

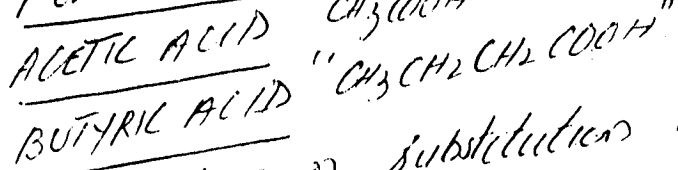
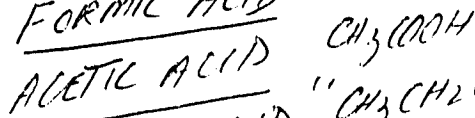
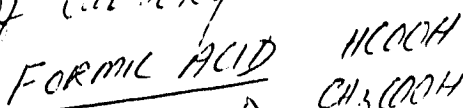
CARBOXYLIC ACIDS D.V.C.

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

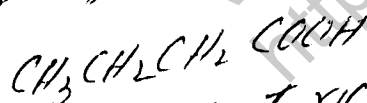
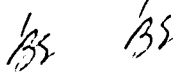
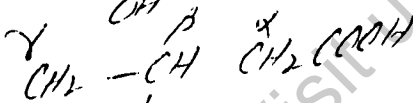
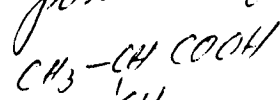
NOMENCLATURE:- There are two systems of nomenclature

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



OBTAINED FROM DISTILLATION OF RED WOODS
 " " VINEGAR (ACETUM)
 " " BUTYRUM means butter

The position of substitution is indicated by α, β, γ , etc.



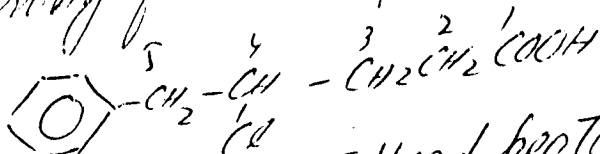
n-Butyric acid



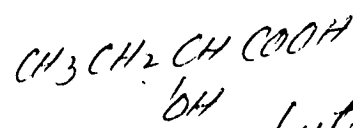
Isobutyric acid

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

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

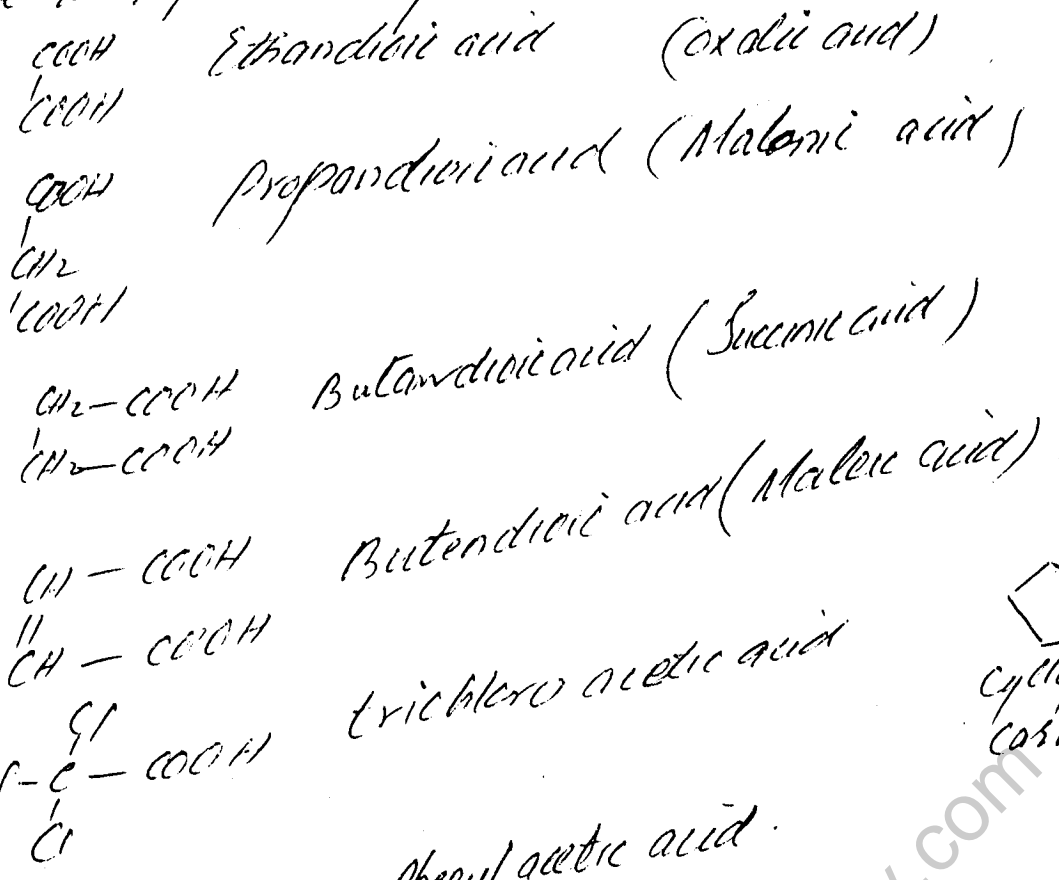


4-Chloro-5-phenyl pentanoic acid

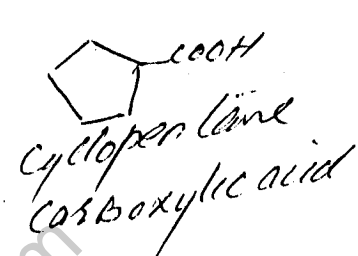


2-Hydroxybutanoic acid

If there are more than one carboxylic acid groups, "e" is replaced by "dioic acid". Some examples are then



