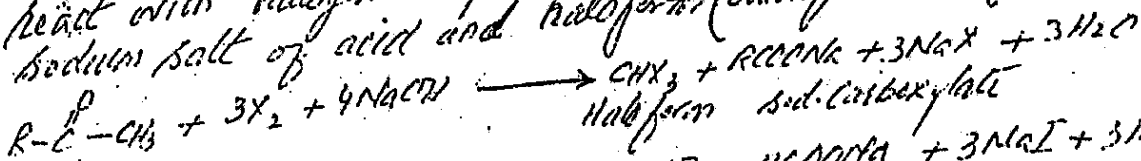


3) HYDROLYSIS & REGENERATION OF BASE

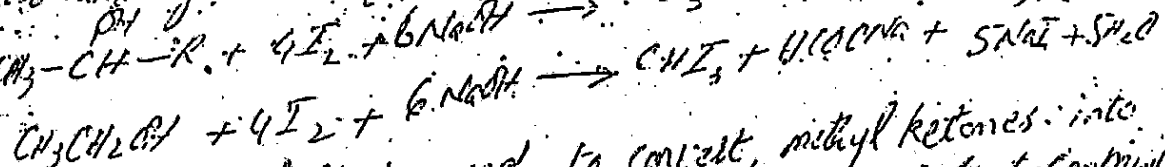
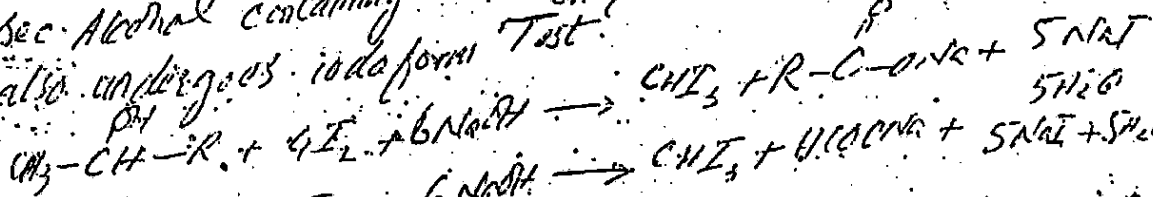


## HALOFORM REACTION

Acetaldehydes and methyl ketones react with halogen in presence of a base to form a sodium salt of acid and haloform (chloroform, bromoform, iodoform)



sec. Alcohol containing -OH on second carbon and Ethanal also undergoes iodoform Test.



APPLICATIONS: It is used to convert methyl ketones into carboxylic acids containing one carbon less than parent compound

2) It is used to distinguish between methanol and Ethanal, Formaldehyde & Acetaldehyde, methyl ketone & other Ketone, Acetaldehyde & other Aldehydes, ETHANOL & OTHER ALCOHOLS.

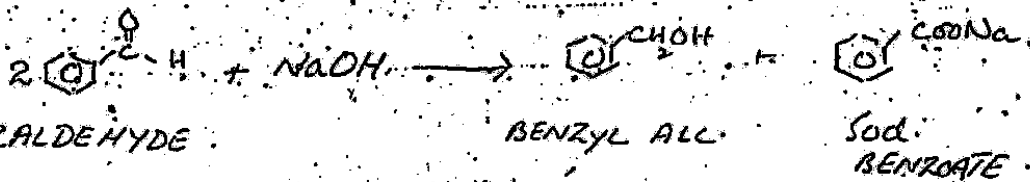
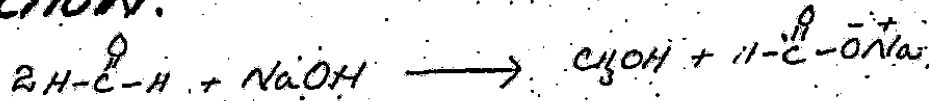
# CANNIZZARO'S REACTION.

Aldehydes having no  $\alpha$ -hydrogen undergo base catalysed self-oxidation reduction reaction. This is called CANNIZZARO'S REACTION.

Two molecules of the aldehyde are involved, one molecule is converted into corresponding alcohol (reduction product) and the other into salt of carboxylic acid (oxidation product).

