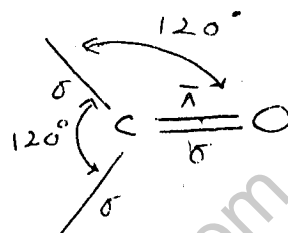
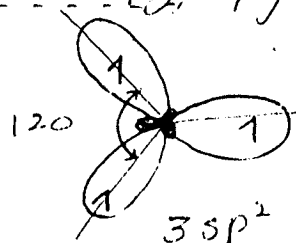
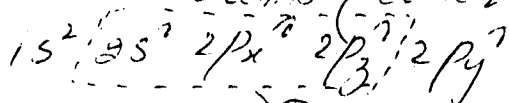


# B.Sc. (Organic) ALDEHYDES AND KETONES.

## STRUCTURE AND REACTIVITY:

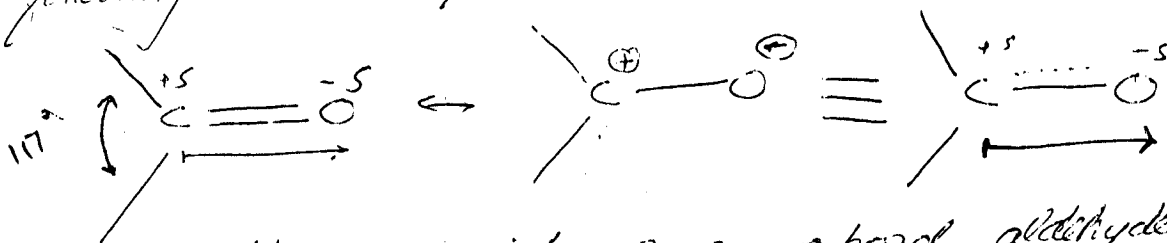
The carbonyl carbon of aldehydes and ketones is  $sp^2$  hybridized. Thus three  $sp^2$  hybridized orbitals are produced which are situated at an angle of  $120^\circ$  from each other. These three hybrid orbitals are planar and used in sigma bond formation.

One  $sp^2$  is used to form sigma bond with oxygen and other two are used to form sigma bonds with two more atoms (either hydrogen or carbons).



The unhybridized  $p$ -orbital of carbon overlaps with  $p$ -orbital of oxygen to form a  $\pi$ -bond. Thus there is a double bond between C & oxygen.

Due to greater E.N. of oxygen, it acquires  $\delta^-$  charge and carbon acquires  $\delta^+$  charge. Thus carbon is an electrophilic centre (electron deficient) and oxygen is electron rich. The  $C=O$  is polarized having dipole moment (2.2 to 3.0 D). Its polar nature can also be explained on the basis of following canonical forms.



As a result of polarity of  $C-O$  bond aldehydes and ketones have higher B.P. than corresponding hydrocarbons.

The carbonyl carbon has +ve charge thus it acts as electrophile and most of reactions of aldehydes and ketones are due to attack of nucleophile on carbonyl carbon. The reactivity of carbonyl carbon towards nucleophilic addition is mainly influenced by following factors.

- (i) Electronic factors (ii) Steric factors.

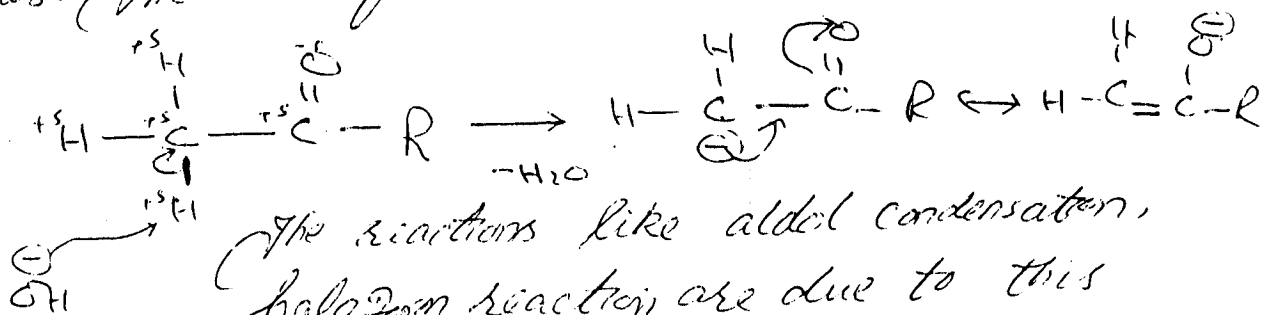
ELECTRONIC FACTORS:-

The ease of nucleophilic attack on carbonyl carbon depends upon magnitude of positive charge on carbonyl carbon. The more is the +ve charge on carbonyl carbon the more easily the nucleophile will attack carbonyl carbon & vice versa.

-I EFFECT | If an electron withdrawing group (-I effect) like  $-NO_2$ ,  $-Cl$ ,  $-F$  etc is present on  $\alpha$ -carbon it will produce more positive charge on carbonyl carbon and make it more liable to attack of nucleophile and reactivity is increased.

+I EFFECT | If an electron donating group like  $-R$  group is attached on  $\alpha$ -carbon it will decrease the positive charge on carbonyl carbon make it less susceptible to attack of nucleophile. Thus reactivity is decreased.

$\alpha$ -HYDROGEN | Due to deficiency of electron on carbonyl carbon, the hydrogen on  $\alpha$ -carbon gets slightly acidic. It can be removed by a strong base. The anion formed is stabilized by resonance.



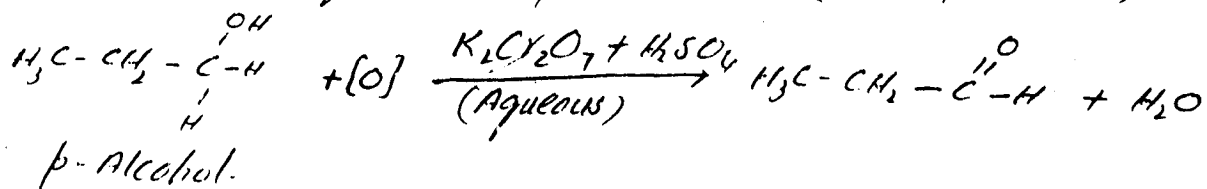
The reactions like aldol condensation, haloform reaction are due to this acidic hydrogen.

## ALDEHYDES AND KETONES: 152

Q: Discuss some general methods of preparation of Aldehydes and Ketones:-

Ans:- PREPARATION OF ALDEHYDES:- Some common methods of preparation of aldehydes are given below.

Oxidation of p-Alcohols:- p-Alcohols on oxidation produce aldehydes. The most common oxidizing agent is potassium dichromate in aqueous sulphuric acid ( $K_2Cr_2O_7 + H_2SO_4$ ).

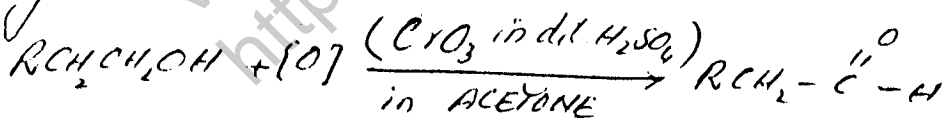


DISADVANTAGE:- Aldehyde produced in this reaction is further oxidized to carboxylic acid, because aldehydes are more easily oxidized as compared to carboxylic acids.

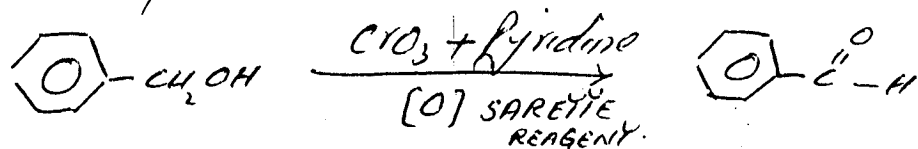
HOW TO AVOID OXIDATION OF ALDEHYDE:-?

There are two common reagents which stop oxidation at aldehyde stage.

(i) JONES REAGENT:-  $CrO_3$  in dil  $H_2SO_4$  in acetone as medium (NON-AQUEOUS MEDIUM) stop oxidation at aldehyde stage



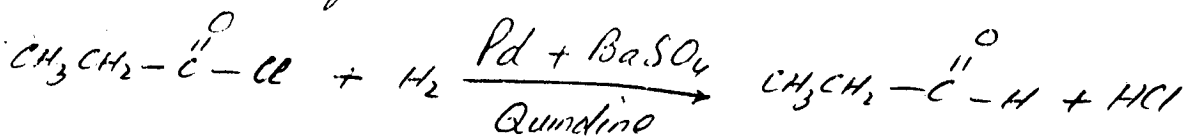
(ii) SARETT REAGENT The oxidizing agent used in this process is  $CrO_3$  in pyridine as solvent.



Rosenmund Reduction:- (REDUCTION OF ACID CHLORIDES)

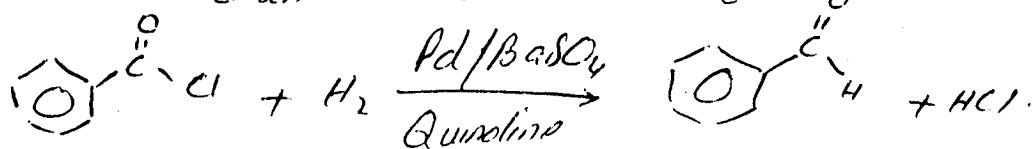
In this method acid chlorides are reduced to aldehydes by catalytic reduction by hydrogenation. The catalyst used is Palladium deposited on barium sulphate poisoned

with lead or quinoline

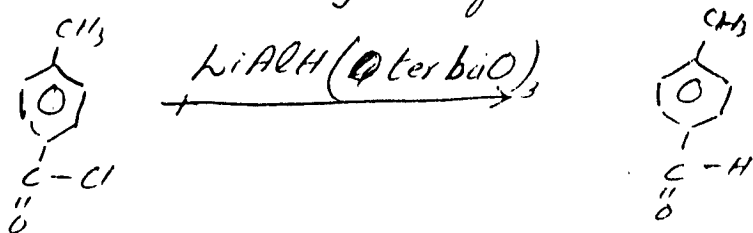


Aldehyde.  
(Propanal)

ADVANTAGE: Acid chlorides are reduced to aldehydes selectively. The product formed (Aldehyde) is less reactive than acid chloride itself.

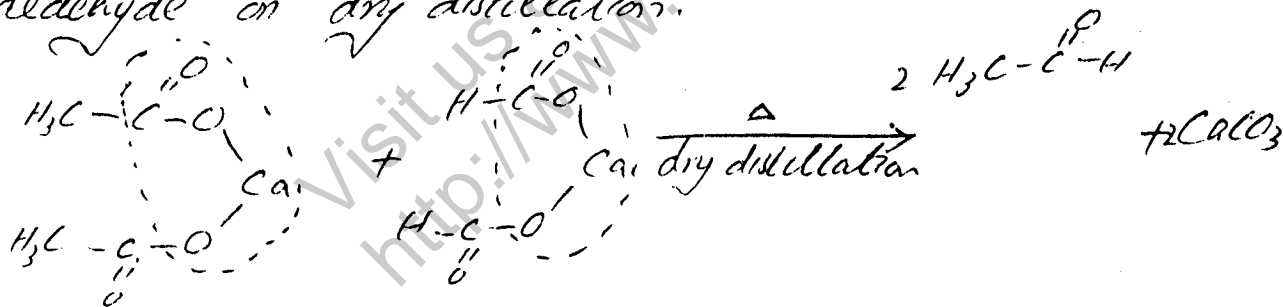


REDUCTION WITH tri-ter butyl <sup>lithium</sup> aluminium hydride  $\text{LiAlH}(\text{tert} \text{C}_4\text{H}_9)_3$  also produces aldehydes from acid chloride.



**FROM CALCIUM SALTS OF CARBOXYLIC ACIDS**

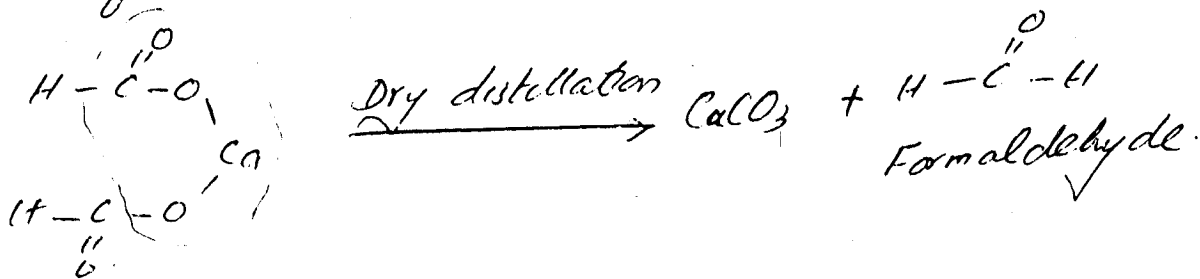
A mixture of calcium salt of formic acid (calcium formate) and calcium salt of any other acid produces aldehyde on dry distillation.



calcium acetate

calcium formate

Formaldehyde and acetate are produced as byproduct. Formaldehyde can be prepared by dry distillation of calcium formate.

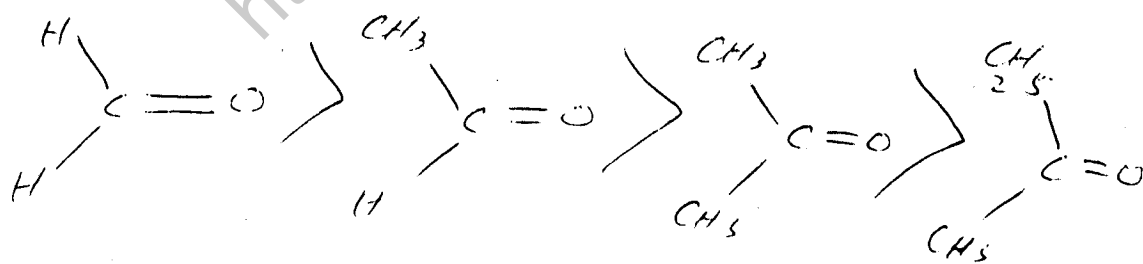


STERIC FACTORS

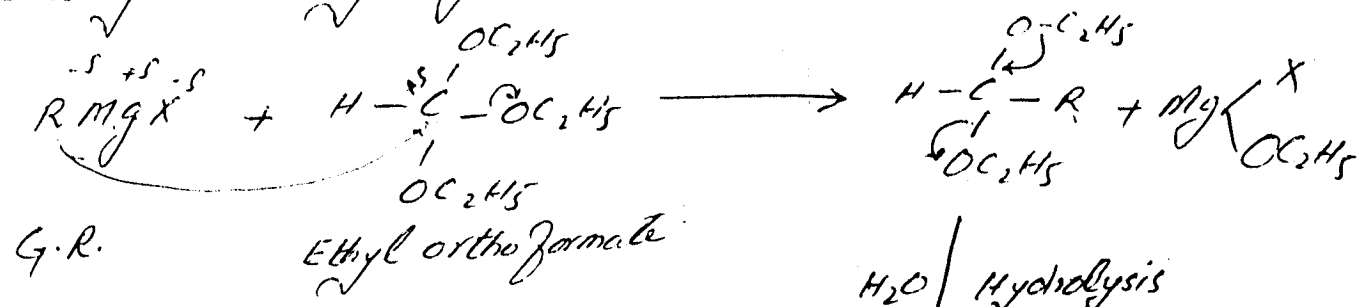
The bulky groups attached to carbonyl carbon decrease reactivity of the aldehydes & ketones. It is due to the fact that carbonyl carbon is  $sp^2$  hybridized having  $120^\circ$  bond angle. The atoms or groups attached to carbonyl carbon are planar. When a nucleophile attacks the carbonyl carbon, its hybridization changes from  $sp^2$  to  $sp^3$  (tetrahedral). Thus the groups bonded to carbonyl carbon get closer to each other in transition state. If there are bulky groups they cause more steric hindrance and destabilize the transition state. Thus reactivity of carbonyl group is decreased due to bulky groups.

Cyclic ketones are more reactive than open chain ketones because in cyclic system there is rigidity or ~~restriction~~ in cyclic structure while open chain structures have greater freedom of motion.

This order of reactivity of aldehydes and ketones is

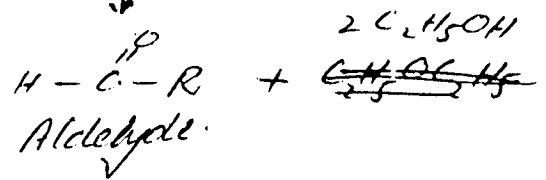


**FROM GRIGNARD REAGENT:-** Grignard reagent on reaction with ETHYL ORTHOFORMATE  $HC(OC_2H_5)_3$  produces aldehyde on hydrolysis.

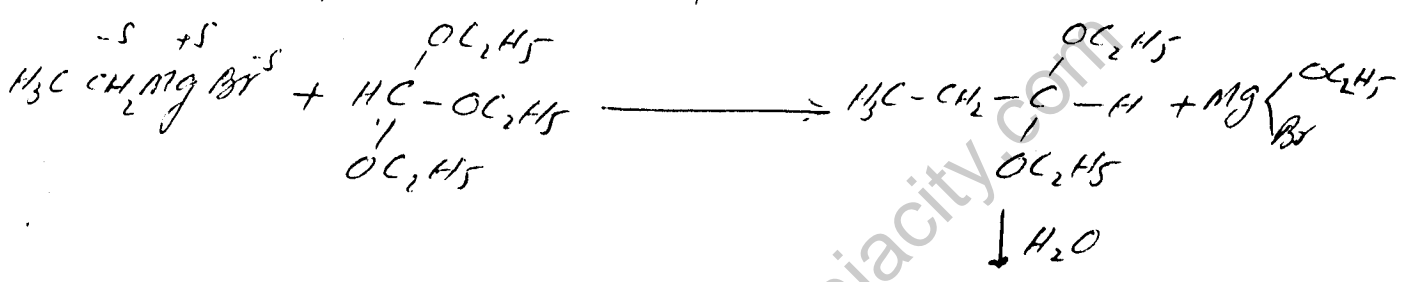


$\downarrow$   $H_2O$  / Hydrolysis

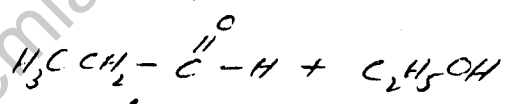
The ethyl orthoformate provides -CHO of aldehyde produced.