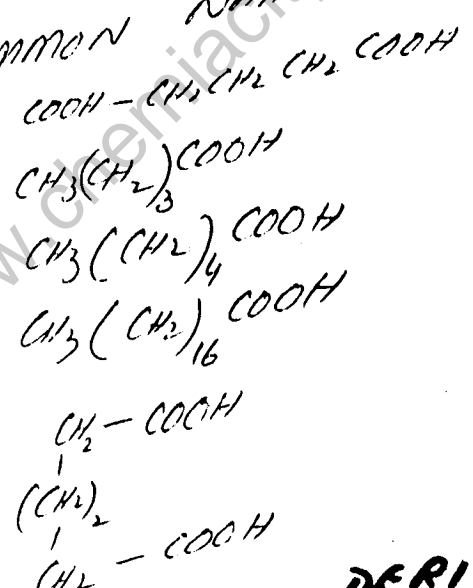
NOTE
SEE SOME MORE COMMON NAMES FROM TEXT BOOK



SOME IMPORTANT

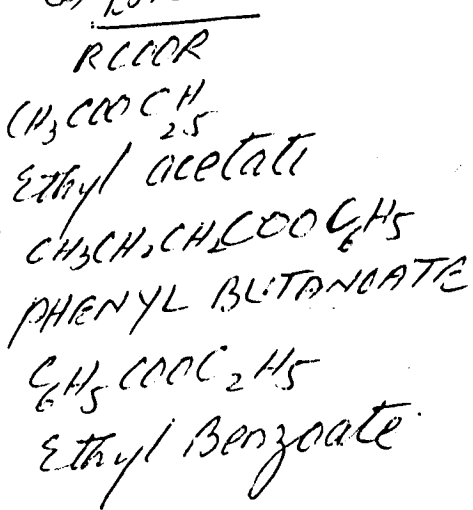
- 1) GLUTARIC ACID
- 2) VALERIC ACID
- 3) CAPROIC ACID
- 4) STEARIC ACID
- 5) ADIPIC ACID

COMMON NAMES

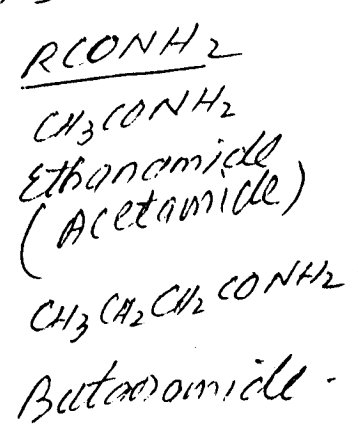


NAMES OF

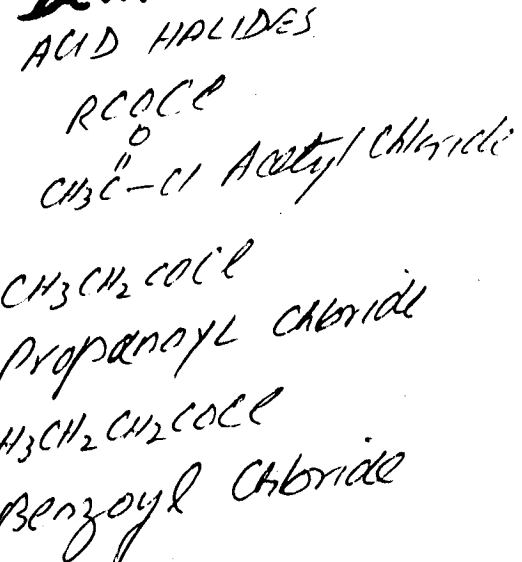
ESTERS



SOME ACID AMIDES



DERIVATIVES

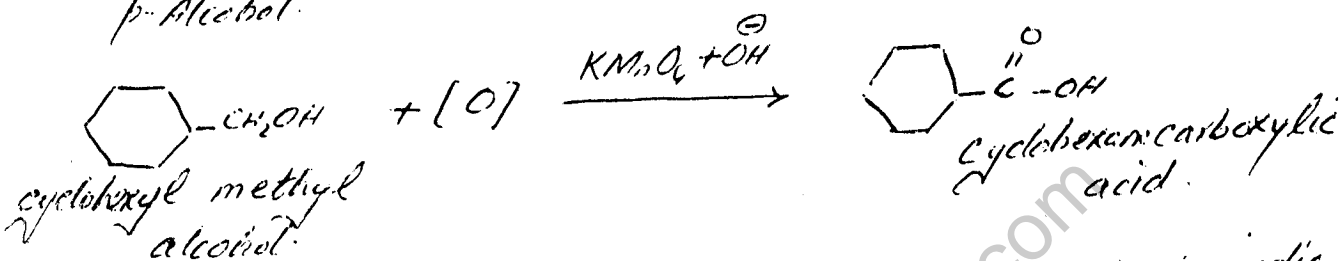
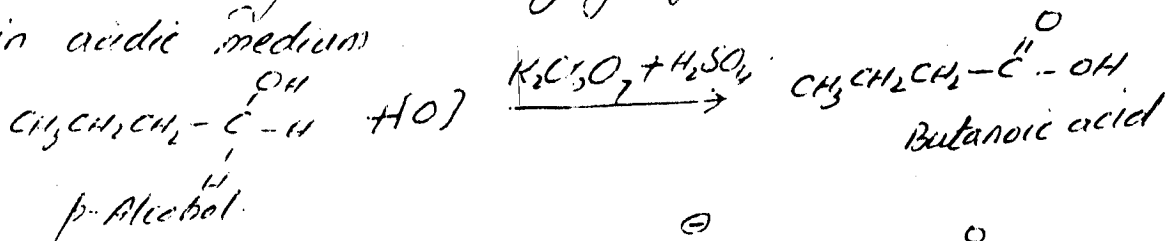


(See Textbook also)

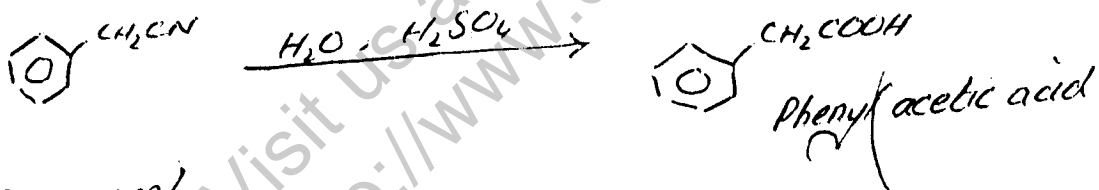
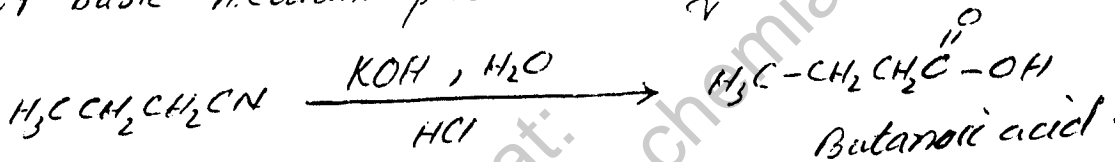
GENERAL METHODS OF PREPARATION OF CARBOXYLIC ACIDS