Reaction is carried out with 50% aq. NaOH at room temperature.

## REACTION.



BENZALDEHYDE

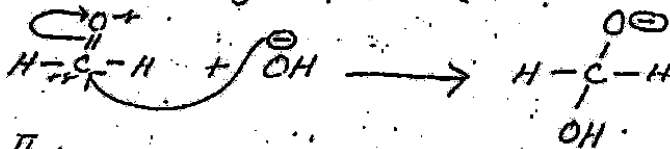
BENZYL ALC.

Sod. BENZOATE

## MECHANISM.

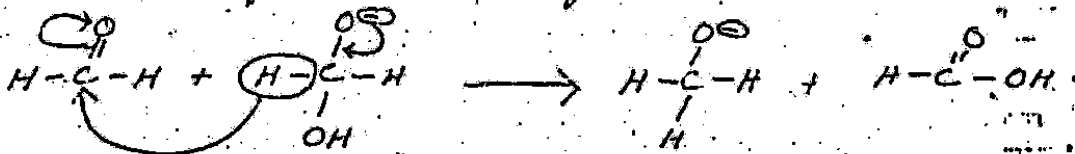
### STEP-I

Hydroxide anion acts as nucleophile and attacks on carbonyl carbon.



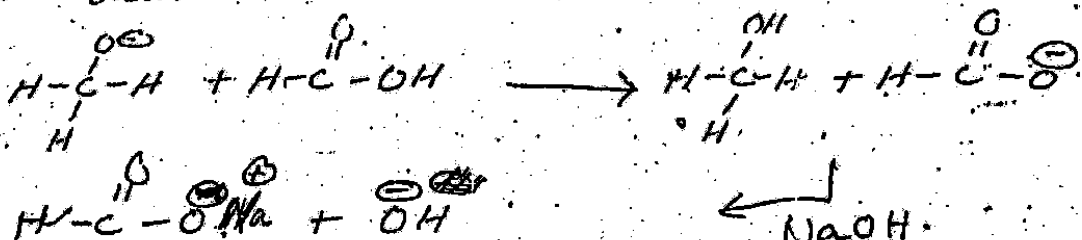
### STEP-II

Anion formed transfers  $\text{H}^+$  to second molecule.