For example propional can be prepared as follows:



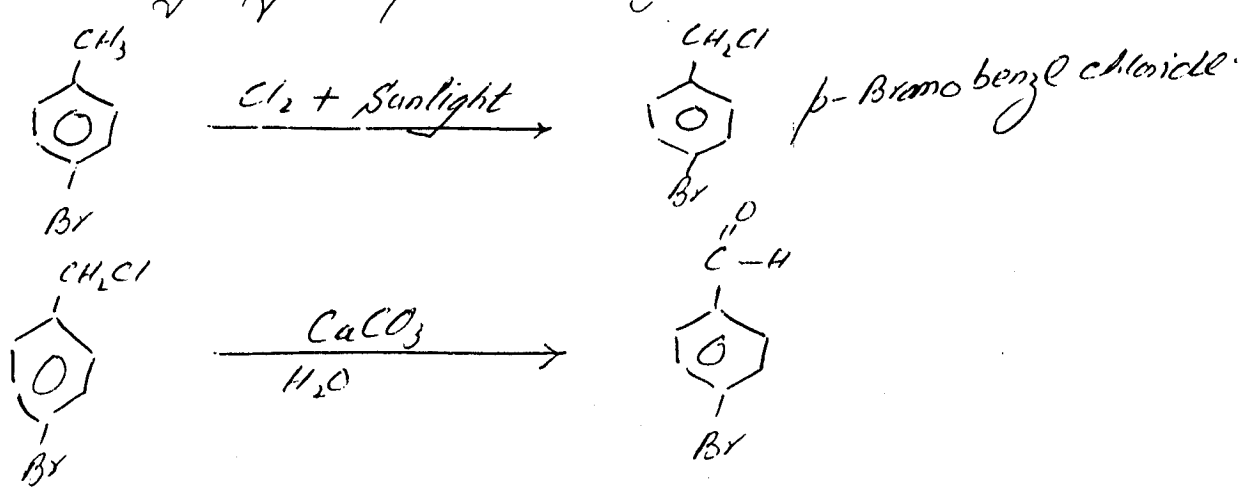
$\downarrow$   $H_2O$



**AROMATIC ALDEHYDES:-** Following reactions are commonly used for preparation of aromatic aldehydes.

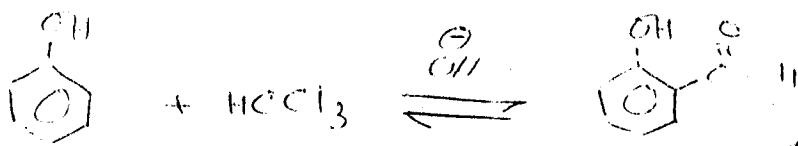
(i) **OXIDATION OF METHYL BENZENE:-**

Methyl benzene is first converted into benzyl chloride by side chain halogenation, and by ~~side chain halogenation~~ the benzyl chloride on basic hydrolysis produce benzaldehyde.

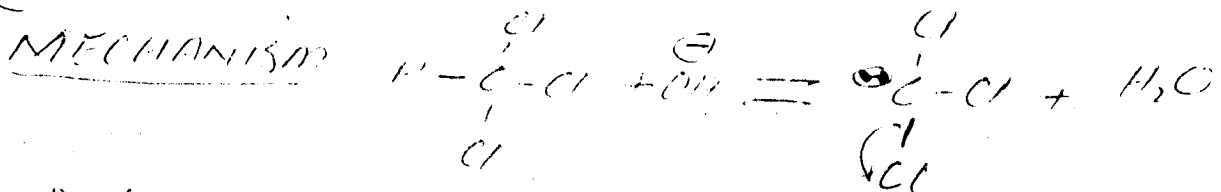


# Reimer-Tiemann Reaction:

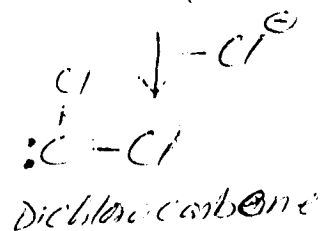
In this reaction phenol is treated with chloroform in basic medium. The product is hydroxy benzaldehyde.



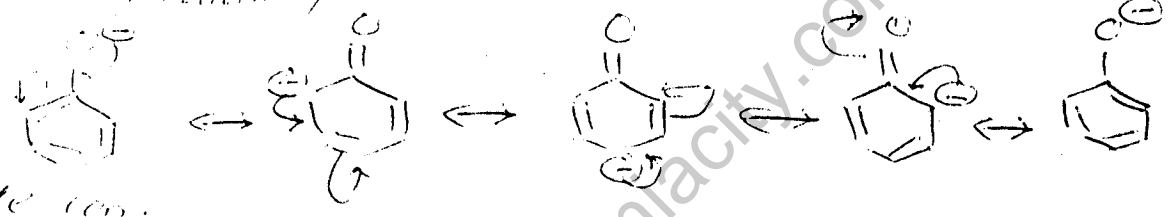
The reaction involves formation of carbene intermediate.



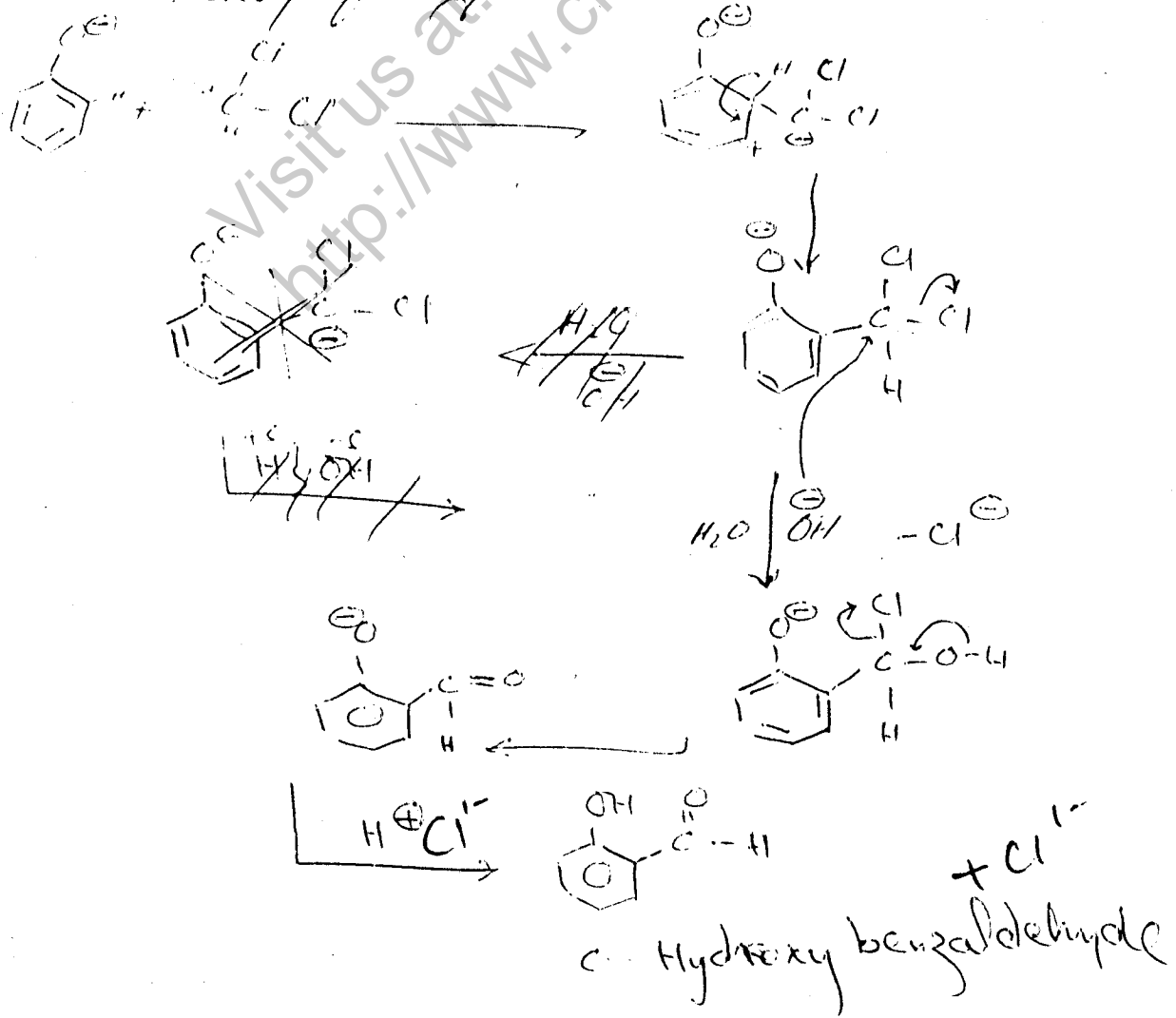
Dichlorocarbene is an electron deficient species (electrophile)



In basic medium phenol exists in ~~ionized~~ ionized form



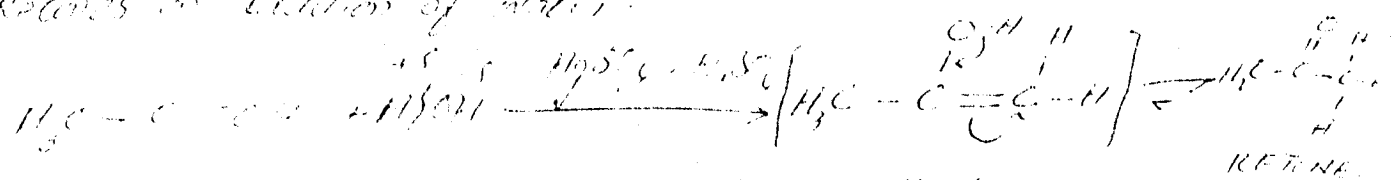
The carbene attacks preferably at ortho position of phenolate ion



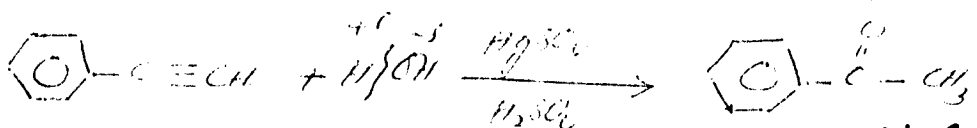




**HYDRATION OF ALKYNES:-** When alkynes are treated with dilute sulphuric acid (10%) in presence of mercuric sulphate, a molecule of water is added across triple bond. The addition of water takes place according to Markovnikov's rule. Thus alkynes other than ethyne produce ketones on addition of water.

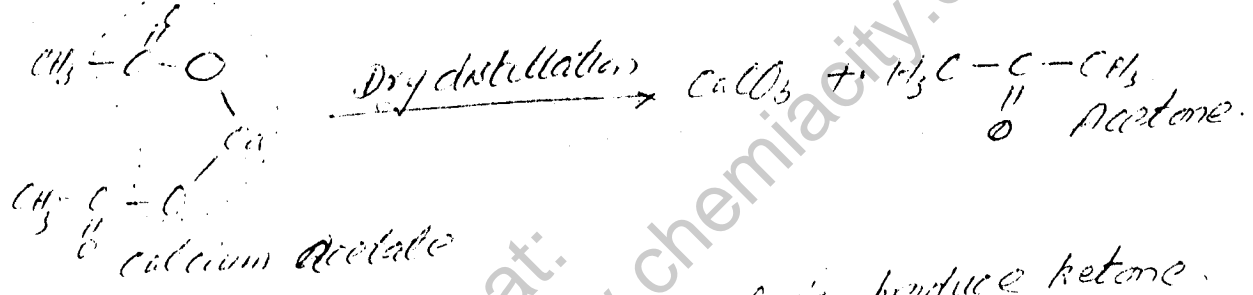


The reaction is useful for preparation of <sup>ENOL</sup> methyl ketones



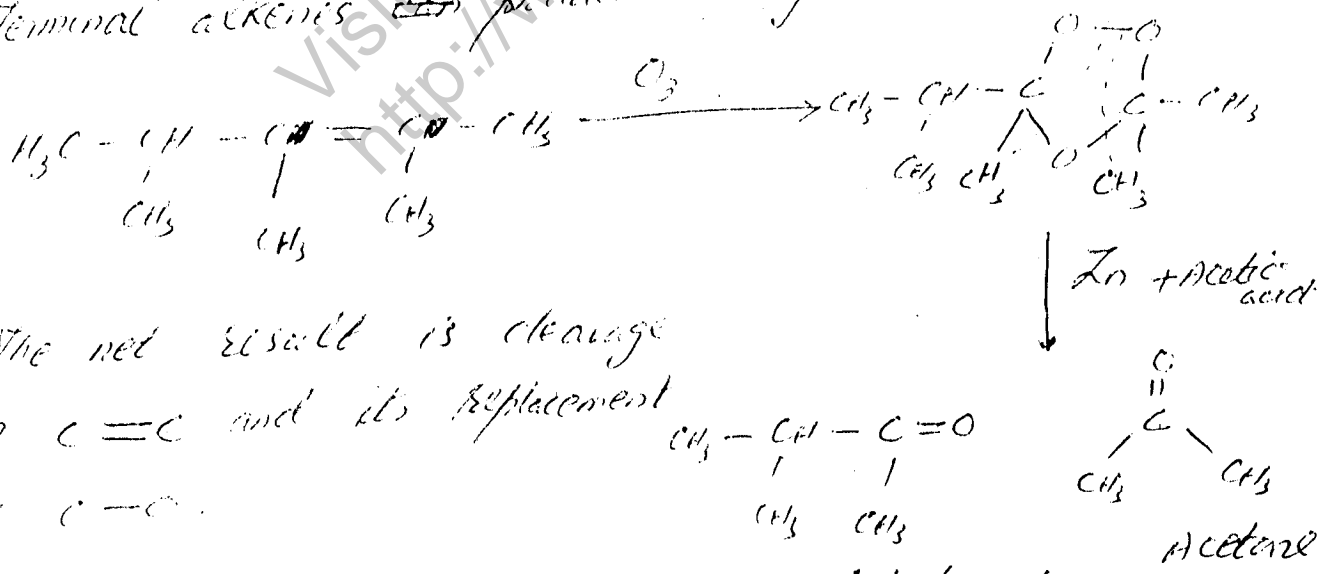
**Dry distillation of Calcium salts of Carboxylic Acids:-**

Dry distillation of calcium salts of carboxylic acids produce symmetric ketones (this is also called decarboxylation reaction).

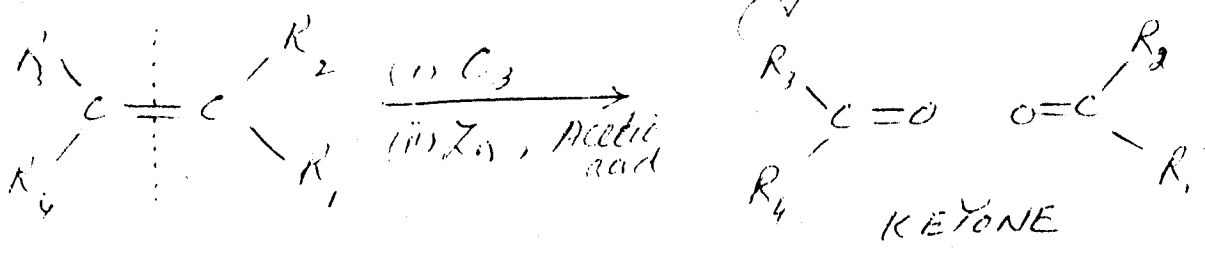
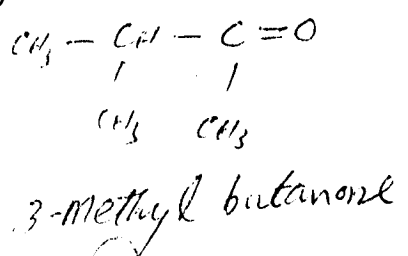


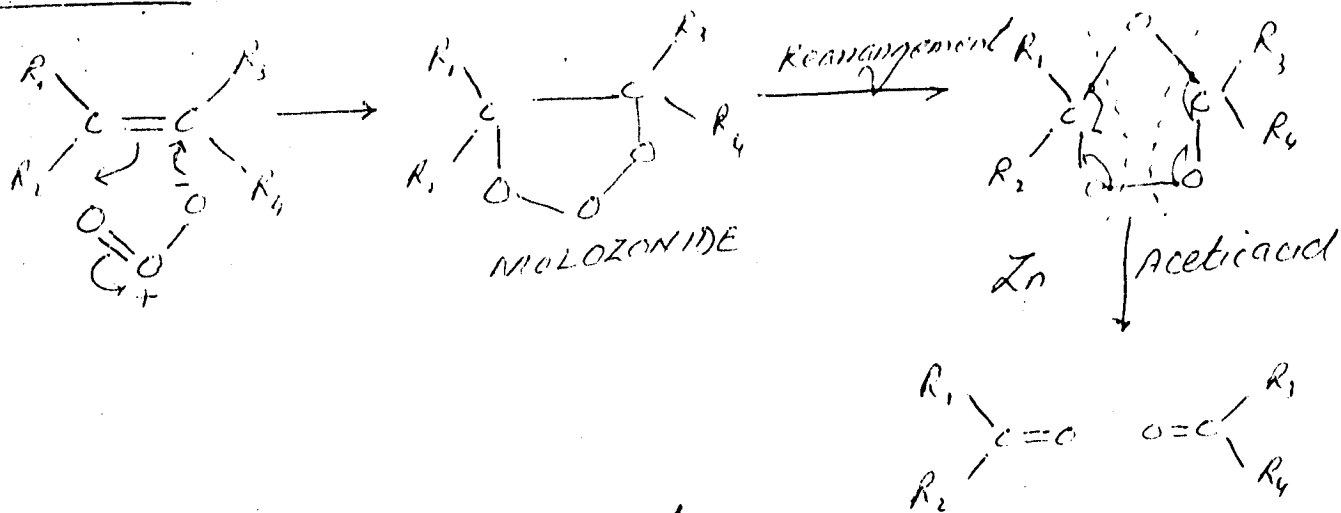
**From Alkenes:-** Alkenes on ozonolysis produce ketone.