The general methods of preparation of carboxylic acids are given below. (PLEASE CONSULT YOUR TEXT BOOK ALSO)

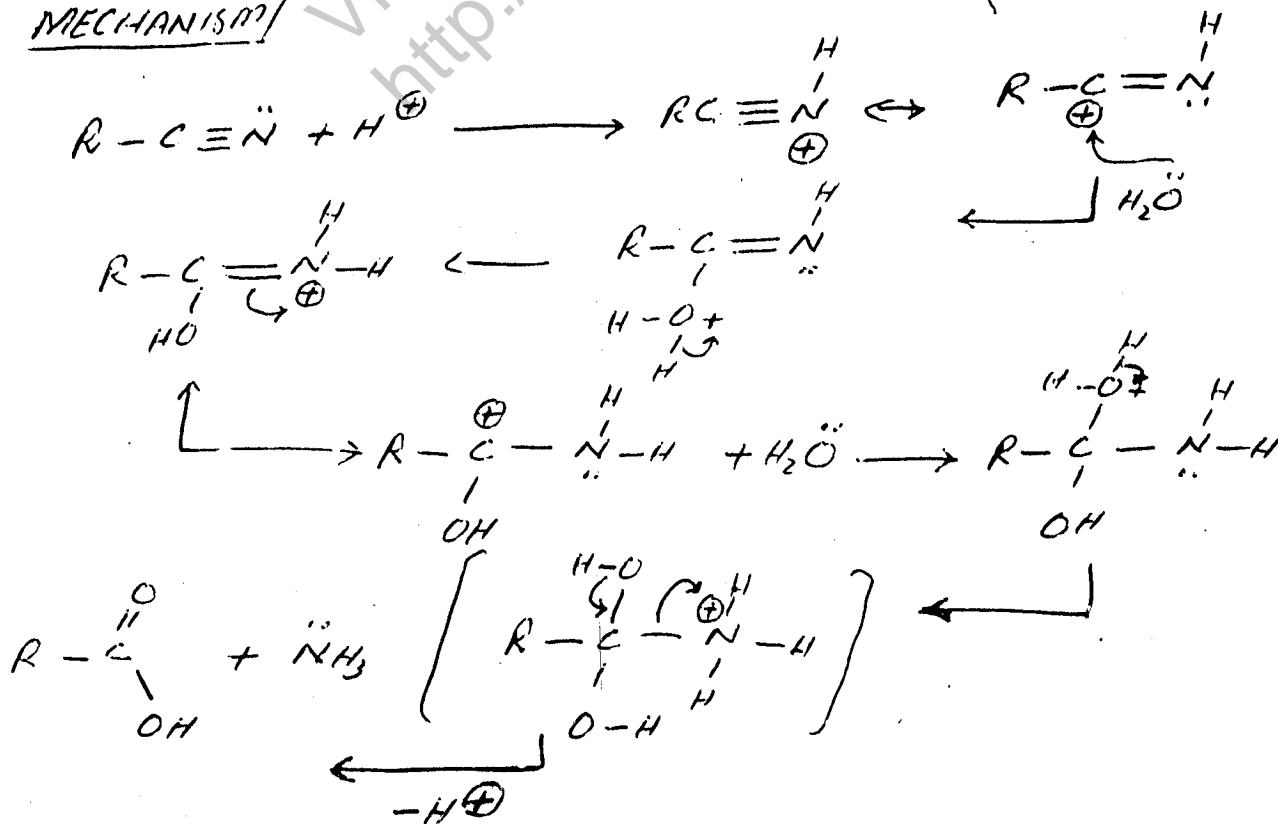
Oxidation of p-Alcohols:- p-Alcohols are oxidized to aldehydes, which are further oxidized to carboxylic acids. The most commonly used oxidizing agent is potassium dichromate in acidic medium.



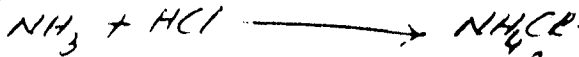
NITRILE SYNTHESIS:- Alkyl nitriles on hydrolysis in acidic or basic medium produce carboxylic acids.



MECHANISM



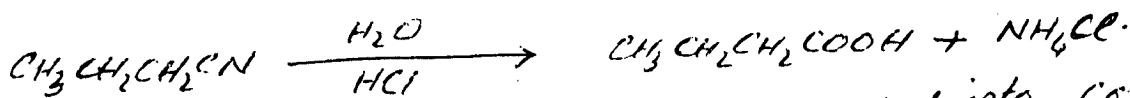
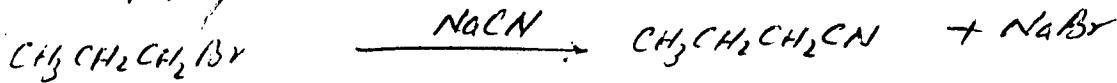
Ammonia formed may react with HCl to form ammonium chloride



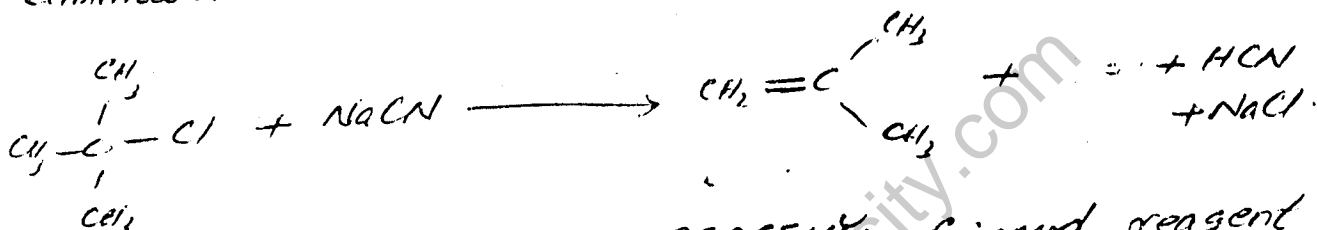
ADVANTAGE The reaction can be used to lengthen carbon chain. For example n-propyl alcohol (1-Propanol) could be converted into butanoic acid by following reaction scheme.