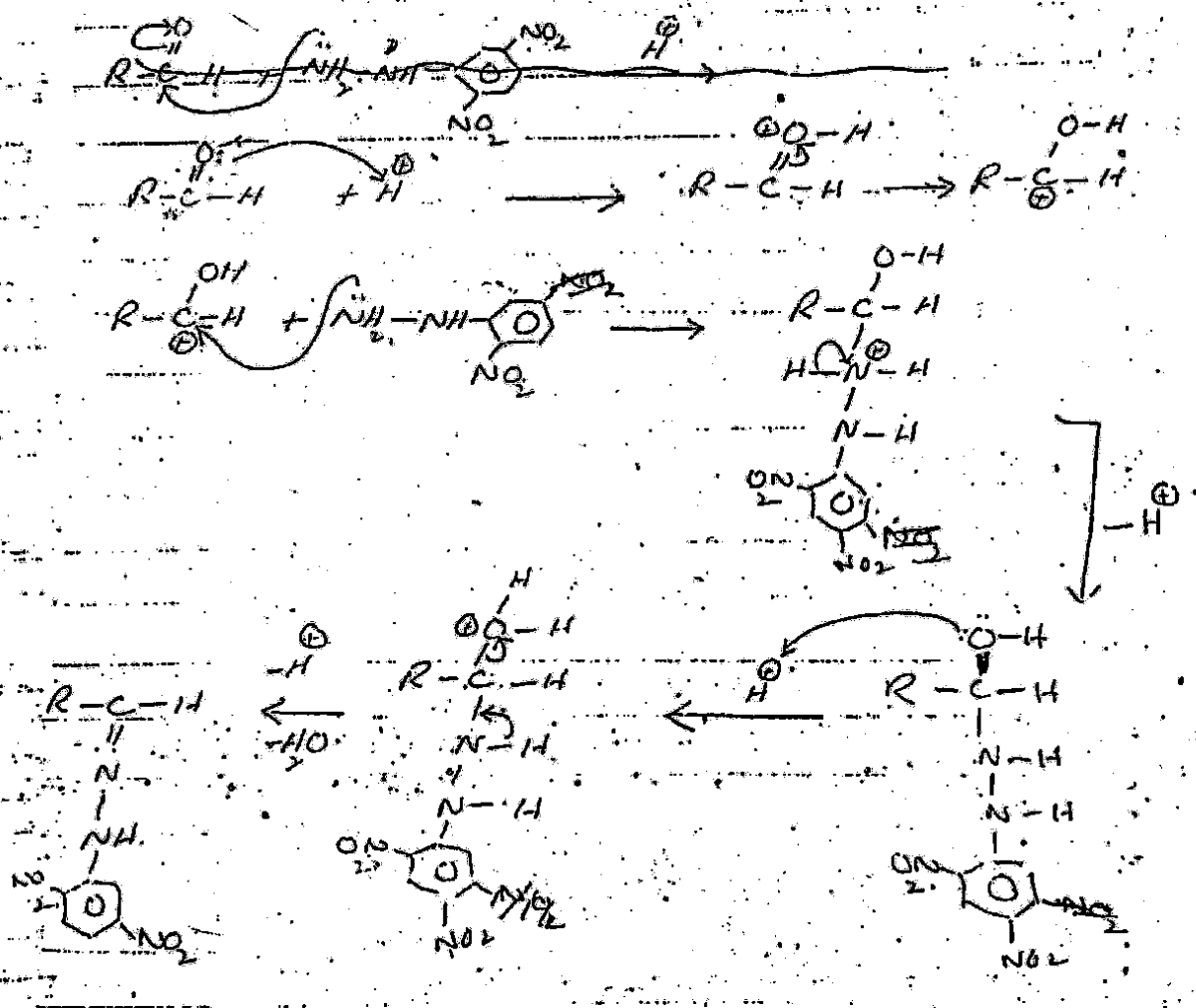
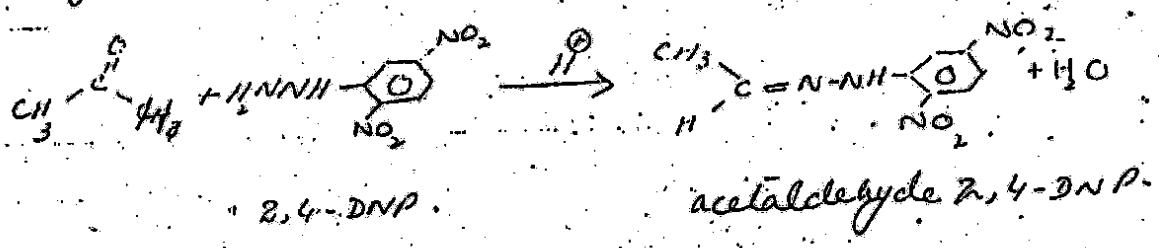
### STEP-III

$\text{CH}_3\text{O}^-$  acts as base and abstracts proton from acid



# REACTION WITH 2,4-DNP.

Aldehydes and ketones react with 2,4 dinitrophenyl hydrazine to form 2,4 dinitrophenyl hydrazones in presence of an acid.