(Terminal alkenes) produce aldehydes on ozonolysis



The net result is cleavage of C=C and its replacement by C-O.

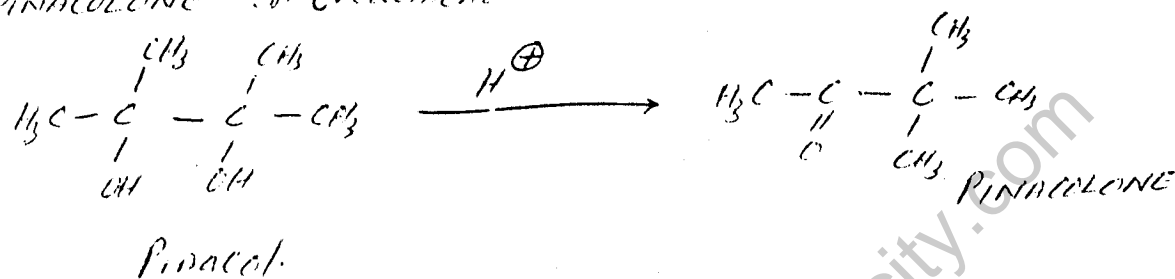




Pinacol Pinacolone Rearrangement:-

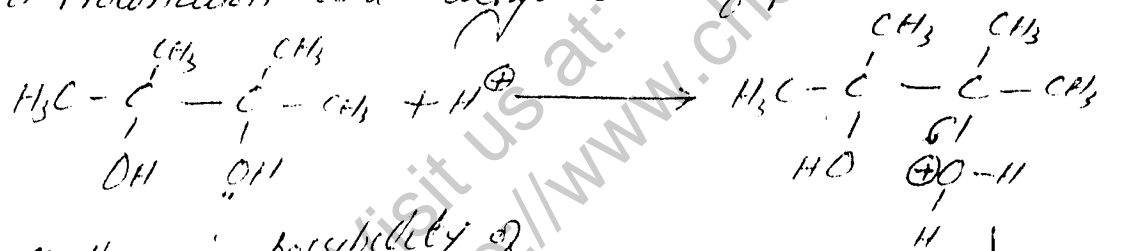
$R_2,3$ -Butanediol (PINACOL) is converted into a ketone called

PINACOLONE on treatment with sulphuric acid.

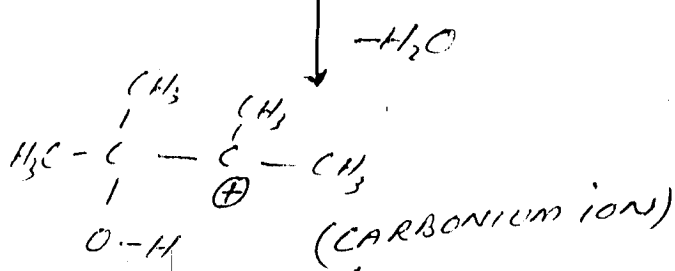


MECHANISM:- (The rearrangement involves following steps)

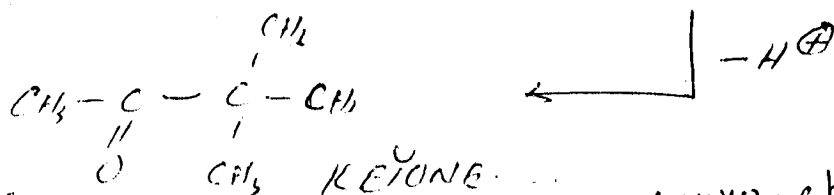
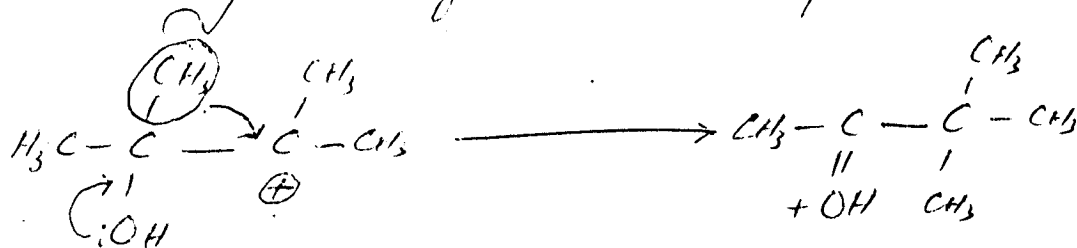
(i) Protonation and dehydration of pinacol to carbocation



If there is possibility of two different carbonium ions then most stable carbonium ion is formed.



(ii) Rearrangement of carbocation to produce ketone



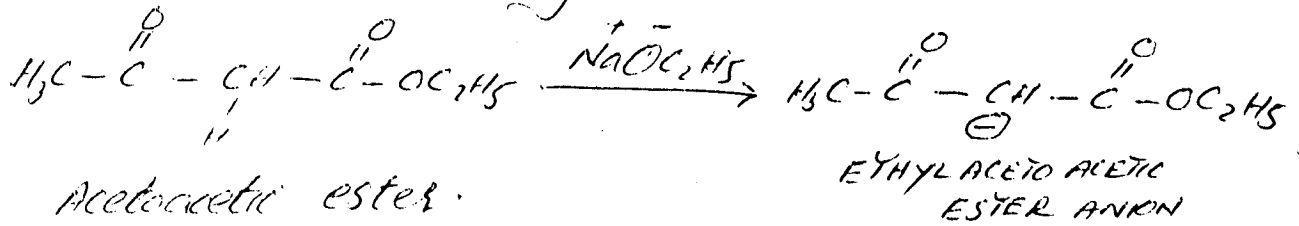
Pinacolone.

KEONE.

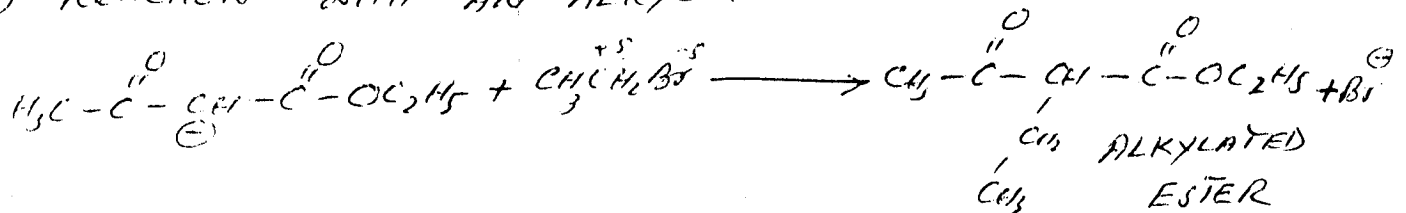
## KEYONES FROM ACETOACETIC ESTER:-

ketones can be produced by ketonic hydrolysis of acetoacetic ester. The reaction involves following steps.

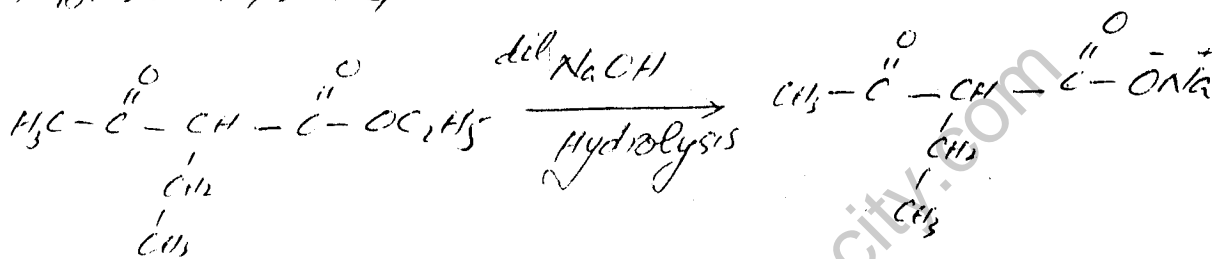
(i) Treatment with a strong base ( $\text{NaOC}_2\text{H}_5$ ).



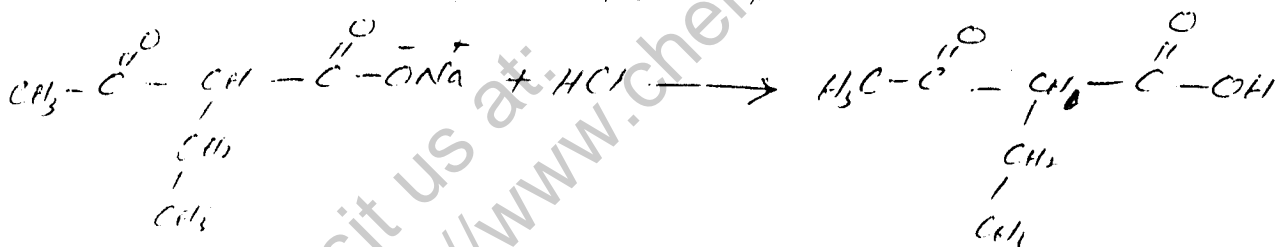
(ii) REACTION WITH AN ALKYL HALIDE.



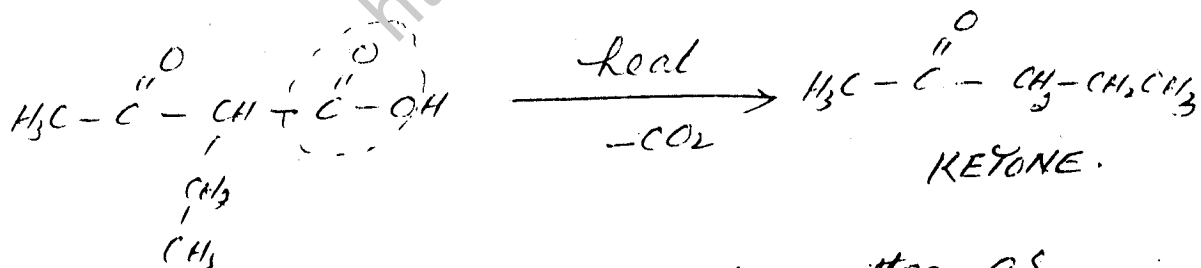
(iii) BASE HYDROLYSIS OF ALKYLATED ESTER.



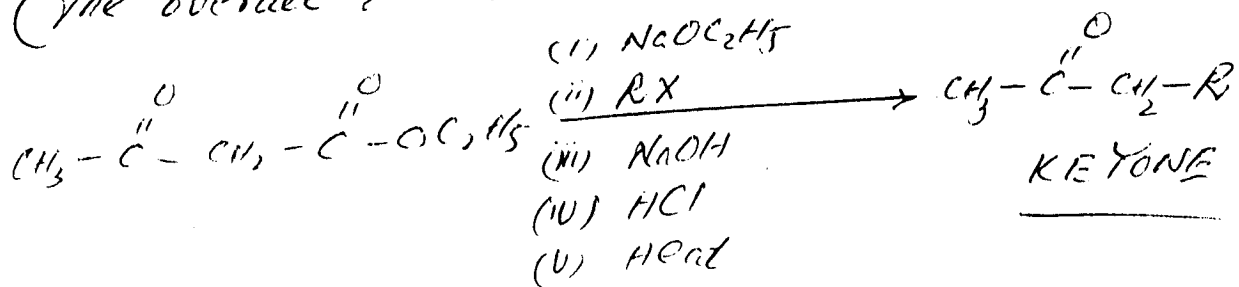
(iv) ACIDIFICATION OF HYDROLYSIS PRODUCT



(v) DECARBOXYLATION ON HEATING.

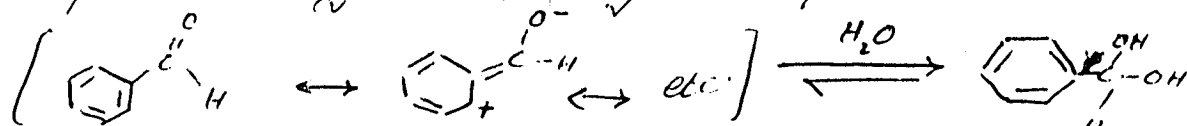


The overall reaction can be written as





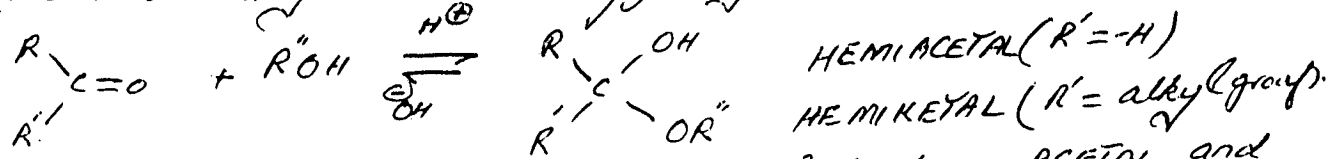
In benzaldehyde, the carbonyl group is stabilized due to electron donating resonance effect of benzene. This stabilization is not possible in hydrate. Thus hydrated product is not formed.



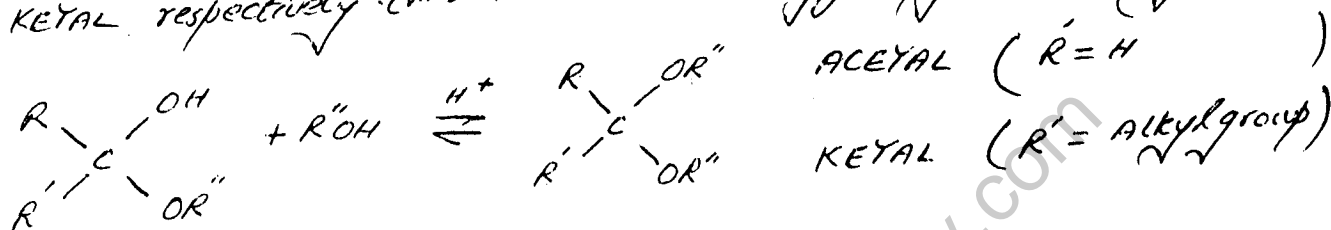
**Addition of Alcohols:-**

Aldehydes and ketones add 1 mole of alcohol to form **HEMIACETAL** and **HEMIKETAL** respectively.

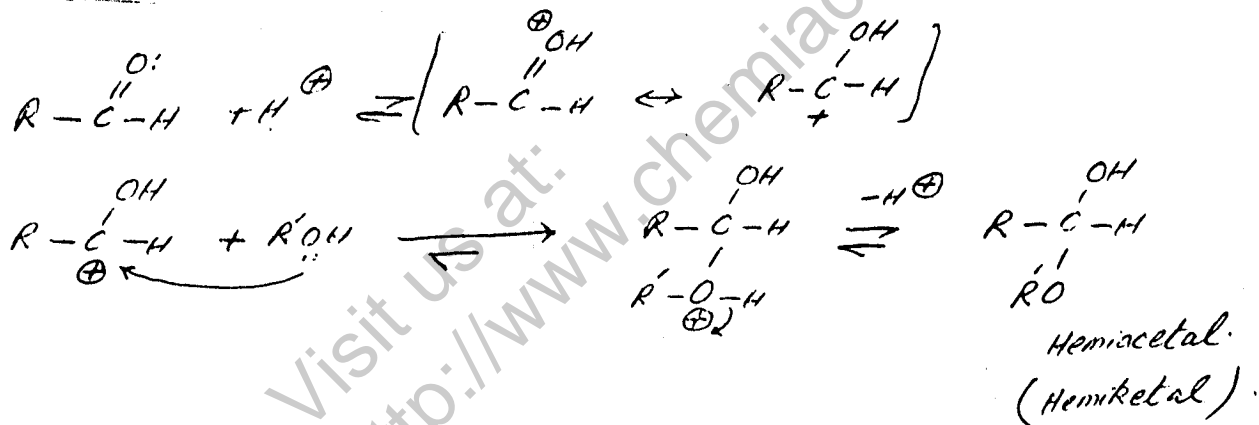
The reaction may be catalyzed by acids or bases.



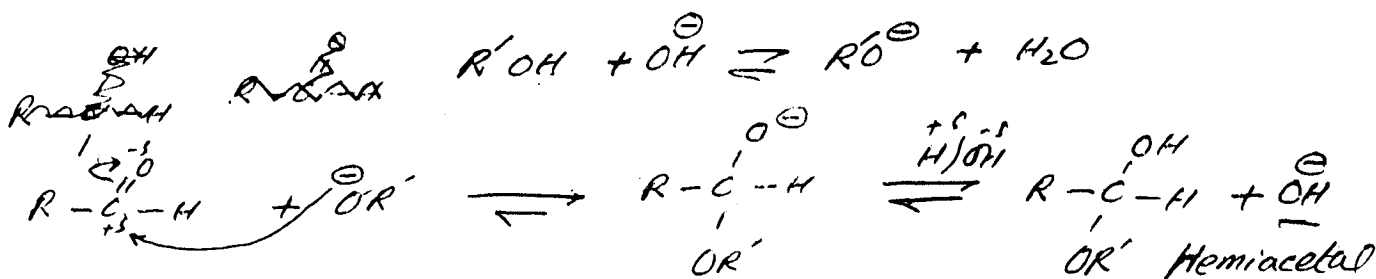
Addition of another mole of alcohol produces **ACETAL** and **KETAL** respectively. This reaction is catalyzed by acids only.