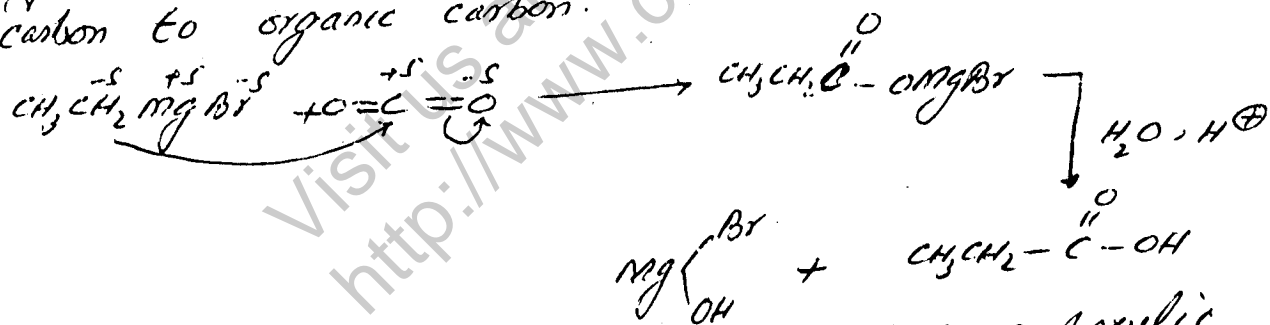
1-Propanol



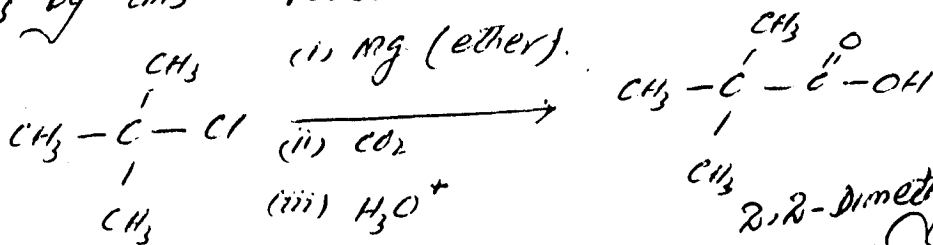
ter. Alkyl halide could not be converted into carboxylic acids by this reaction scheme because these undergo elimination reaction on treatment with CN^- ion.



CARBONYLATION OF GRIGNARD REAGENT: Grignard reagent on treatment CO_2 followed by hydrolysis produces carboxylic acids. The reaction is used to convert inorganic carbon to organic carbon.



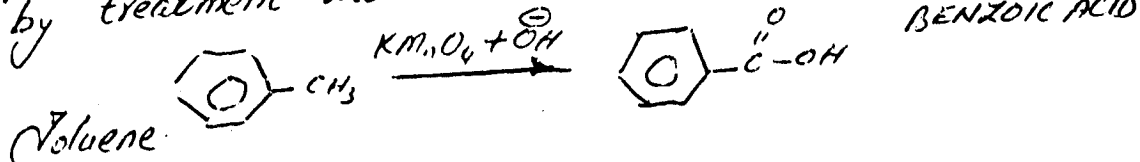
Alkyl halides could be converted into carboxylic acids by this reaction scheme.



2,2-Dimethyl propanoic acid

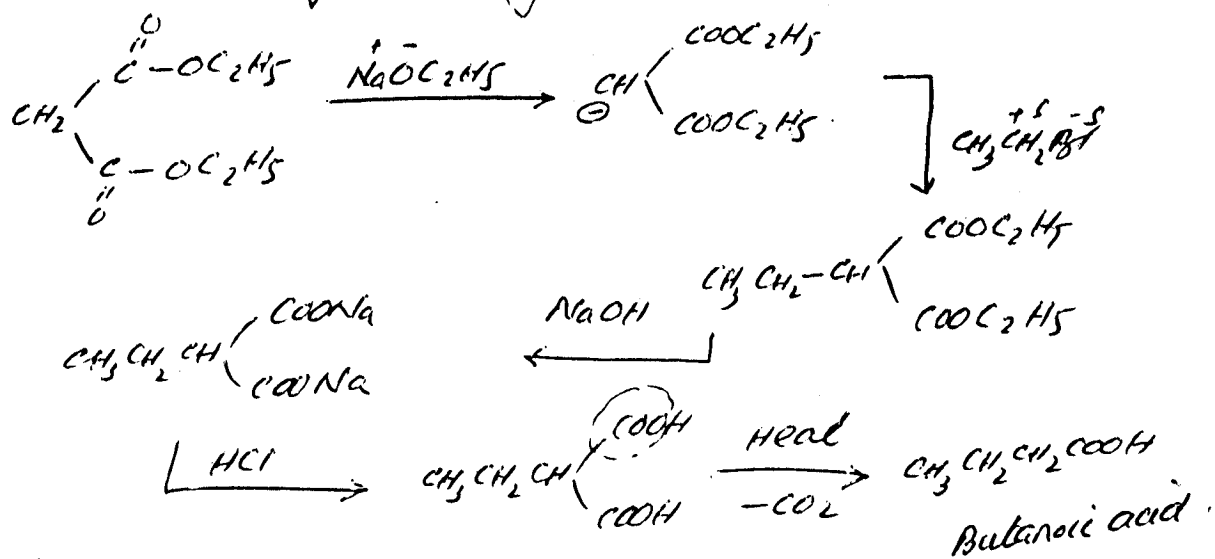
SIDE CHAIN OXIDATION OF AROMATIC HYDROCARBONS. acid.