## 2,4-dinitrophenyl hydrazone.

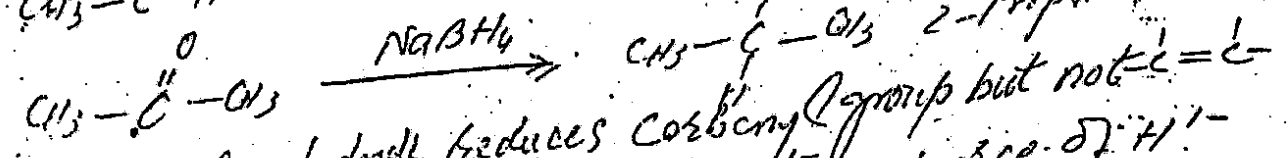
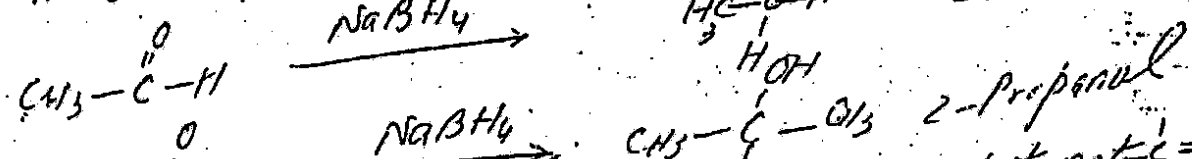
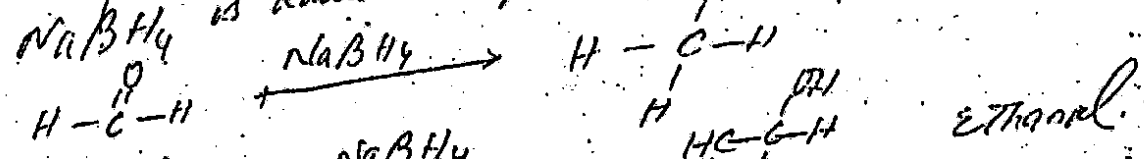
Hydrazones are usually yellow or orange crystalline solids. This reaction is used to identify carbonyl group in a compound.

WRITE NOTE ON REDUCTION OF CARBONYL COMPOUND

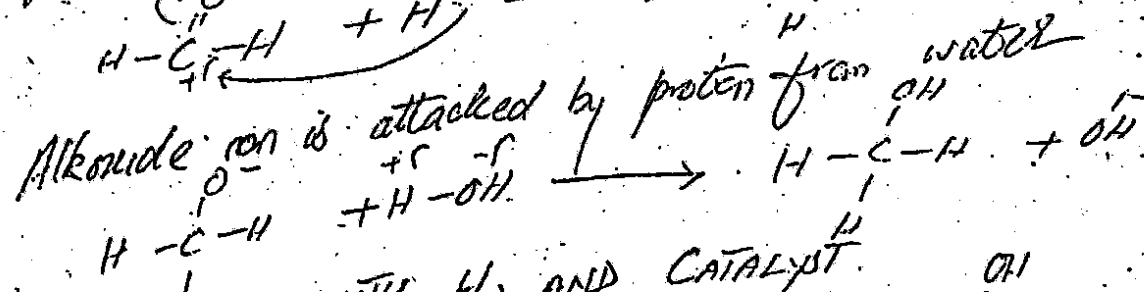
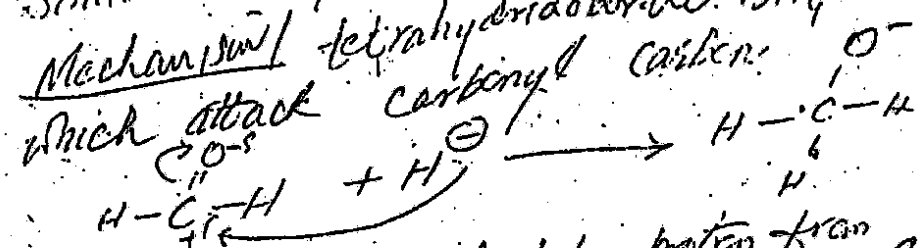
Carbonyl group is reduced to alcoholic group. Aldehydes are reduced to p-Alcohols while ketones are reduced to sec. Alcohols. There are different methods of reduction.