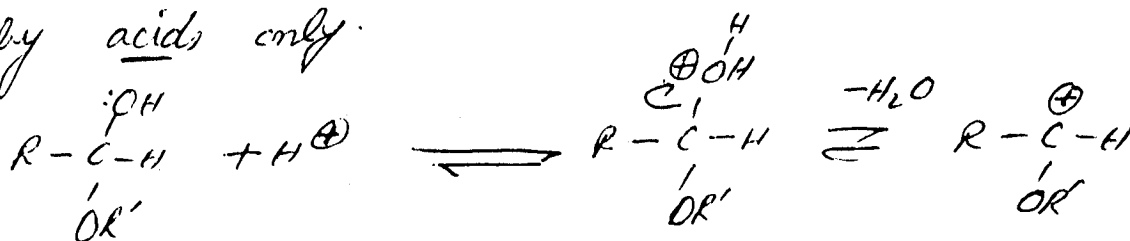
MECHANISM: (ACID CATALYSED MECHANISM)

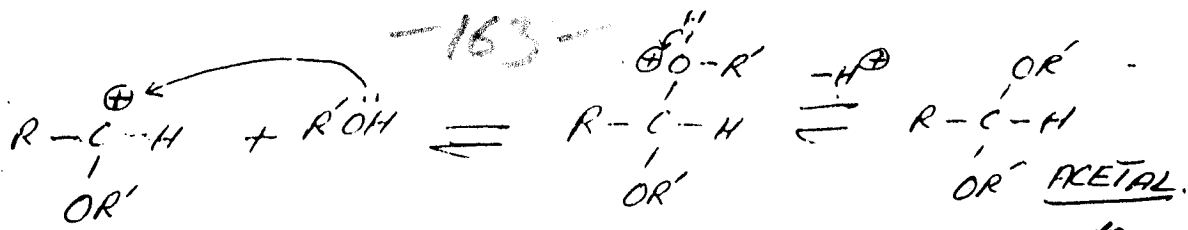


BASE CATALYSED MECHANISM OF HEMIACETAL & HEMIKETAL



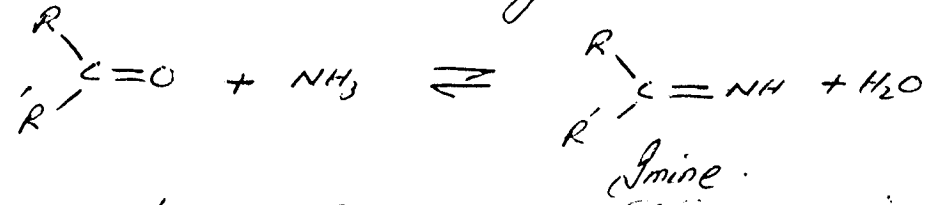
The ACETAL and KETAL formation is catalyzed by acids only.



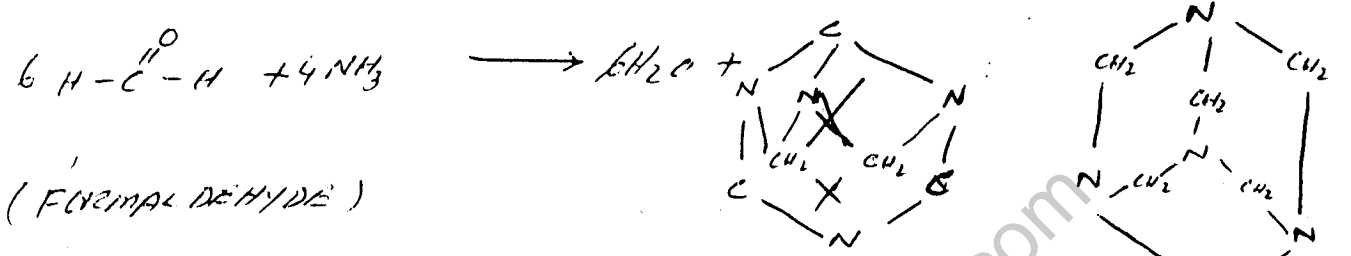


**ADDITION OF AMMONIA AND DERIVATIVES OF AMMONIA:-**

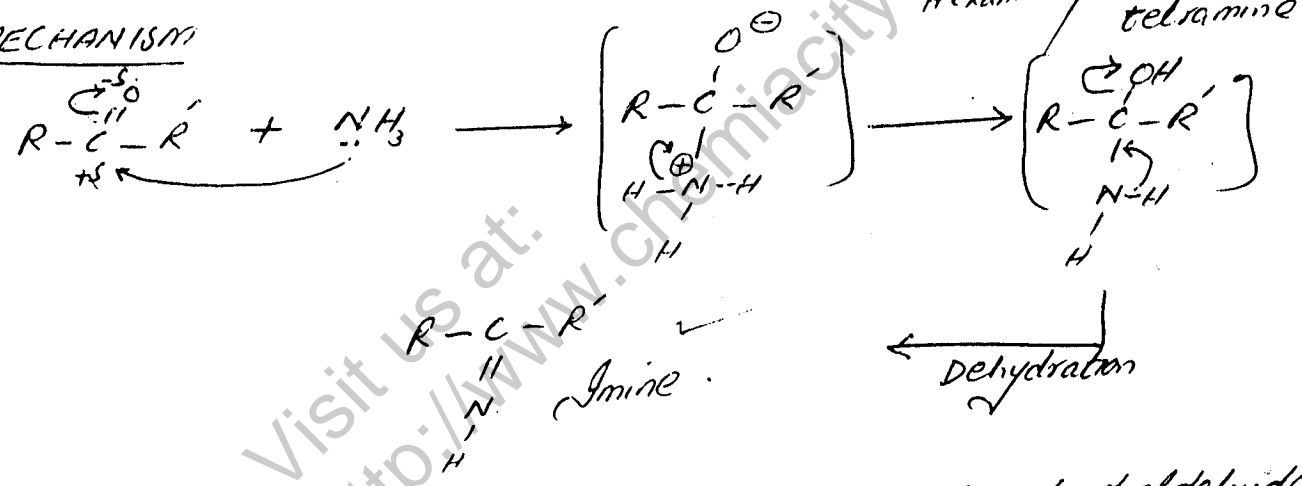
**AMMONIA:-** Aldehydes and ketones react with ammonia to form imines having C=N bonds.



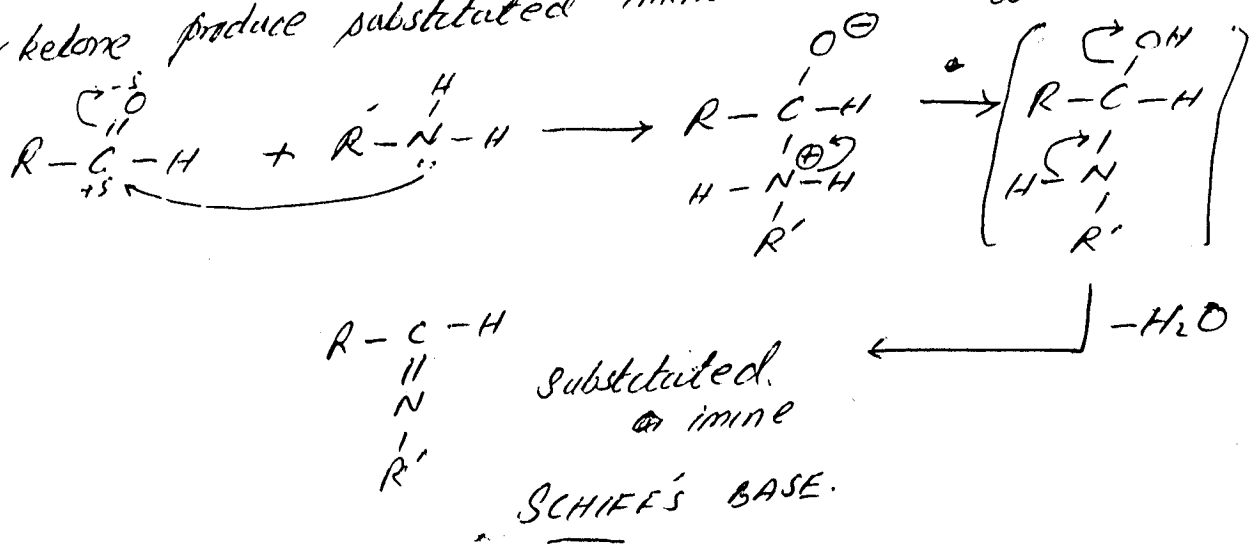
The reaction of formaldehyde with ammonia being an exception. It produces Hexamethylene tetramine.



MECHANISM

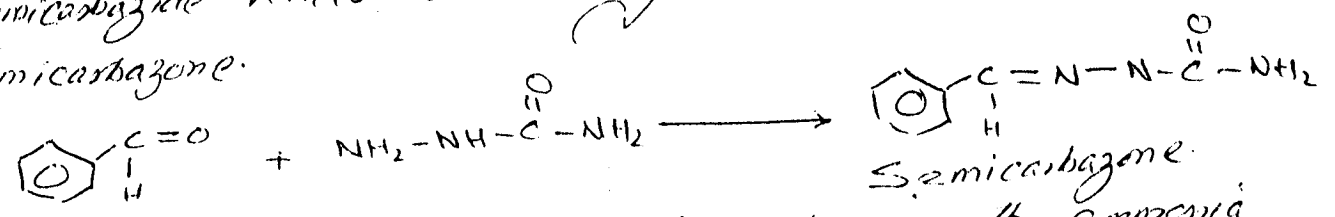


ADDITION OF PRIMARY AMINE:- p-Amine on addition to aldehyde or ketone produce substituted imine called Schiff's base.

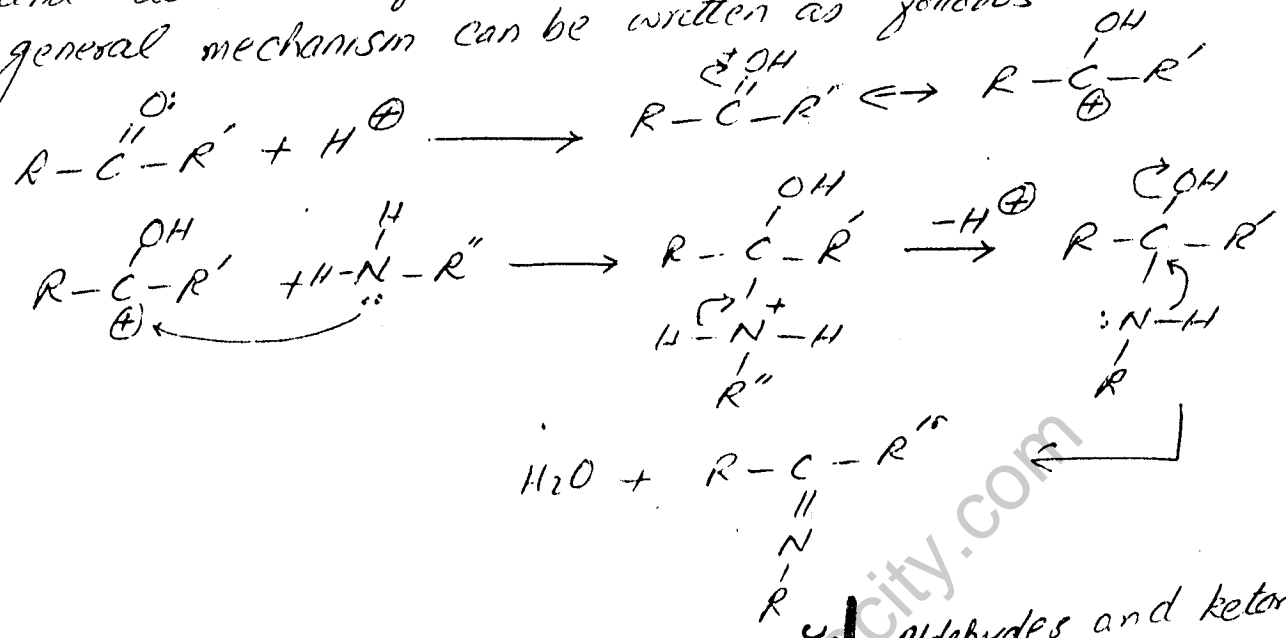




ADDITION OF SEMICARBAZIDE:  $\text{NH}_2 \cdot \text{NH} \cdot \text{C}(=\text{O}) \cdot \text{NH}_2$   
 Semicarbazide reacts with aldehydes and ketones to form Semicarbazone.



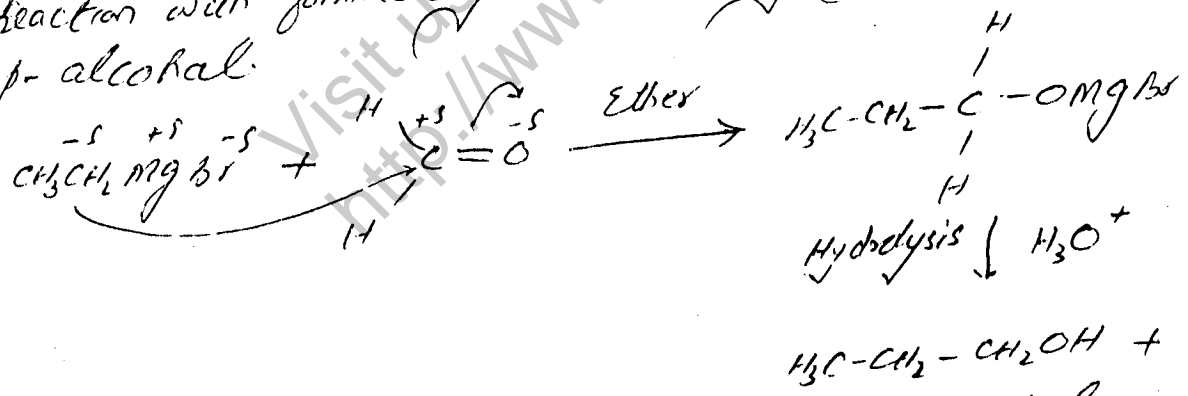
The reactions of aldehydes and ketones with ammonia and derivatives of ammonia are acid catalyzed. The general mechanism can be written as follows.



REACTION WITH GRIGNARD REAGENT:

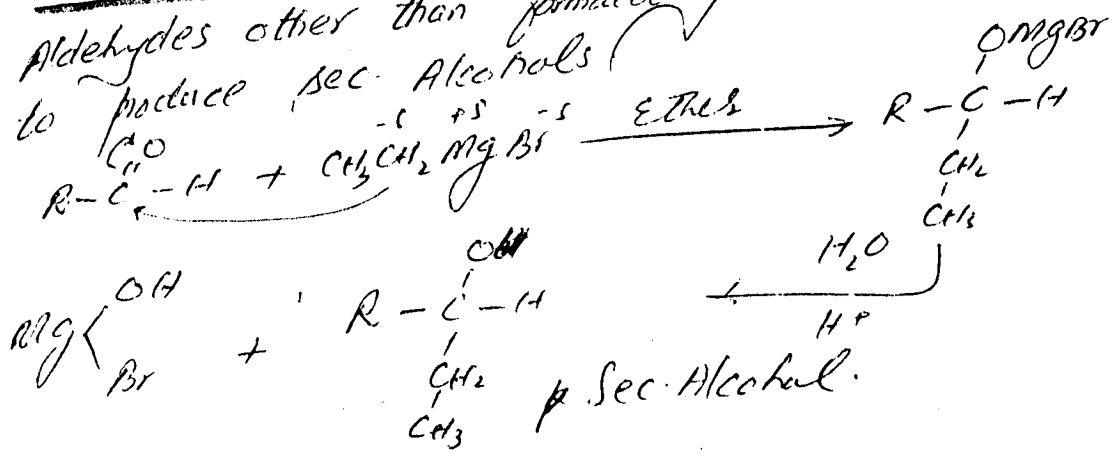
Aldehydes and ketones react with G.R. to form alcohols.

REACTION WITH FORMALDEHYDE: Grignard reagent on reaction with formaldehyde followed by hydrolysis produce p-alcohol.



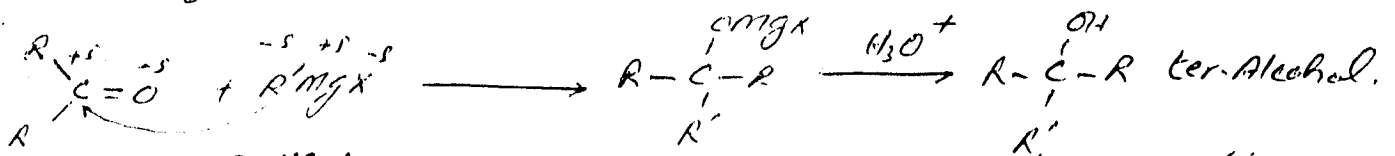
REACTION WITH OTHER ALDEHYDES:

Aldehydes other than formaldehyde react with G.R. to produce sec. Alcohols.

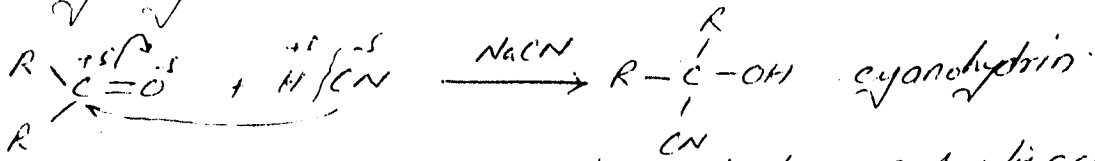




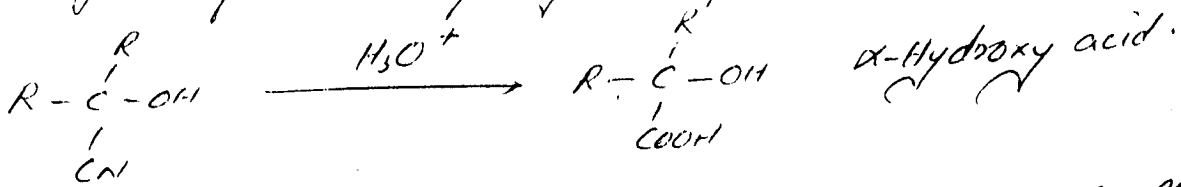
Reaction with ketones Grignard reagent reacts with ketone to form ter-Alcohols.



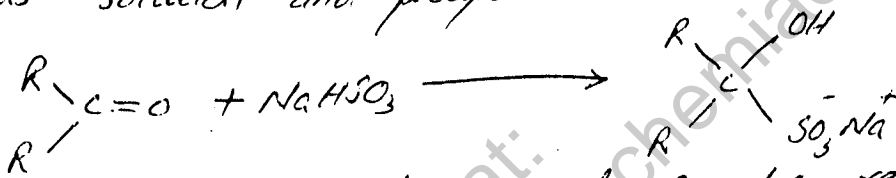
**Addition of HCN:-** Hydrogen cyanide adds to carbonyl compound to form cyanohydrins.