The alkyl side chain of benzene ring is oxidized to " $-\text{COOH}$ " group by treatment with alkaline KMnO_4

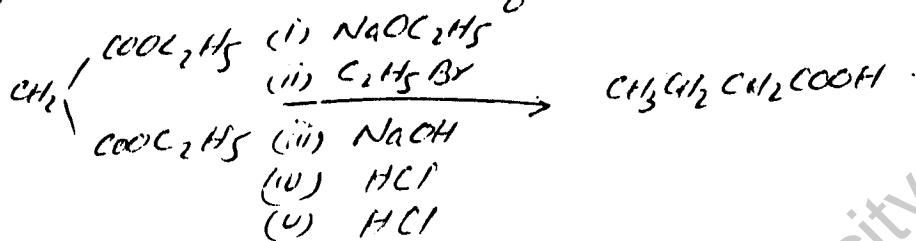


Toluene

FROM MALONIC ESTER: - Carboxylic acids can also be prepared by reaction of an alkyl halide with malonic ester by following reaction scheme.

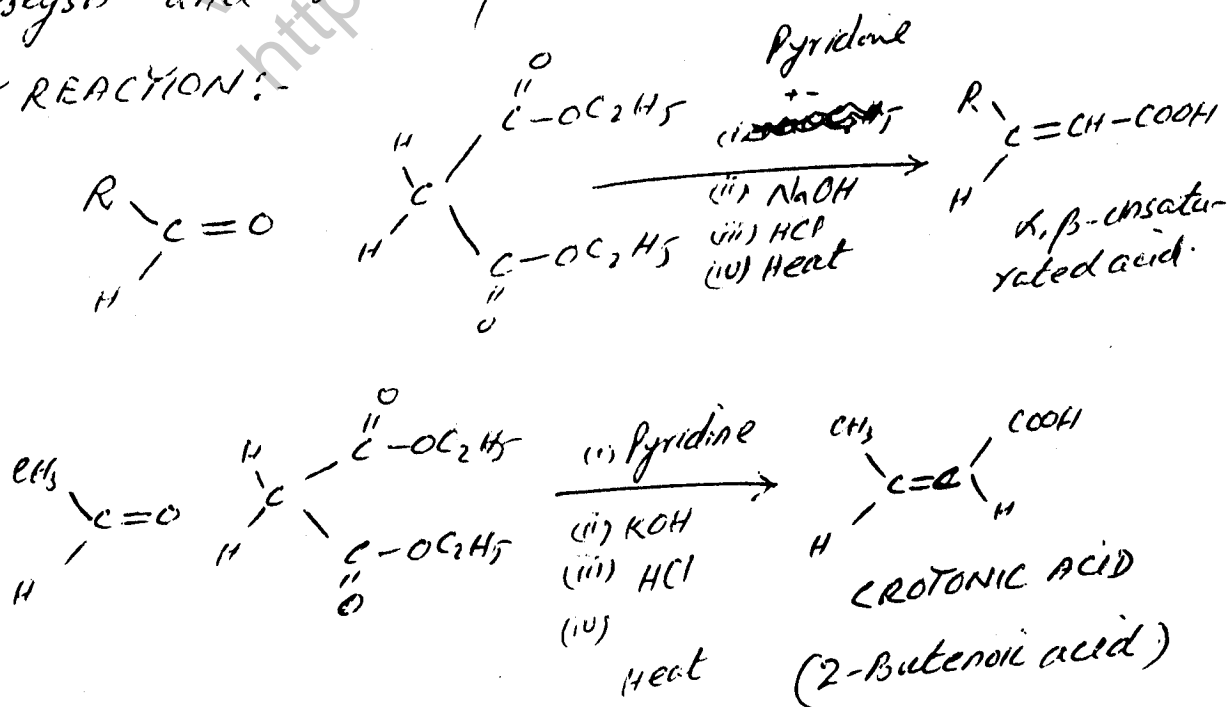


It can be written as follows:

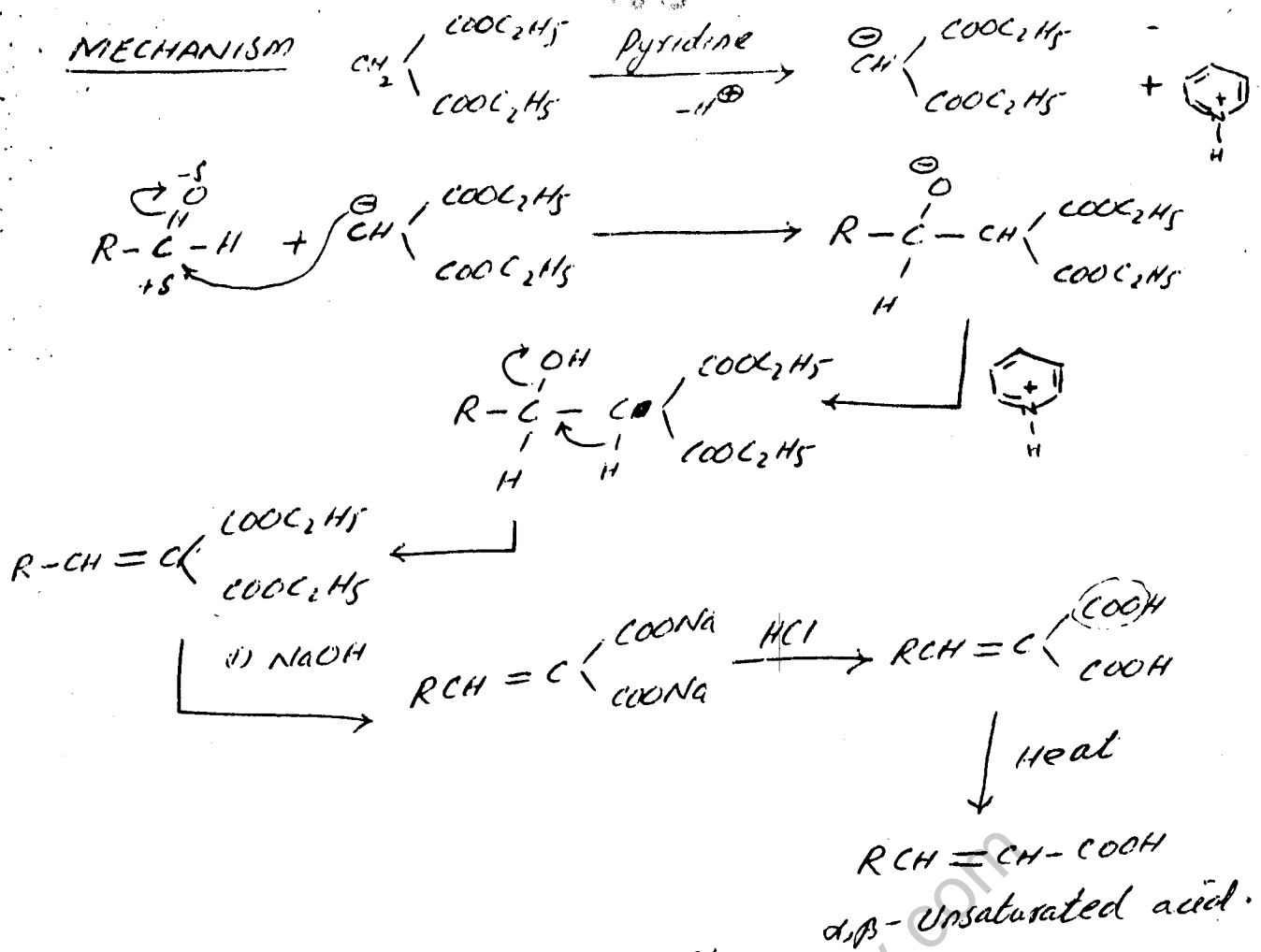


Imp. KUNVENAGEL REACTION: - The reaction is used to prepare α, β -unsaturated carboxylic acids. In this reaction an aliphatic aldehyde is treated with an active methylene group compound (MALONIC ESTER etc) in presence of an organic base, pyridine followed by hydrolysis and decarboxylation.

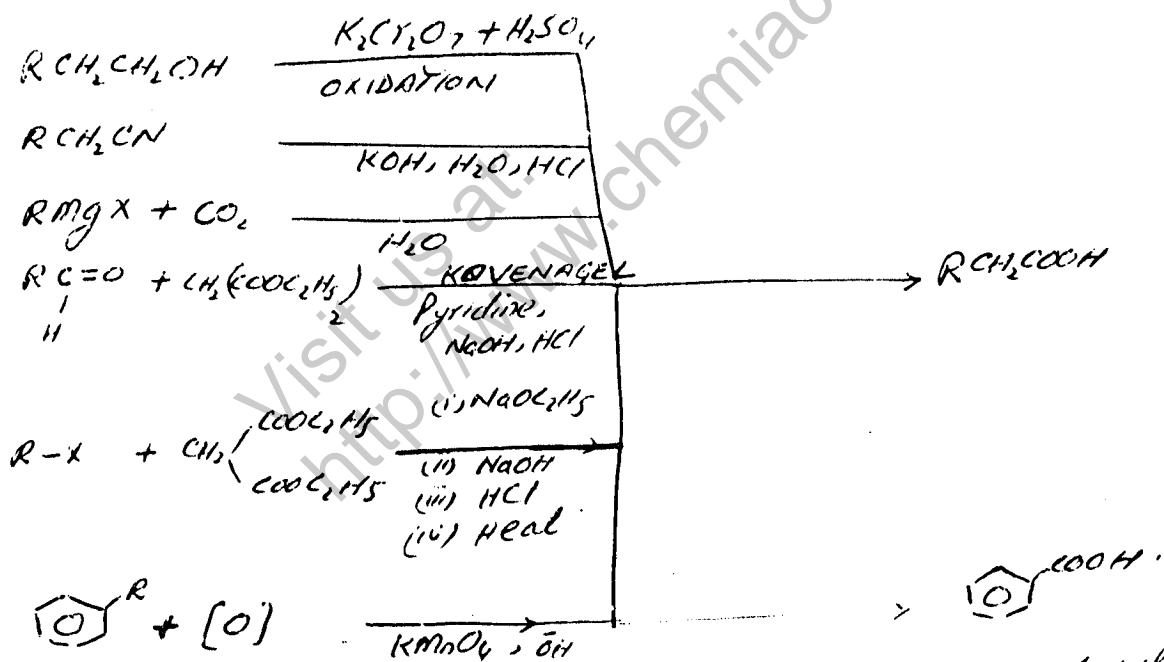
NEY REACTION:



MECHANISM



SUMMARY

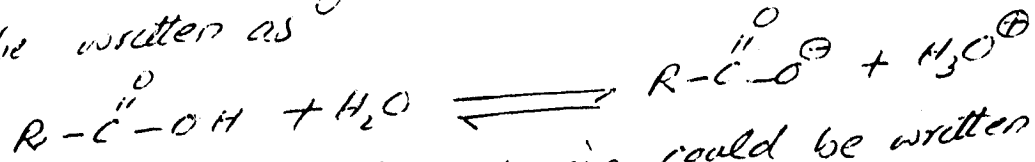


PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS :- Carboxylic acids

have higher B.P. and M.P as compared to corresponding alkanes. It is due to hydrogen bonding in carboxylic acids. The first few carboxylic acids are liquids while higher acids are solids. Carboxylic acids of low m.wt (up to 5 carbons) are water soluble. The higher are sparingly soluble and carboxylic acids of high m.wt are insoluble. The densities of formic acid and acetic acid are higher than water due to strong hydrogen bonding.

Discuss acidity of carboxylic Acids? What is effect of various substituents on acid strength? An acid is defined as a proton donor species. Carboxylic acids donate their hydroxylic hydrogen as proton, thus they act as Acids.