REDUCTION WITH SODIUM BOROHYDRIDE

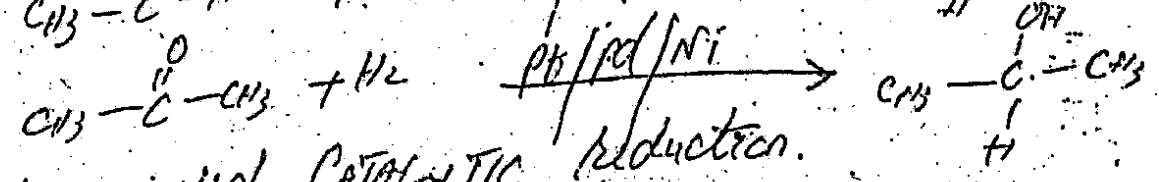
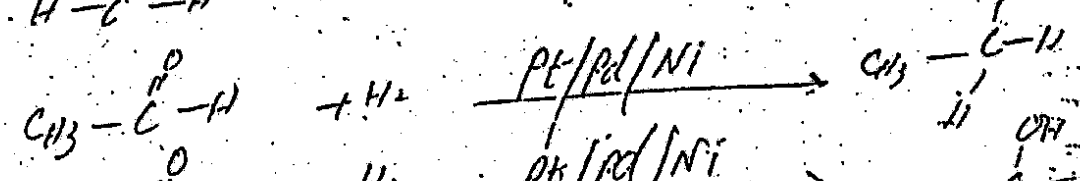
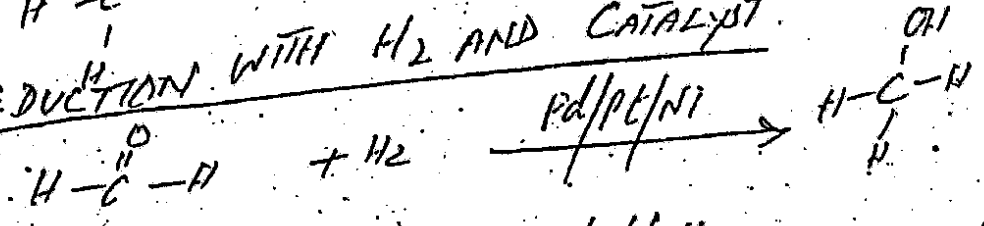
Aldehydes or ketones are reduced to Alcohols when NaBH<sub>4</sub> is added to aq. sol. of carbonyl compound.



Sodium Borohydride reduces carbonyl group but not C=C. Mechanism: tetrahydridoborate. BH<sub>4</sub> is source of H<sup>-</sup> which attack carbonyl carbon.



REDUCTION WITH H<sub>2</sub> AND CATALYST



Above called CATALYTIC reduction.



## IDENTIFICATION OF $\overset{\text{O}}{\parallel}{\text{C}}$ -COMPOUNDS.

Aldehydes and ketones can be detected by following tests

### i. 2,4 DNP TEST.

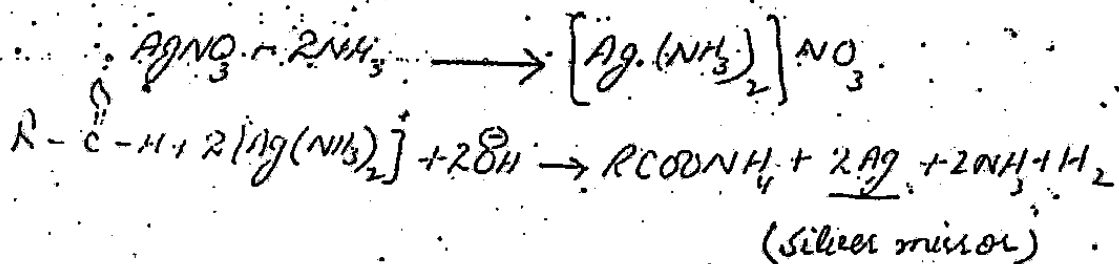
Aldehydes and ketones form a yellow or red precipitates with 2,4 dinitrophenyl hydrazine solution.

### ii. SODIUM BISULPHITE TEST.

Aldehydes and methyl ketones form a crystalline white precipitates with saturated sodium bisulphite solution.

### iii. TOLLEN'S TEST.

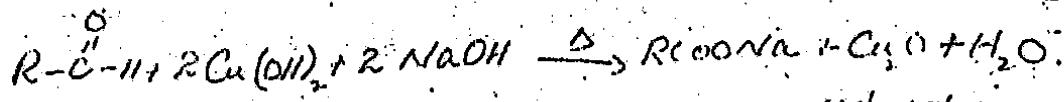
Aldehydes form silver mirror with Tollen's reagent (ammoniacal silver nitrate solution). Tollen's reagent is added to solution of aldehyde in a test tube and warm. Silver mirror is formed on the inside of the test tube.



Ketones don't give this test.