The cyano compounds on hydrolysis produce carboxylic acids.

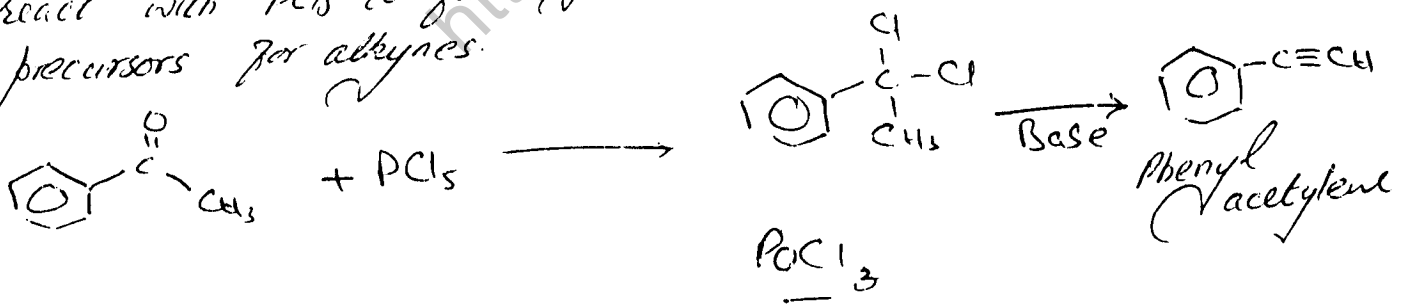


**ADDITION OF SODIUM BISULPHITE:-** (SODIUM HYDROGEN SULPHITE). Sodium hydrogen sulphite  $NaHSO_3$  in aqueous solution readily adds to aldehydes and ketones to form addition product. The concentrated addition product is insoluble in concentrated aqueous solution and precipitates out.



The parent carbonyl compound can be regenerated by addition of aqueous acid or base.

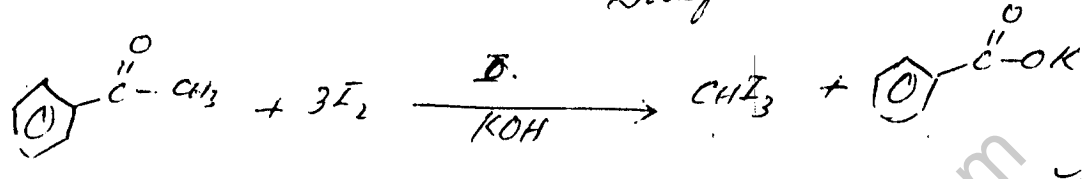
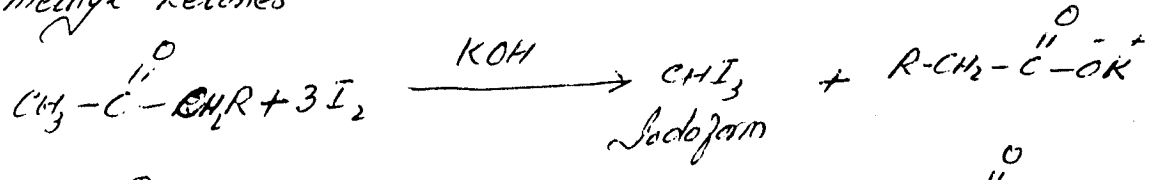
**REACTION WITH HALOGENS:-**  $PCl_5$  :- Aldehydes and ketones react with  $PCl_5$  to form gem-dichlorides which are suitable precursors for alkynes.



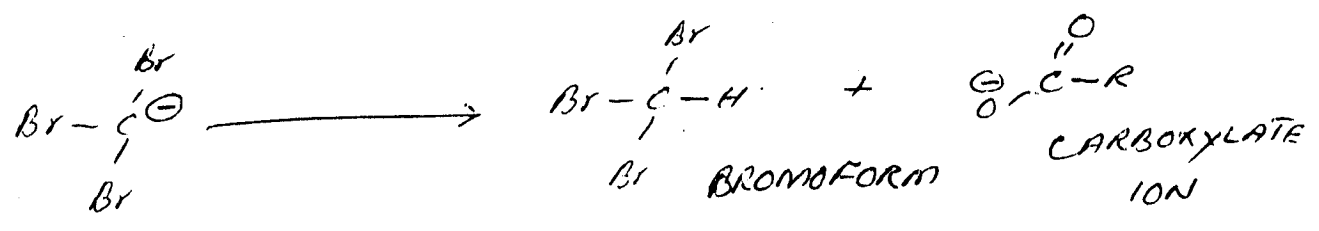
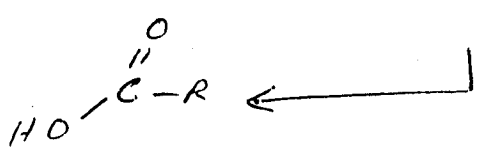
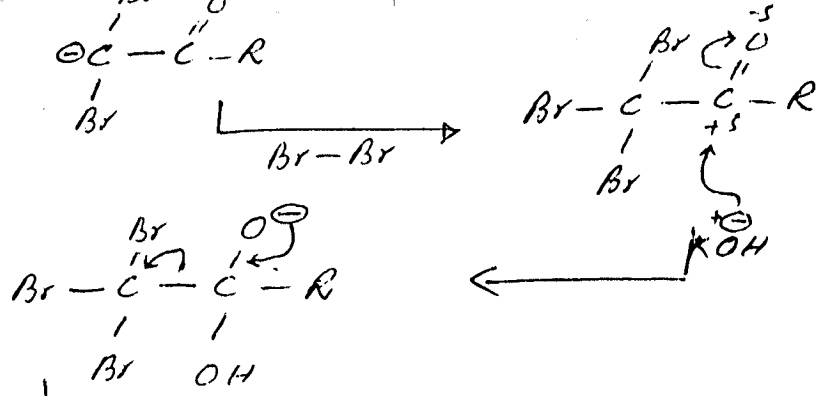
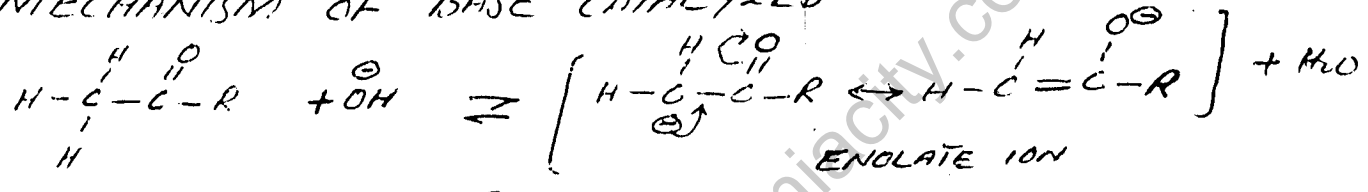
WRITE A NOTE ON EACH OF FOLLOWING REACTIONS.

**HALOFORM REACTION:-** The acetaldehyde and methyl ketones react with halogen in presence of BASE to form trihalomethane commonly called haloform and carboxylate salt. This is called HALOFORM REACTION.

When halogen used is iodine, the product is triiodomethane commonly called Iodoform. It is a yellow crystalline solid. This test is used to identify presence of methyl ketones.



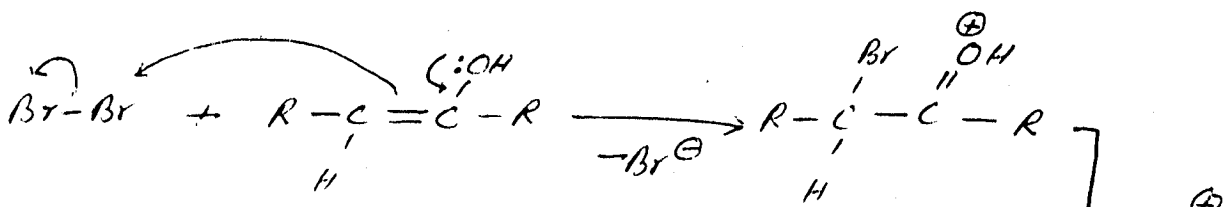
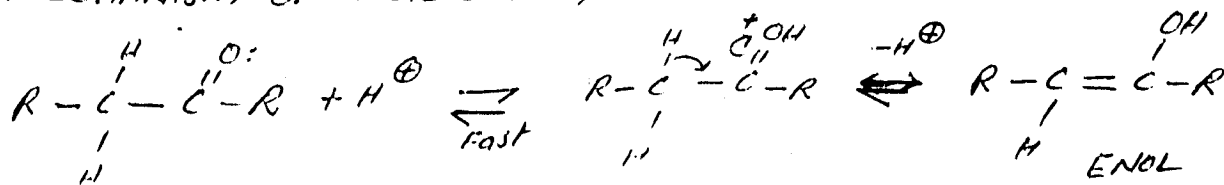
**MECHANISM OF BASE CATALYZED HALOGENATION:-**



$\alpha$ -halogenation increases acidity of  $\alpha$ -hydrogen and base catalyzed halogenation proceed favourably until all  $\alpha$ -hydrogens are removed by  $\text{OH}^-$ .

**ACID CATALYZED HALOGENATION:** Aldehydes and ketones that having at least one  $\alpha$ -hydrogen can undergo  $\alpha$ -halogenation in presence of ~~base~~ ACID also

**MECHANISM OF ACID CATALYZED HALOGENATION**



The introduction of a halogen at  $\alpha$ -position decreases reactivity of  $\alpha$ -hydrogen. Thus further halogenation is slower.

Thus acid catalyzed halogenation can be stopped at mono halostage.

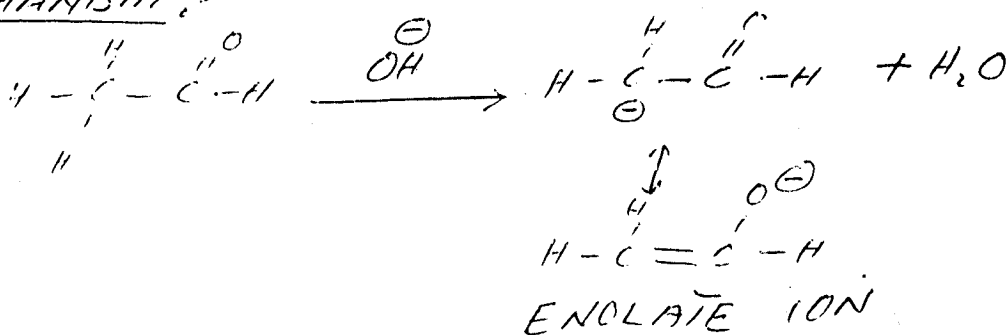
**ALDOL CONDENSATION:**

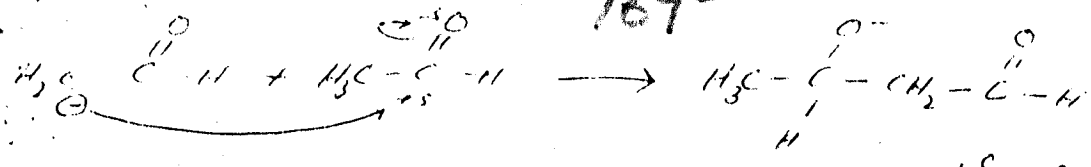
The aldehydes and ketones having at least one  $\alpha$ -hydrogen undergo self base catalyzed self addition reaction called ALDOL CONDENSATION. The reaction proceeds through formation of enolate ions.

For example ACETALDEHYDE when treated with aqueous NaOH gives following ALDOL

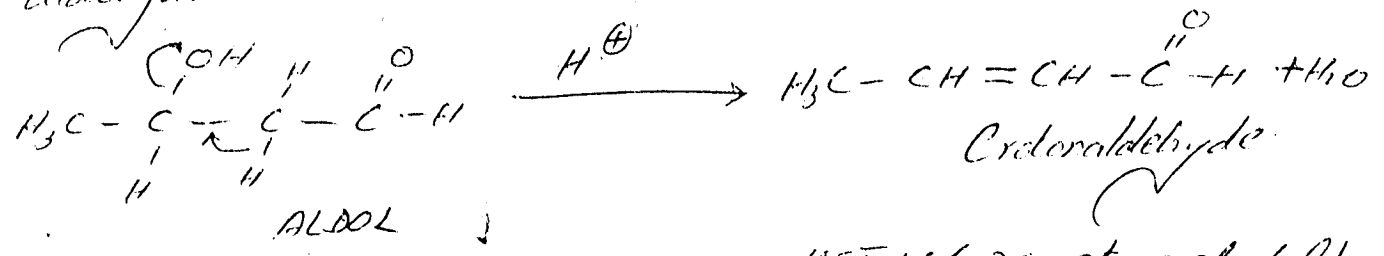
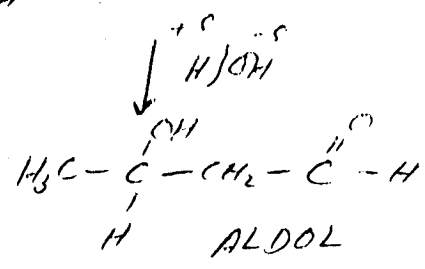
$$2 \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \xrightarrow{\text{OH}^-} \text{H}_3\text{C}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \quad \text{ALDOL}$$

**MECHANISM:-**

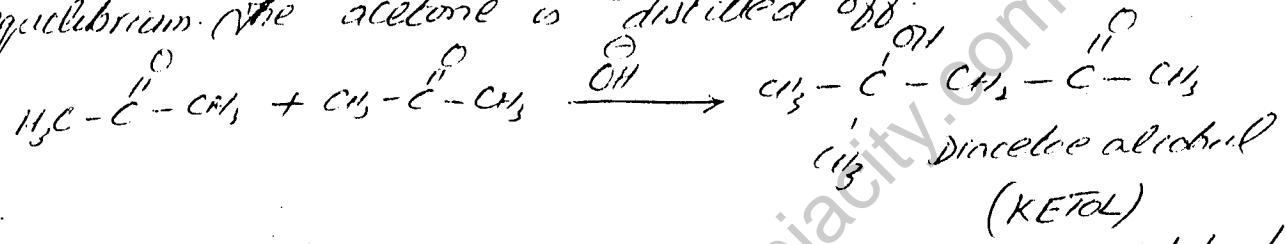




The aldols are stable in basic medium but dehydrate in acidic medium to form unsaturated aldehydes.

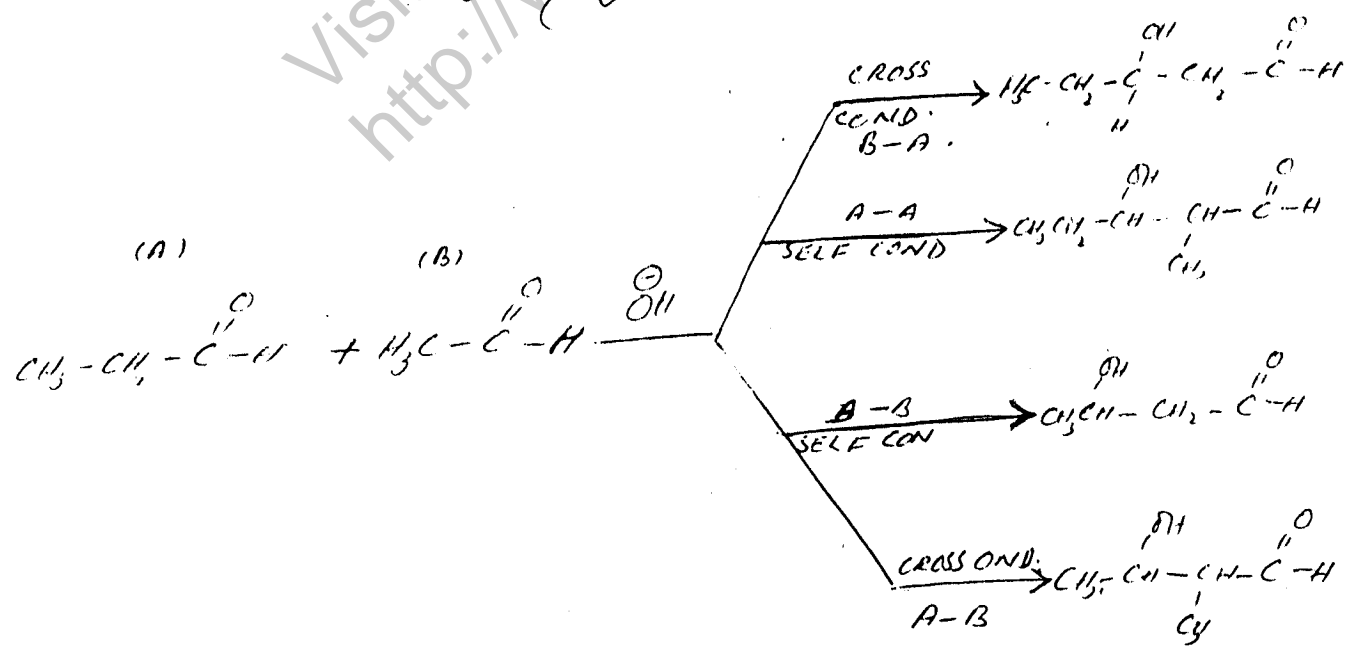


The ketones on condensation give KETOLS (Diacetone alcohol) but ketols cannot be isolated under basic conditions. However it can be isolated by removing base catalyst after attaining equilibrium. The acetone is distilled off.