The ionization of carboxylic acid in water can be written as



The equilibrium constant expression could be written as

$$K_c = \frac{[RCOO^-][H_3O^+]}{[RCOOH][H_2O]}$$

Since water is used in large excess so its concentration almost remains constant. The above expression could be written as

$$K_c [H_2O] = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

" K_a " is called Acid dissociation constant. The value of " K_a " is measure of acid strength. The greater the value of " K_a " the stronger is the acid and vice versa. The " K_a " of most of carboxylic acids is of the order of 10^{-2} to 10^{-5} . Thus strength of acid is mostly expressed as pK_a .

$$pK_a = -\log K_a$$

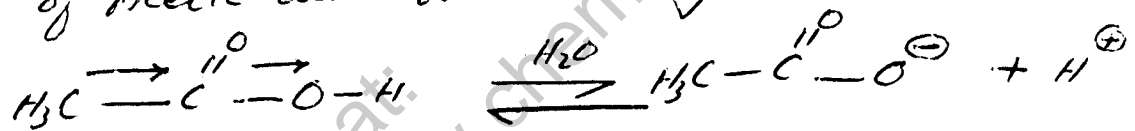
For example when $K_a = 10^{-2}$ $pK_a = 2$
 when $K_a = 10^{-5}$ $pK_a = 5$

The greater the value of pK_a the weaker is the acid.

The pK_a of formic acid is 3.75 while pK_a of Acetic acid is 4.76. Thus formic acid is almost ten times as strong as Acetic acid.

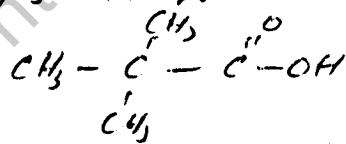
Hydrogen of formic acid by electron donating group decreases acid strength while an electron withdrawing group increases acid strength.

ACETIC ACID IS WEAKER ACID THAN FORMIC ACID. It is due to the fact that methyl group is an electron donating group which inhibits removal of proton from $-OH$. Further it destabilizes the anion formed. The anion recaptures proton released. Thus proton of acetic acid is not easily available to base.



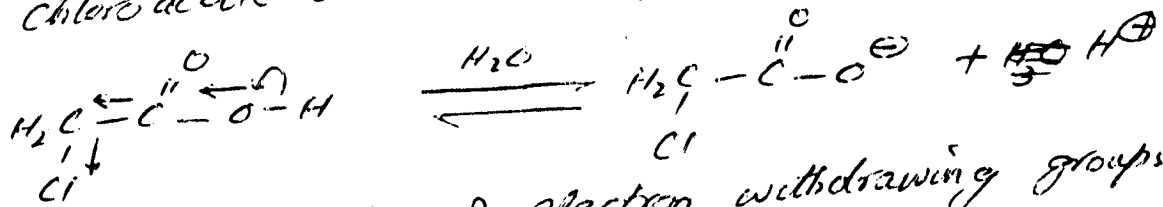
$$pK_a = 4.76$$

Further addition of the length of alkyl group has minor effect on acid strength. However crowding of alkyl groups on α -carbon decreases acid strength appreciably.



$$pK_a = 5.0$$

ELECTRON WITHDRAWING GROUPS ($-OH, -OCH_3, -X$) -
 at α -position increase acid strength because they
 favour a removal of proton from hydroxylic group
 and stabilize anion formed after removal of proton.
 Thus chloroacetic acid is stronger than Acetic acid



The greater the number of electron withdrawing groups
 at α -position the stronger is the acid. For example
 decreasing order of acid strength is

Trichloroacetic acid > Dichloroacetic acid > Chloroacetic acid

The electron withdrawing inductive effect decreases
 appreciably with distance from $-COOH$ group. Thus
 decreasing order of acid strength is

2-chlorobutanoic acid > 3-chlorobutanoic acid > 4-chlorobutanoic acid

The $-I$ effect of halogens depend upon electronegativity of halogens. For example order of acid strength is

Iodoacetic acid > Chloroacetic acid > Bromoacetic acid > acetic acid

RESONANCE EFFECT: - The groups which show electron donating resonance effect decrease resonance effect acid strength while group with electron withdrawing resonance effect increase acid strength.

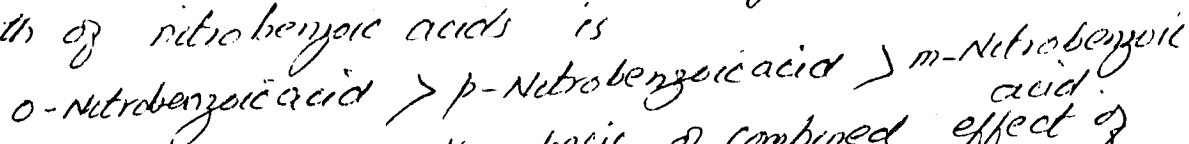
BENZOIC ACID IS WEAKER ACID AS COMPARED TO FORMIC ACID.

The pK_a of benzoic acid is 4.2 while that of formic acid is 3.75

It is due to the fact that in benzene carbon is sp^2 hybridized. Thus it is less electron withdrawing as compared to hydrogen of formic acid. Hydrogen uses its $1s$ -orbital in bond formation. The order of electronegativity is $s > sp > sp^2 > sp^3$. Thus benzoic acid

is weaker acid as compared to formic acid -
but ~~is~~ stronger acid as compared to Acetic acid.

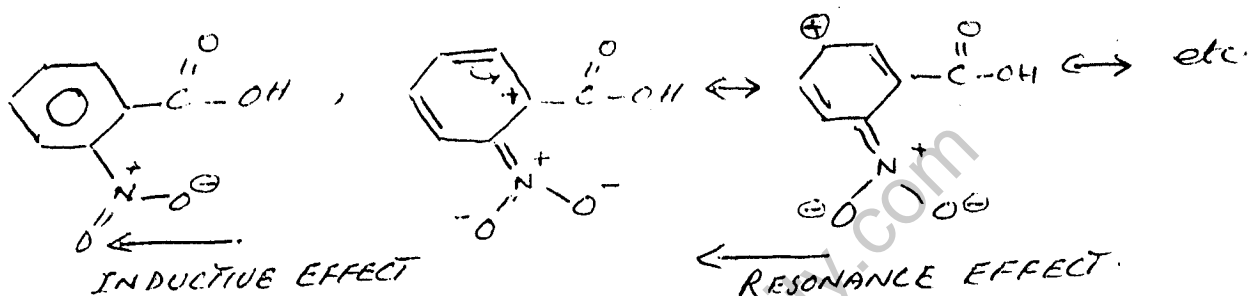
NITRO BENZOIC ACIDS :- The decreasing order of acid strength of nitrobenzoic acids is