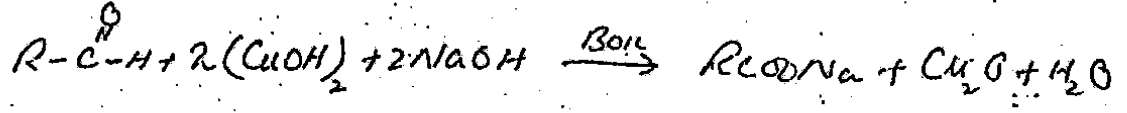
### iv. FEHLING'S SOLUTION TEST. (alt. CUPRIC YACINATE)

Aliphatic aldehydes form brick-red precipitates with Fehling's solution. To the solution of aldehyde add Fehling's solution and boil. Brick red ppt of  $\text{Cu}_2\text{O}$  is formed. Ketones don't give this test.



V- **BENEDICT'S TEST:** (ALKALINE CURRIC CITRATE COMPLEX ION)

Aliphatic aldehydes form a brick-red precipitate with Benedict's solution.



(Brick red)

VI- **SODIUM NITROPRUSSIDE TEST.**

Ketones produce wine red or orange red ppt. colour on adding alkaline sod. nitroprusside solution dropwise.

Aldehydes do not give this test.

**WRITE IMPORTANT USES OF FORMALDEHYDE.**

Formaldehyde is a very important chemical. Some important uses of formaldehyde has been discussed below.

(1) **FORMALIN:** A 40% aqueous solution of formaldehyde containing 8% methyl alcohol is called Formalin. It is used to prepare synthetic resins.

(2) Formalin is used for preparation of bakelite.

(3) It is also used as disinfectant, antiseptic, sedative agent.

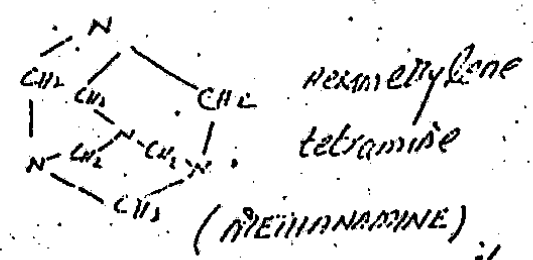
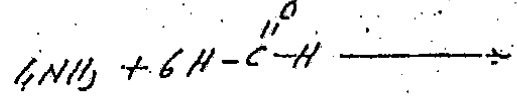
(4) Formalin is used to preserve biological specimen.

(5) Formalin is used to prepare water insoluble gelatin.

(6) Formaldehyde is used to prepare antitoxic vaccines. The alive pox viruses are rendered harmless by formaldehyde. (These harmless viruses are injected as vaccines)

(7) Formaldehyde is used to prepare dyes and dyestuffs.

(8) It is used to prepare cyclonite which is an explosive.



Melamine on treatment with conc. NITRIC ACID PRODUCES CYCLONITE WHICH IS AN EXPLOSIVE

It is used to prepare Formamint (Formaldehyde + Lactose)<sup>19</sup> used as throat lozenges

It is used as decolorizing agent in vat dyeing.

It is used in making dyes such as indigo, para-resorcinol

### USES OF ACETALDEHYDE

1- It is used to prepare acetic acid, Acetic anhydride, n-butanol, ethanol, 2-ethyl hexanol, vinyl acetate, paraldehyde, ethyl acetate.

2- It is used to prepare Acetaldehyde ammonia, used as rubber Accelerator.

3- It is used to make chloral hydrate, ethanol trimer, tetramer. Chloral hydrate, and ethanol trimer both are used as hypnotic drugs whereas ethanol tetramer is used as slug poison.

4- It is used as antiseptic inhalant in nasal infections.

5- It is used in silvering of mirrors.

6- It is used to prepare phenolic resins and synthetic drugs.

### ADDITION OF ALCOHOL TO CARBONYL COMPOUNDS

Aldehydes and Ketones when treated with Alcohols in presence of ~~the~~ dry acid (HCl) they produce acetals and Ketals. The reaction is used to protect Carbonyl group against Alkaline oxidizing agents. The acetal on hydrolysis regenerates Aldehyde or Ketone.