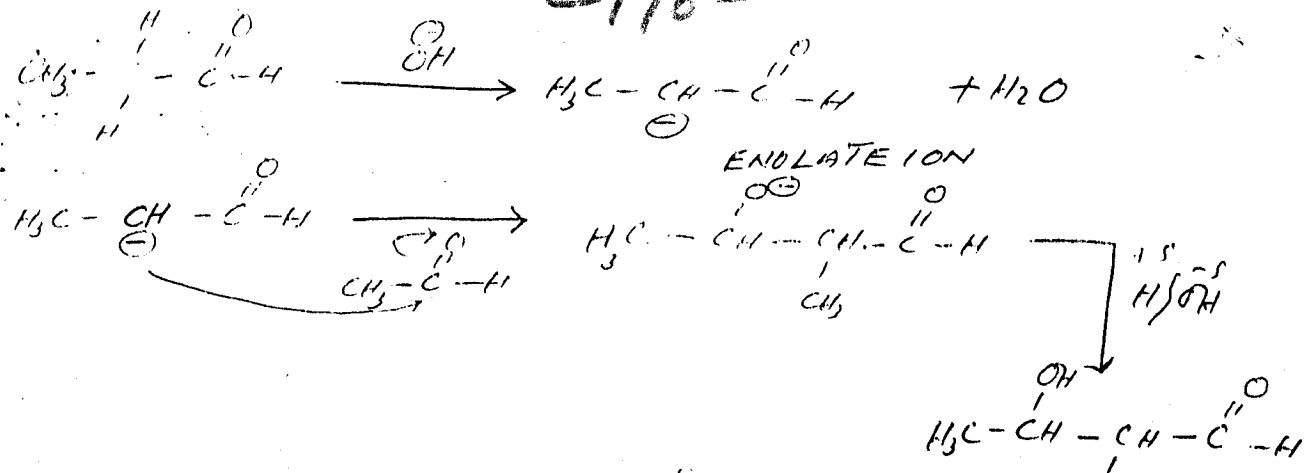


**CROSS ALDOL CONDENSATION:** When a mixture of aldehydes is used both with  $\alpha$ -hydrogens then a mixture of aldols is produced due to self and cross condensations.

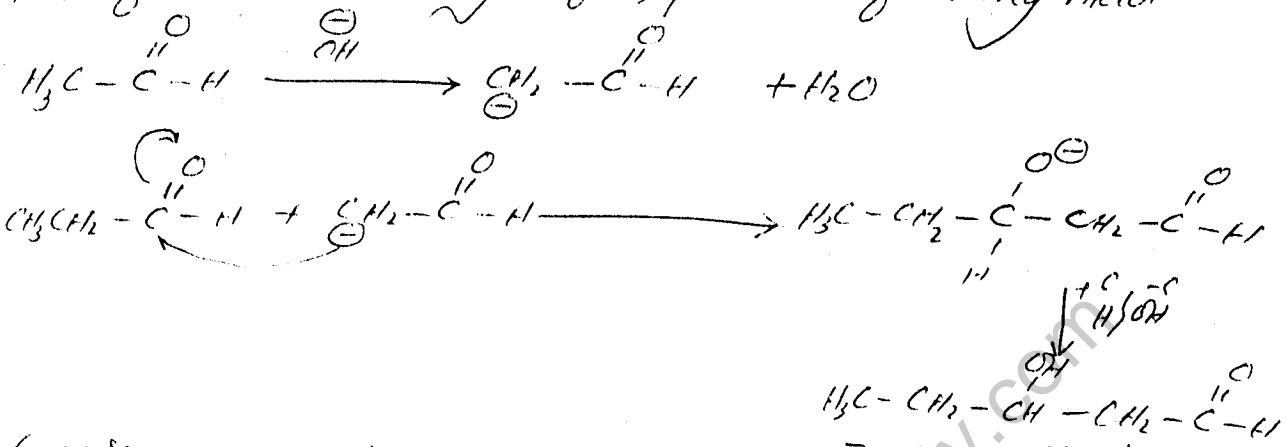
Let us consider following example



Let us consider mechanism of cross condensation of "A" and "B"



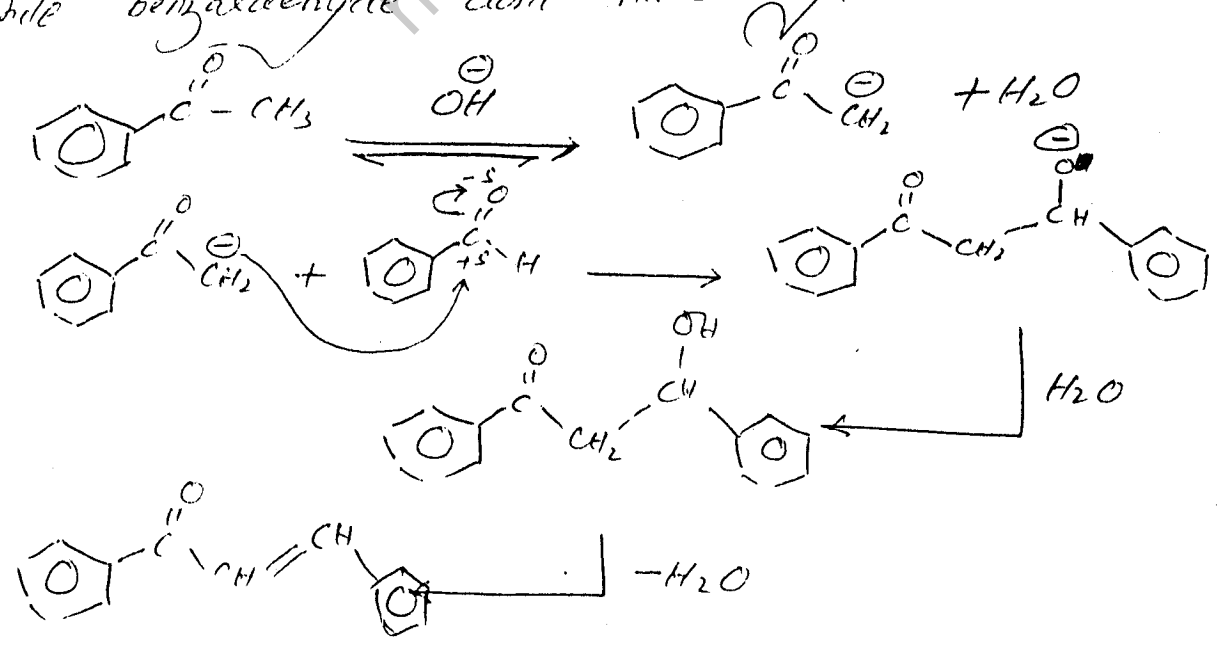
Similarly cross condensation of "B" and "A" (i.e enolate ion of B and carbonyl of A) produces following Aldol.



(WRITE MECHANISM OF SELF CONDENSATION YOURSELF).

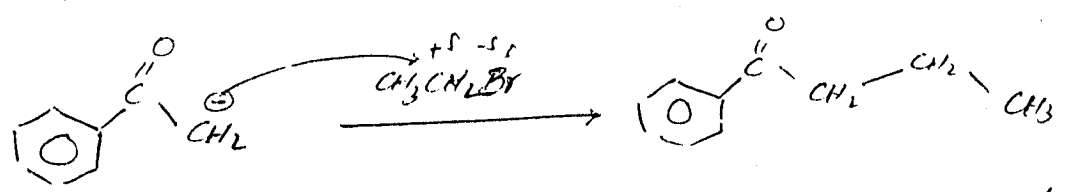
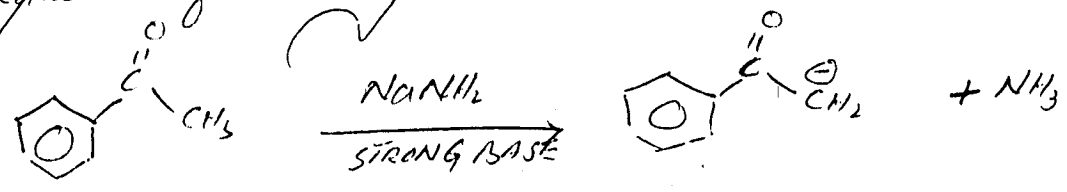
When a mixture of aldehydes is used one with  $\alpha$ -hydrogen and other without  $\alpha$ -hydrogen then only two products are obtained one due to self condensation and one due to cross condensation.

Let us consider condensation of benzaldehyde and ACETOPHENONE. Only acetophenone has  $\alpha$ -hydrogen while benzaldehyde don't have any.

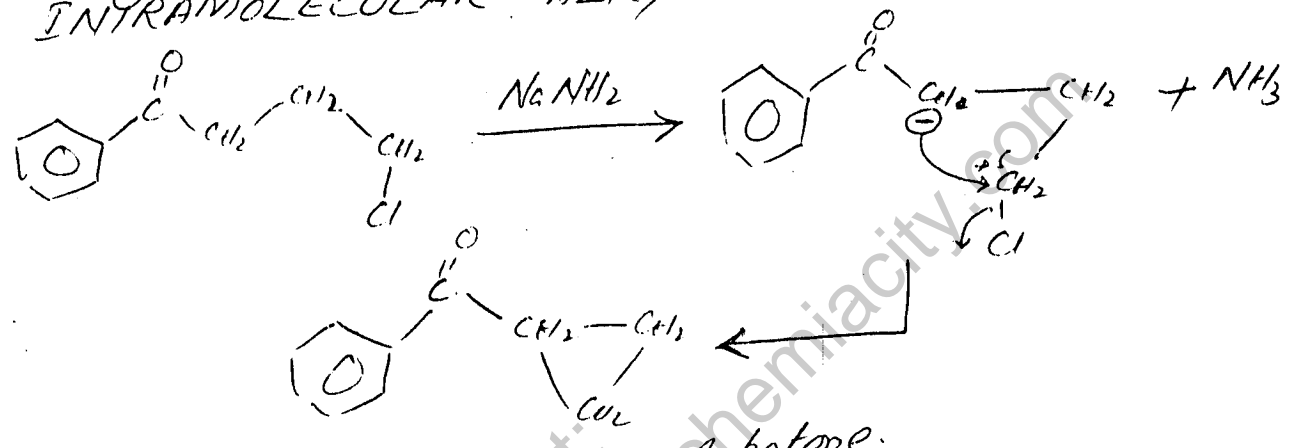


ALKYLATION OF ALDEHYDES AND KETONES.

Another application of acidity of  $\alpha$ -hydrogen is that, these ends can act nucleophiles. Thus they react with alkyl halides which act as electrophile. By this reaction alkylation of aldehydes and ketones can be carried out



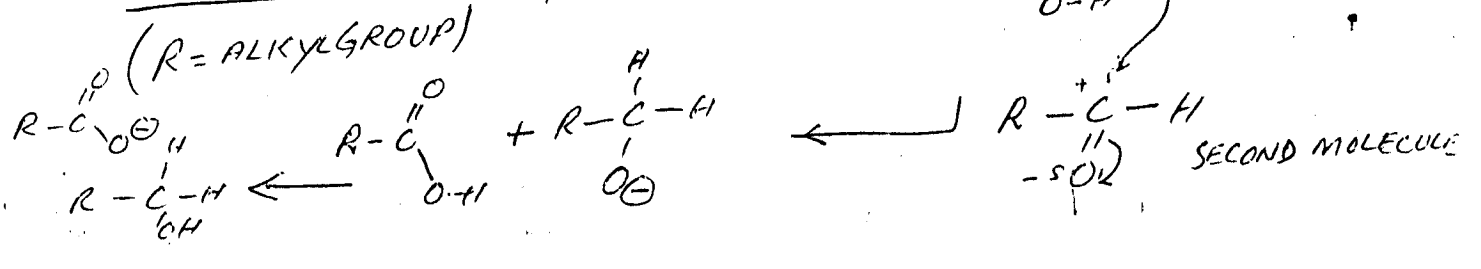
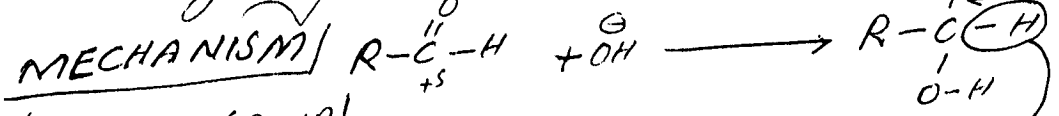
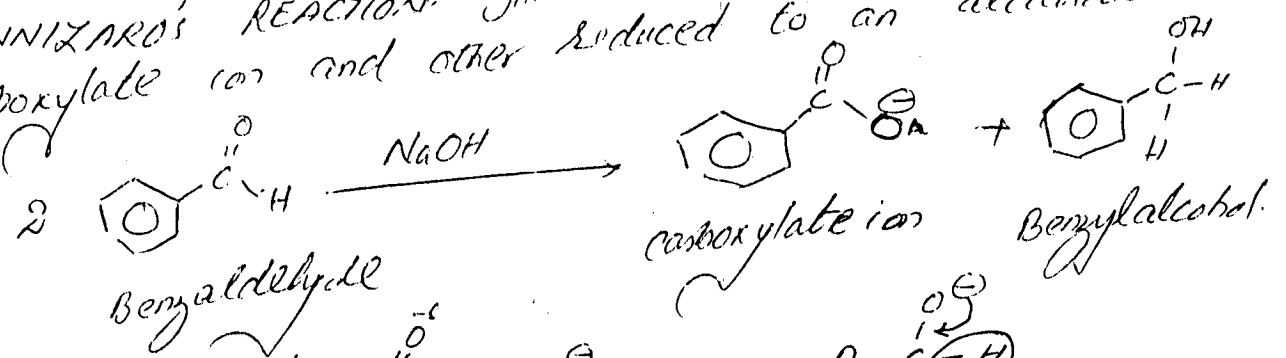
INTRAMOLECULAR ALKYLATION is also possible.



cyclopropyl phenyl ketone.

Imp:- CANNIZAROS REACTION

Those aldehydes and ketones which don't have any  $\alpha$ -hydrogen undergo base catalyzed self oxidation reduction reaction commonly called CANNIZAROS REACTION. One molecule is oxidized to carboxylate ion and other reduced to an alcohol.



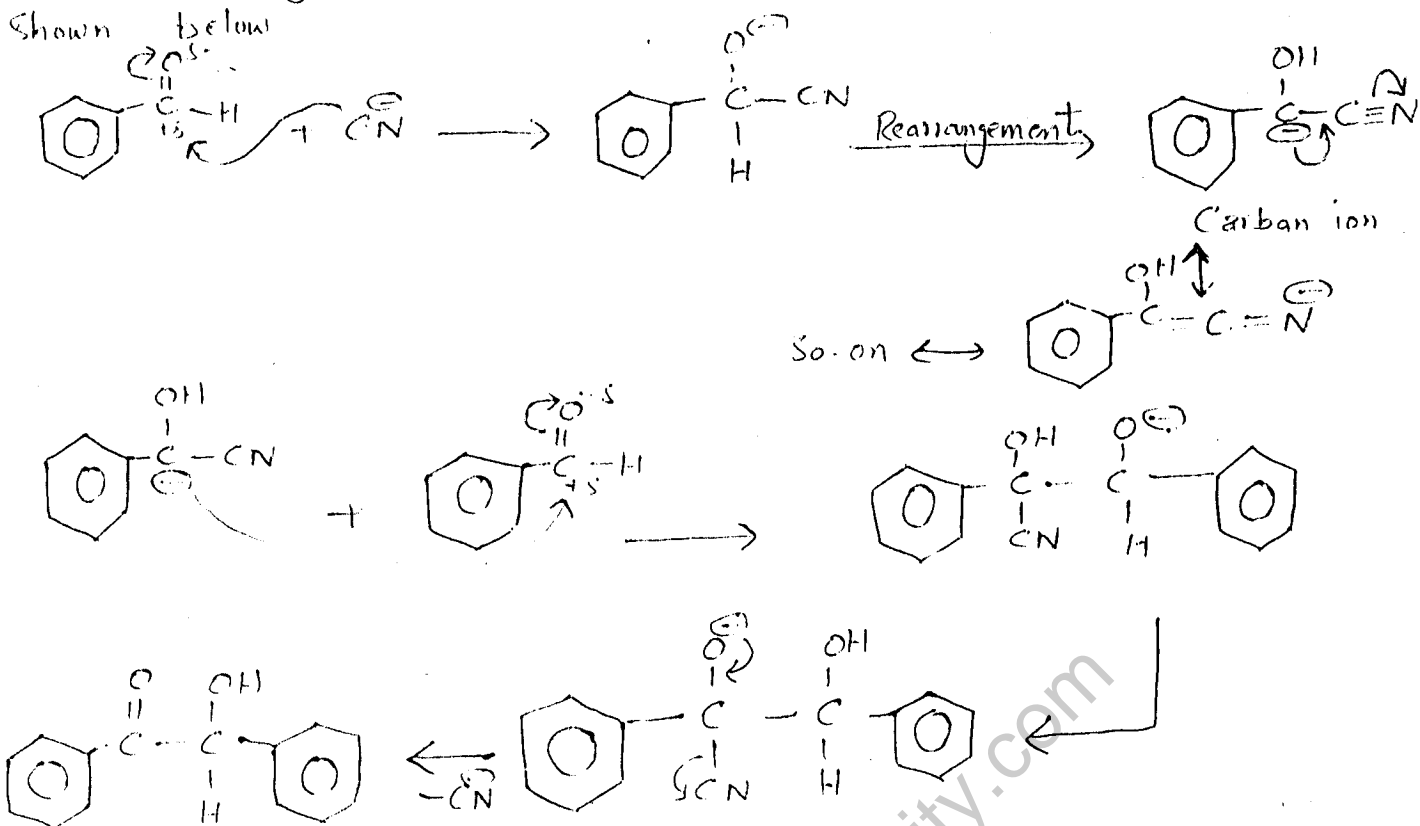
# BENZOIN CONDENSATION :-

organic

(4)

The Condensation of benzaldehyde in presence of Cyanide is called benzoin Condensation. The reaction mechanism is

shown below



Benzoin

Reaction involves following steps:

- i) Attack of  $\text{CN}^-$  on Carbonyl Carbon.
- ii) Shift of proton from carbon to oxygen produce a Carbanion stabilized by resonance.
- iii) The Carbanion attacks another benzaldehyde molecule.
- iv) Shift of proton.
- v) Removal of  $\text{CN}^-$  and formation of a  $\alpha$ -hydroxy ketone called Benzoin.

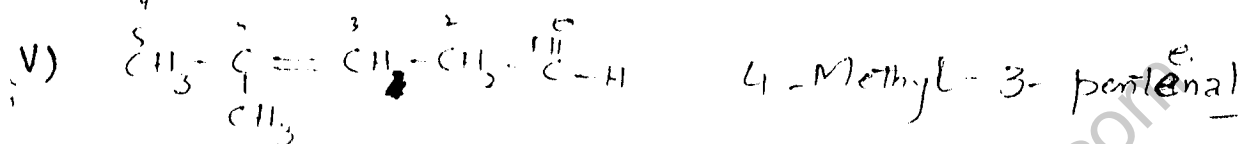
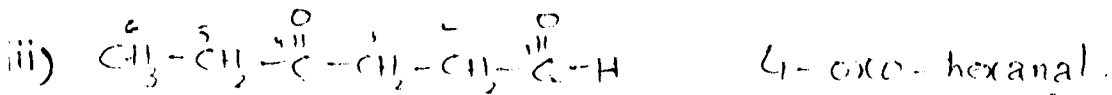
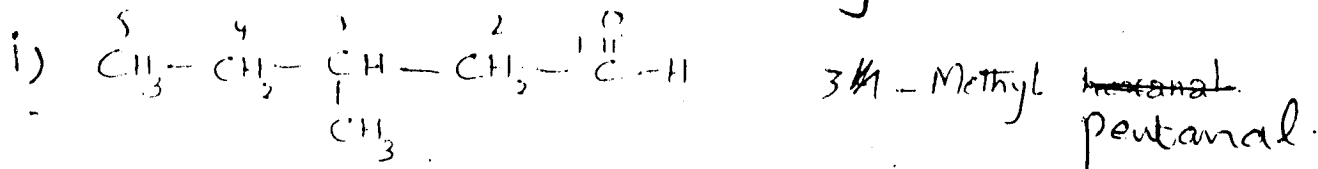
# Aldehydes And Ketones (EXERCISE)

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QUESTION NO. 2 :-

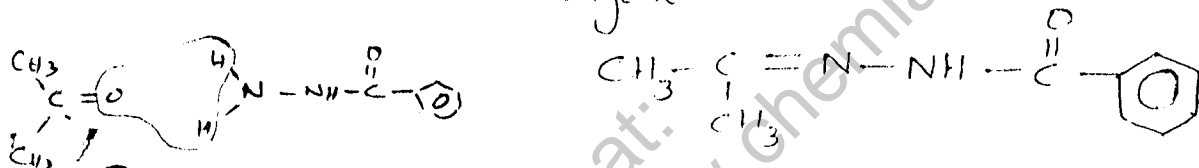
Write names of following :-



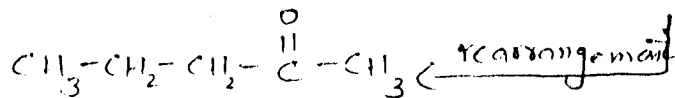
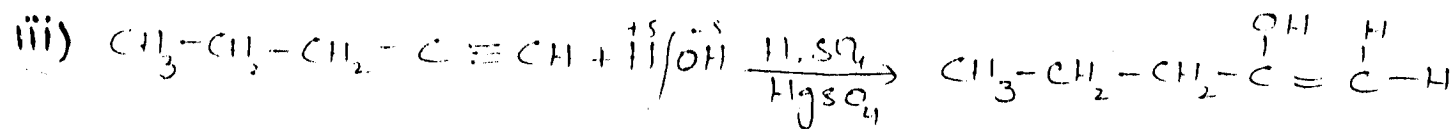
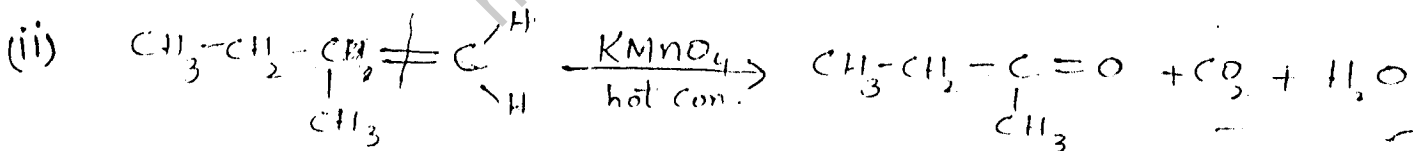
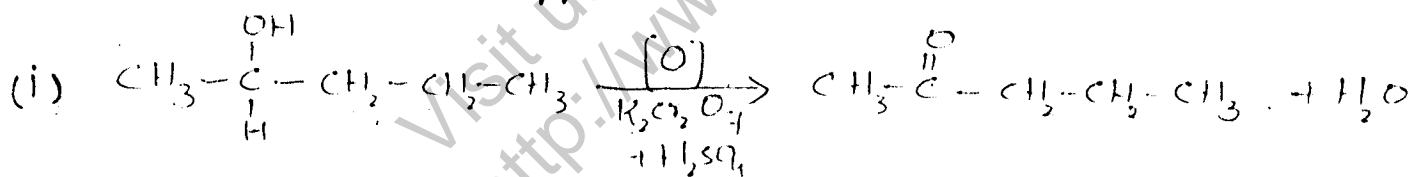
QUESTION NO. 3 :-

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(v) Acetone Semi Carbazone

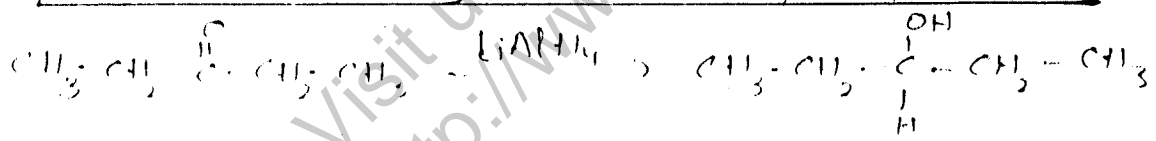
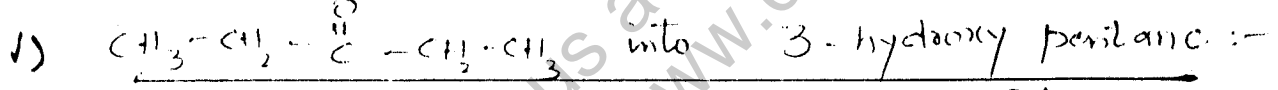
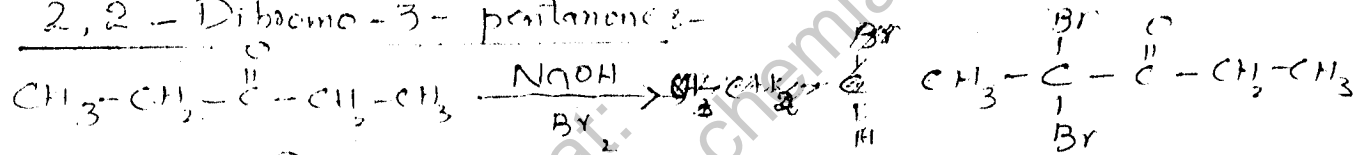
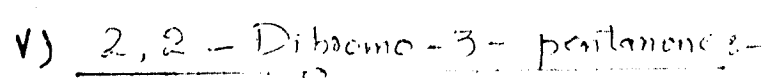
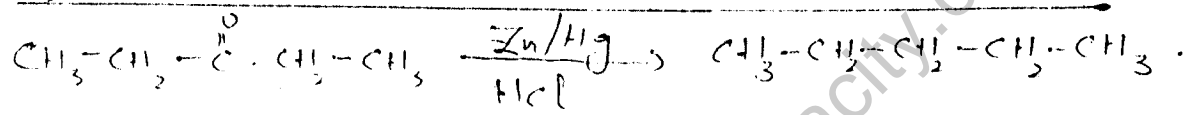
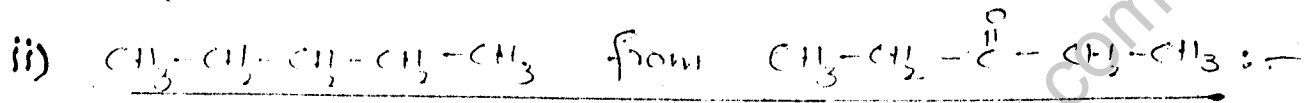
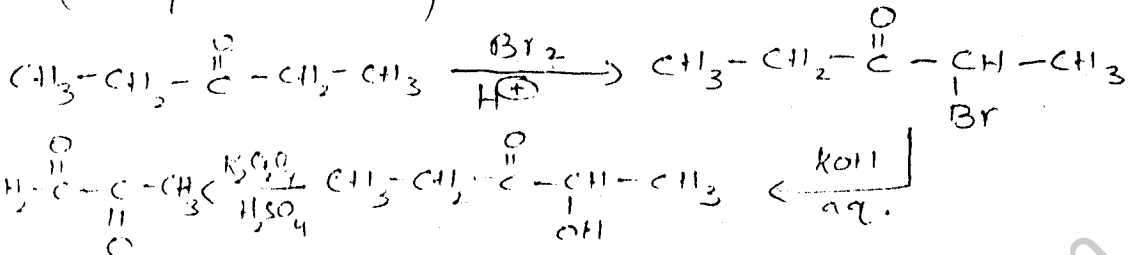
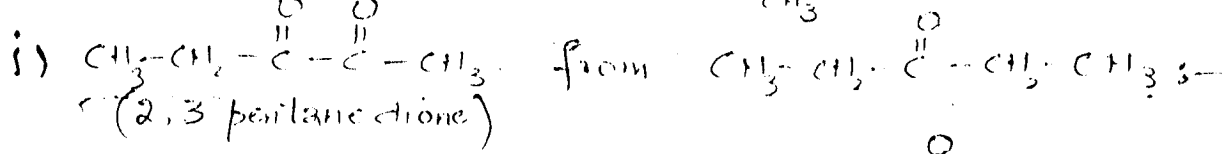
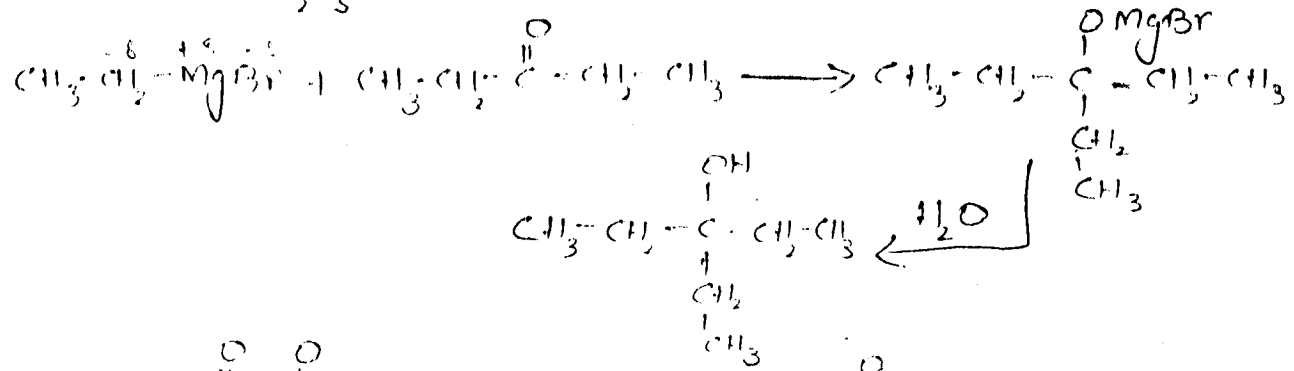
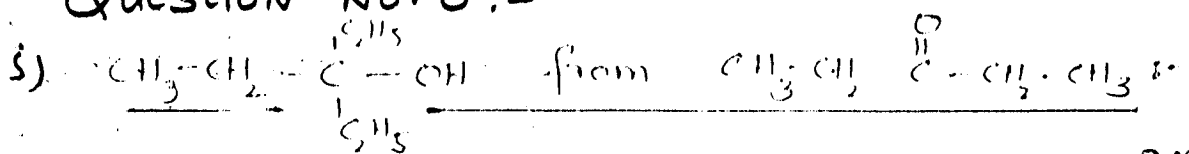


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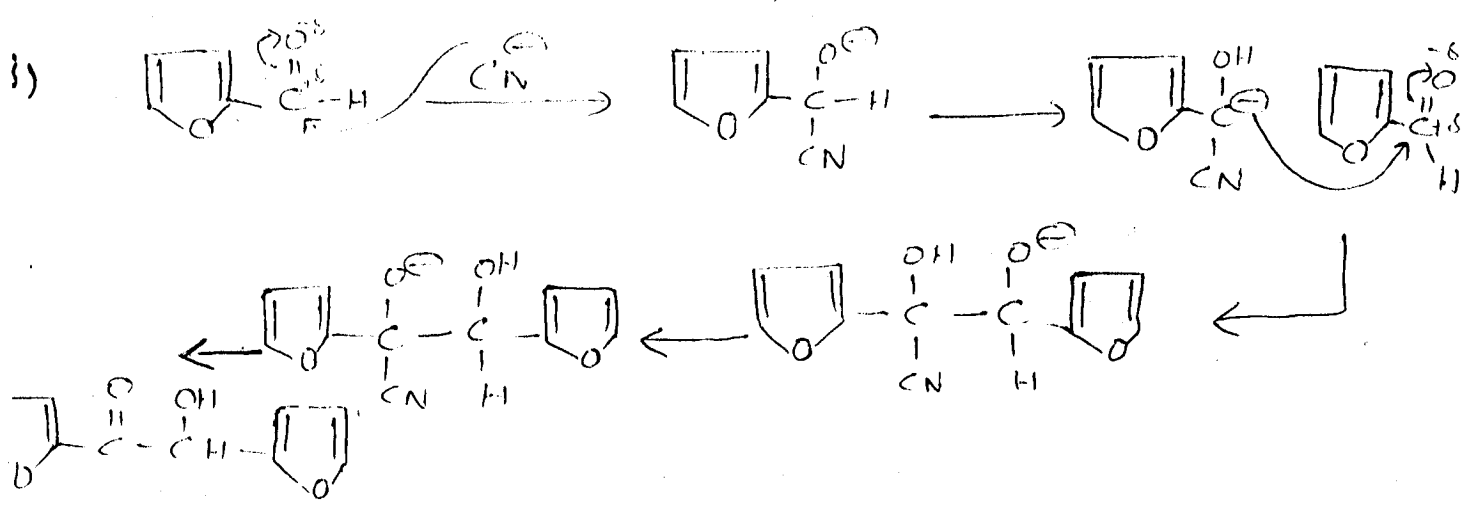
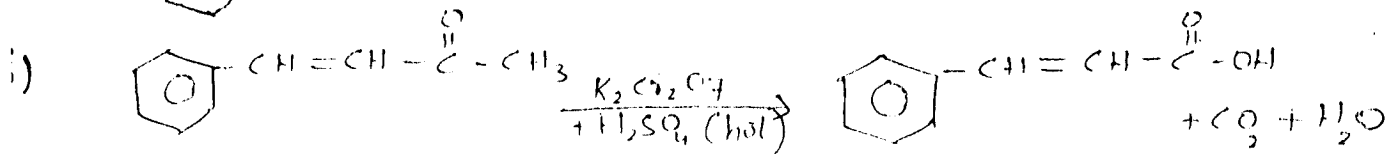
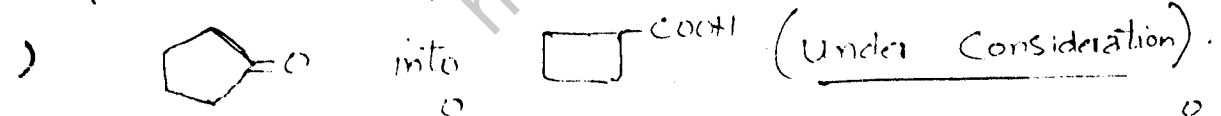


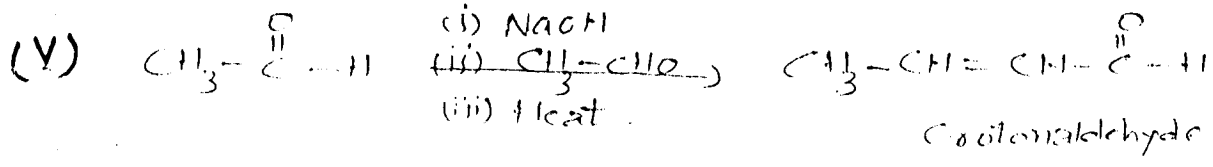
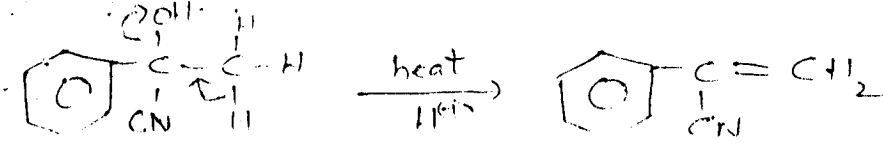
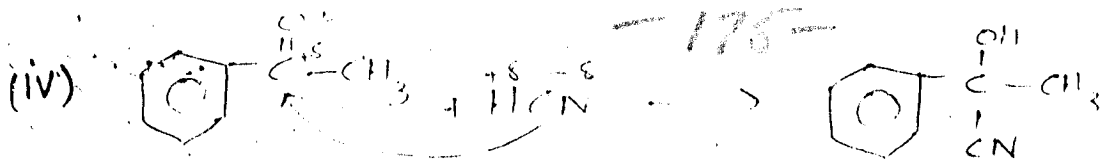


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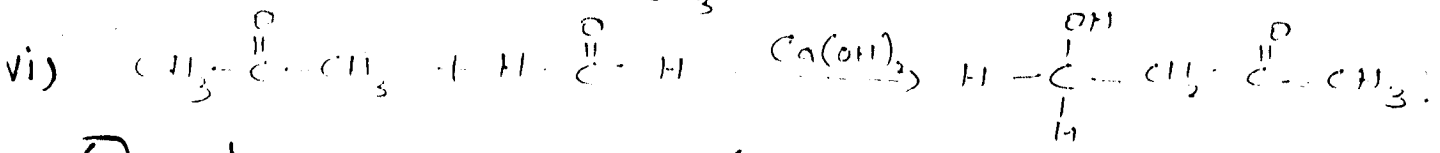
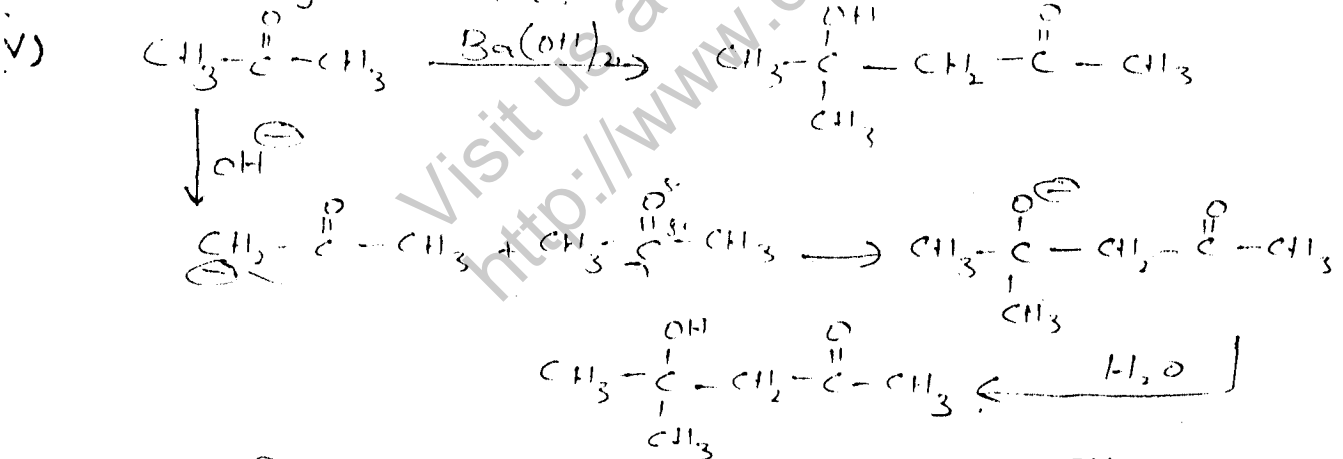
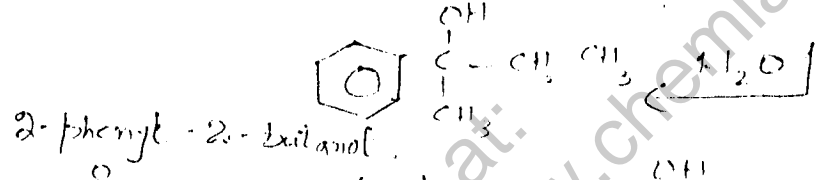
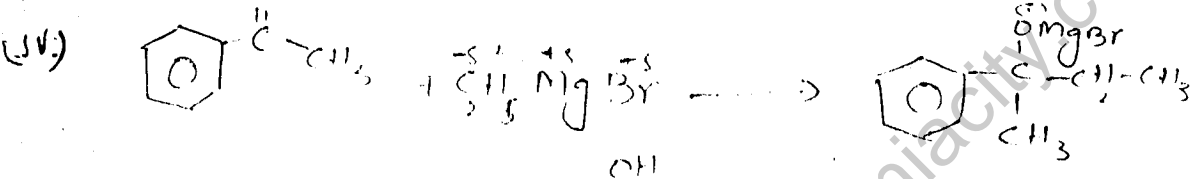
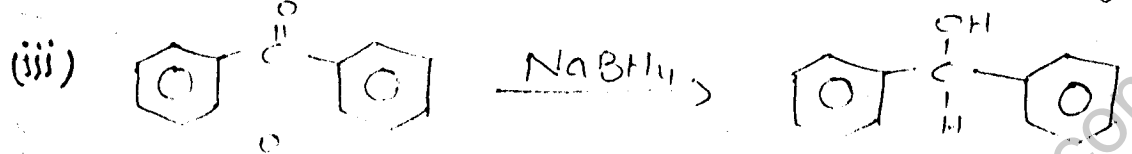
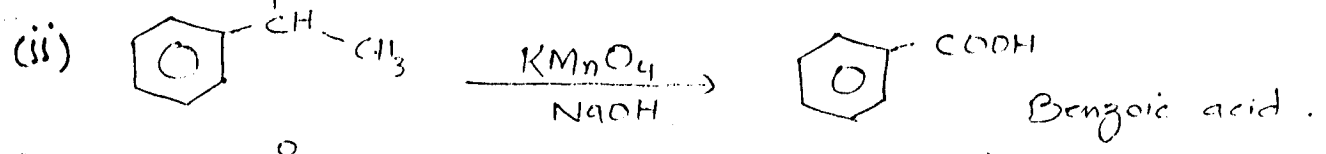
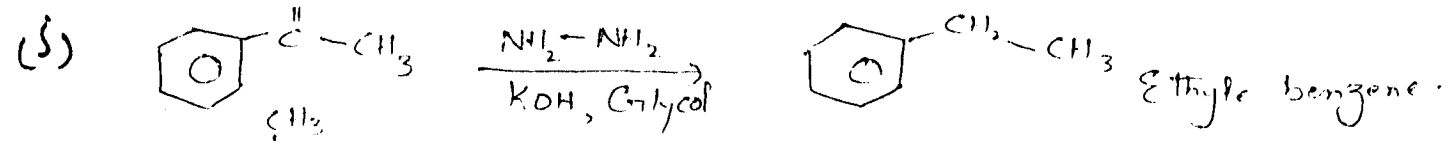


Question No. 7 :-





Question no. 9 :-



Question No. 11 :-

Resemblances :-

- Both are Carbonyl Compounds.
- In both Carbonyl Carbon is sp<sup>2</sup> hybridized
- The Carbonyl Carbon is electrophile with +ve charge

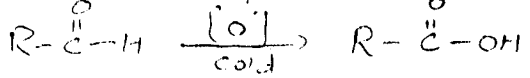
Both undergo base catalyzed and acid catalyzed reaction like, aldol condensation, hemiacetal, acetal etc.

Both can be prepared from corresponding alcohols by their oxidation. In contrast these are reduced to alcohol on reduction.

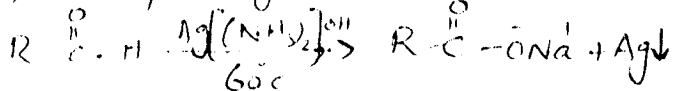
## Differences :-

### Aldehyde

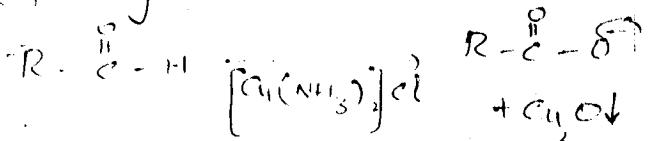
Aldehydes are easily oxidized to Carboxylic acids



Aldehydes give silver mirror test

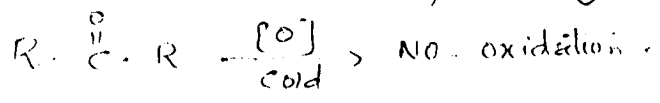


Aldehydes give red ppt with cuprous ammonical chloride (Fehling's solution)



### Ketone

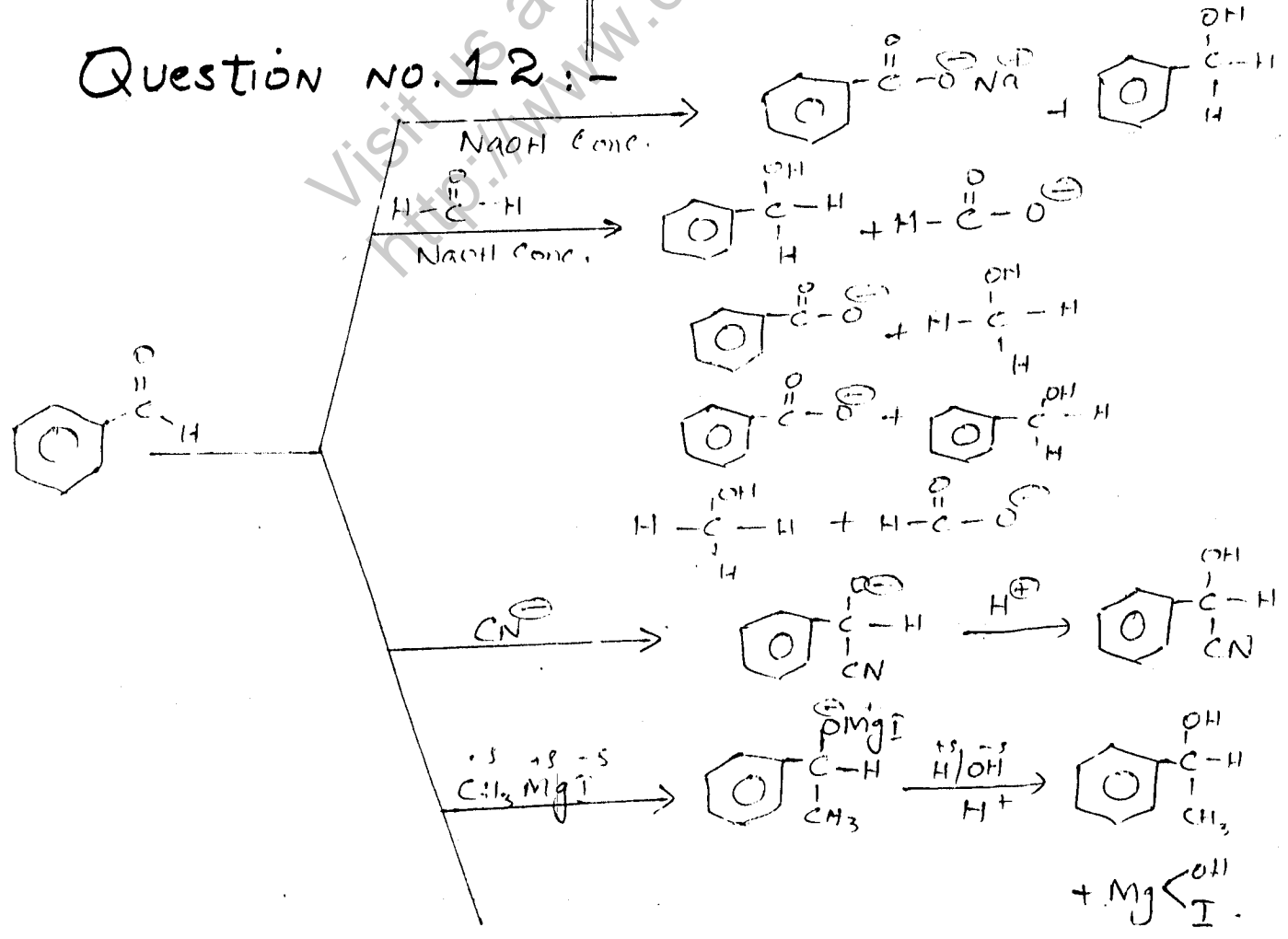
Ketones are not easily oxidized



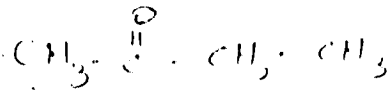
Ketones does not give silver mirror test.

Ketones give no red ppt with Fehling's solution.

## Question NO. 12 :-

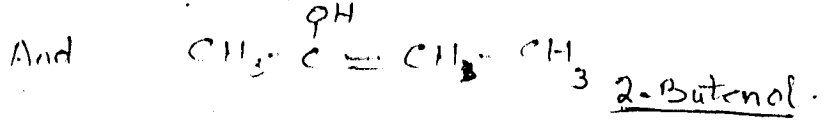
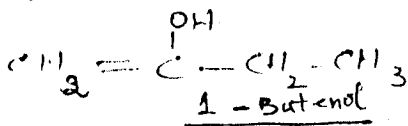


Question NO. 16 :- -177-

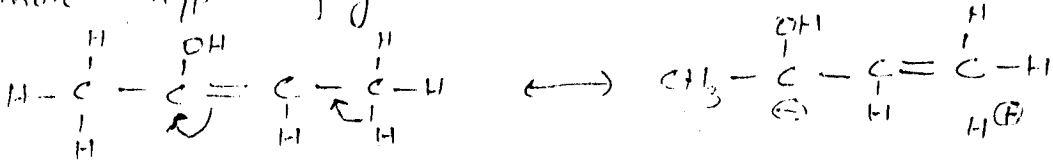


C<sub>7</sub>

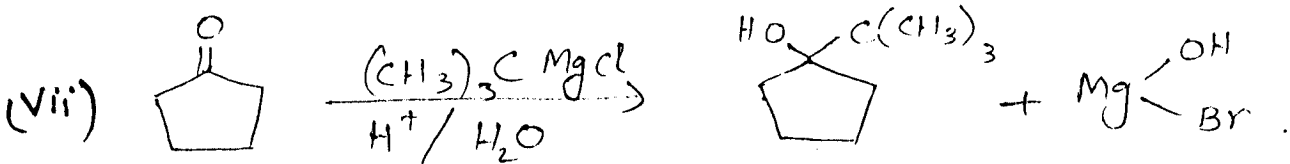
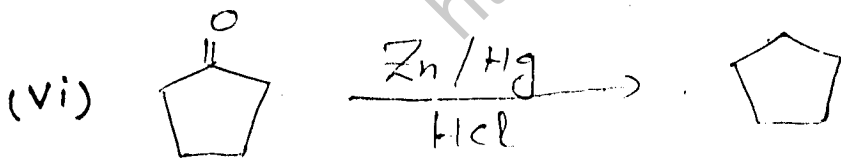
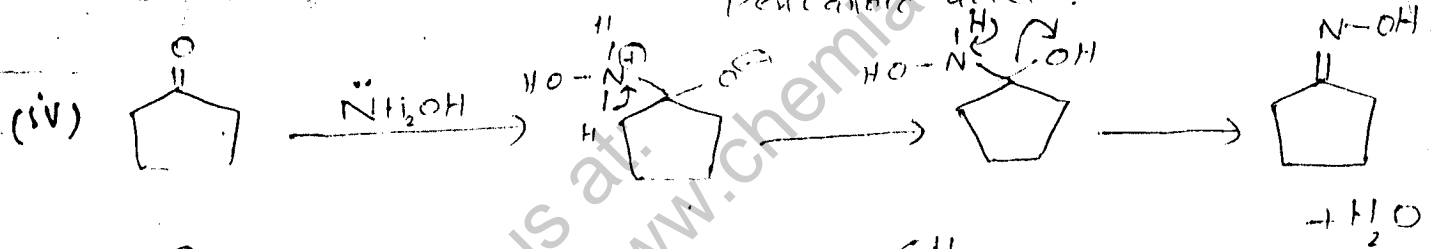
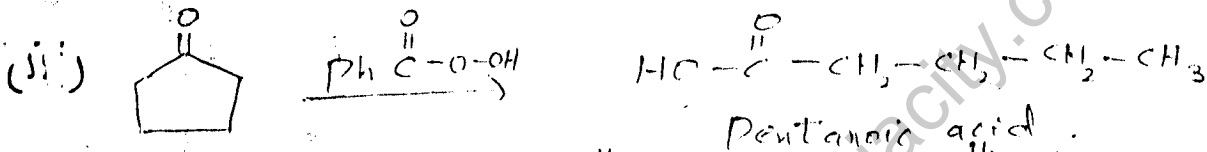
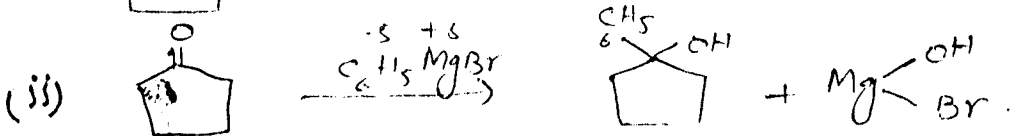
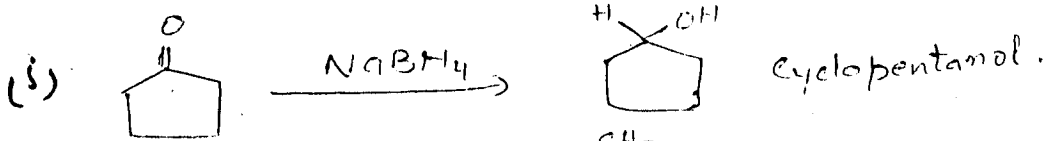
There are two possible enol forms.



2-Butenol is more stable than 1-Butenol due to more hyperconjugated structures.



Question NO. 18 :-



# CARBOXYLIC ACIDS

**INTRODUCTION:-** Organic compounds having carboxyl group (-COOH) are called CARBOXYLIC ACIDS. These may be monocarboxylic acids or dicarboxylic acids having one or two ~~also~~ carboxylic acid groups respectively. The general formula of monocarboxylic acids is  $RCOOH$ . "R" may be aliphatic or Aromatic or heterocyclic compound.

ALIPHATIC MONOCARBOXYLIC ACIDS are sometimes called fatty acids because they are obtained from hydrolysis of fats (For example PALMITIC acid  $C_{16}H_{31}COOH$ ).

**NOMENCLATURE:-** There are two systems of nomenclature

**COMMON NAMES:-** These names are based upon the source of carboxylic acids. Some examples are given below.

FORMIC ACID	$HCOOH$	OBTAINED FROM DISTILLATION OF RED ANTS
ACETIC ACID	$CH_3COOH$	" " " " " " " " " " " "
BUTYRIC ACID	$CH_3CH_2CH_2COOH$	" " " " " " " " " " " "

Butyrum means butter

The position of substitution is indicated by  $\alpha, \beta, \gamma$ , etc.

$CH_3-CH(OH)-COOH$   $\alpha$ -Hydroxy propionic acid

$CH_2(Br)-CH(Br)-CH_2COOH$   $\beta, \gamma$ -dibromo butyric acid

$CH_3CH_2CH_2COOH$  n-Butyric acid

$CH_3-CH(CH_3)-COOH$  Isobutyric acid

**I.U.P.A.C. NOMENCLATURE:-** Rules of I.U.P.A.C.

- Select largest carbon chain and write name of corresponding parent alkane
- Replace "e" of parent alkane by -oic acid.
- To indicate position of substituent number the carbon chain starting from carboxylic carbon.