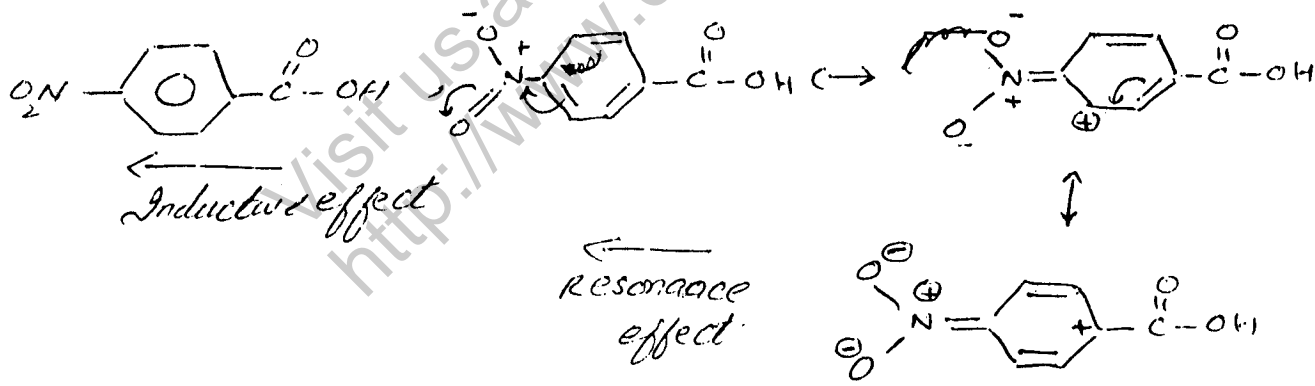
It can be explained on the basis of combined effect of Resonance and Inductive effect.

In ortho nitro benzoic acid there is an electron withdrawing **INDUCTIVE EFFECT** and **electron withdrawing RESONANCE EFFECT**.

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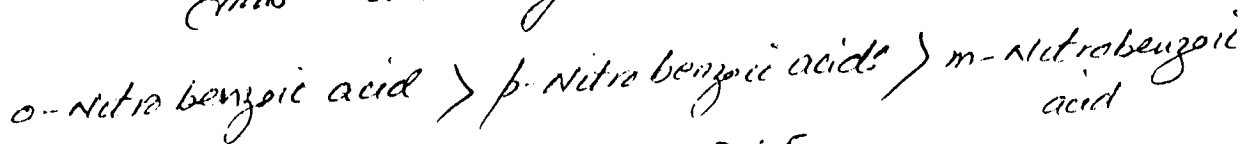


The same is case with *p*-Nitrobenzoic acid but due to farther position of -NO_2 group, inductive effect is less pronounced.



In *m*-Nitrobenzoic acid **INDUCTIVE EFFECT** is there but there is no ^{direct} Resonance effect. Thus it is stronger acid than formic acid but weaker than *o*- and *p*-nitro benzoic acids.

Thus decreasing order of acid strengths is



$$pK_a = 2.17$$

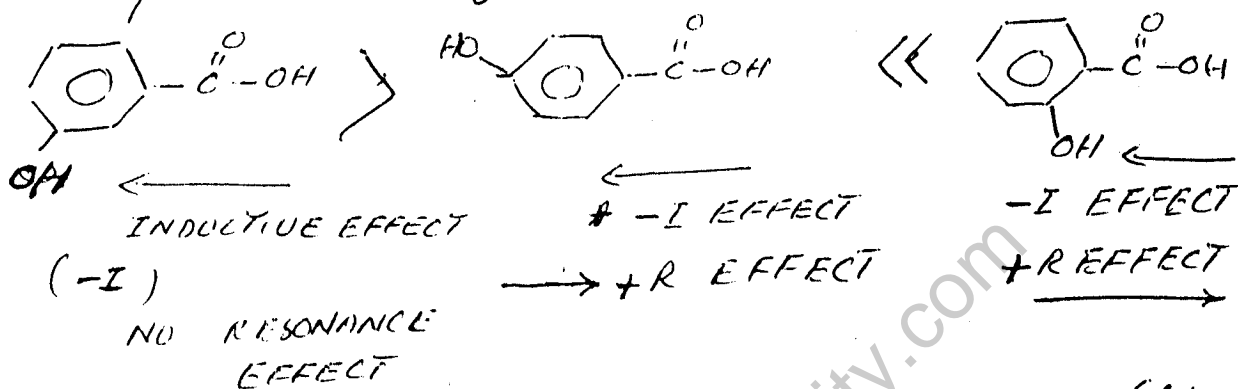
$$pK_a = 3.45$$

$$pK_a = 3.49$$

Groups such as $-OH$, $-OR$, $-NH_2$ have electron attracting inductive effect and electron donating resonance effect when present at ortho and para position.

p -HYDROXY BENZOIC ACID IS WEAKER THAN m -HYDROXY BENZOIC ACID. This is due to the fact that at p position ^{electron donating resonance} effect is much more pronounced as compared to electron withdrawing inductive effect. At m -position there is NO resonance effect and only a inductive effect is there.

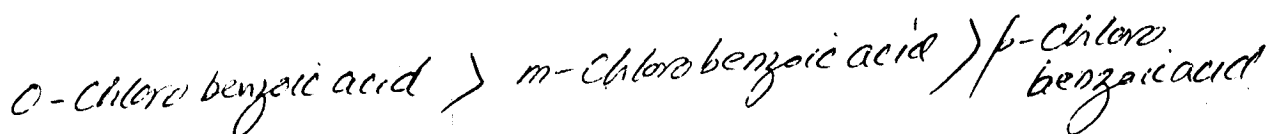
The expected order of acid strength is



O -HYDROXY BENZOIC ACID is quite strong acid ($pK_a = 2.97$) because of intramolecular hydrogen bonding which stabilize carboxylate anion.



HALOGEN SUBSTITUTED BENZOIC ACIDS :- In case of halogen substitution m electron withdrawing inductive effect is much more pronounced as compared to resonance effect. Thus decreasing order of acid strength is

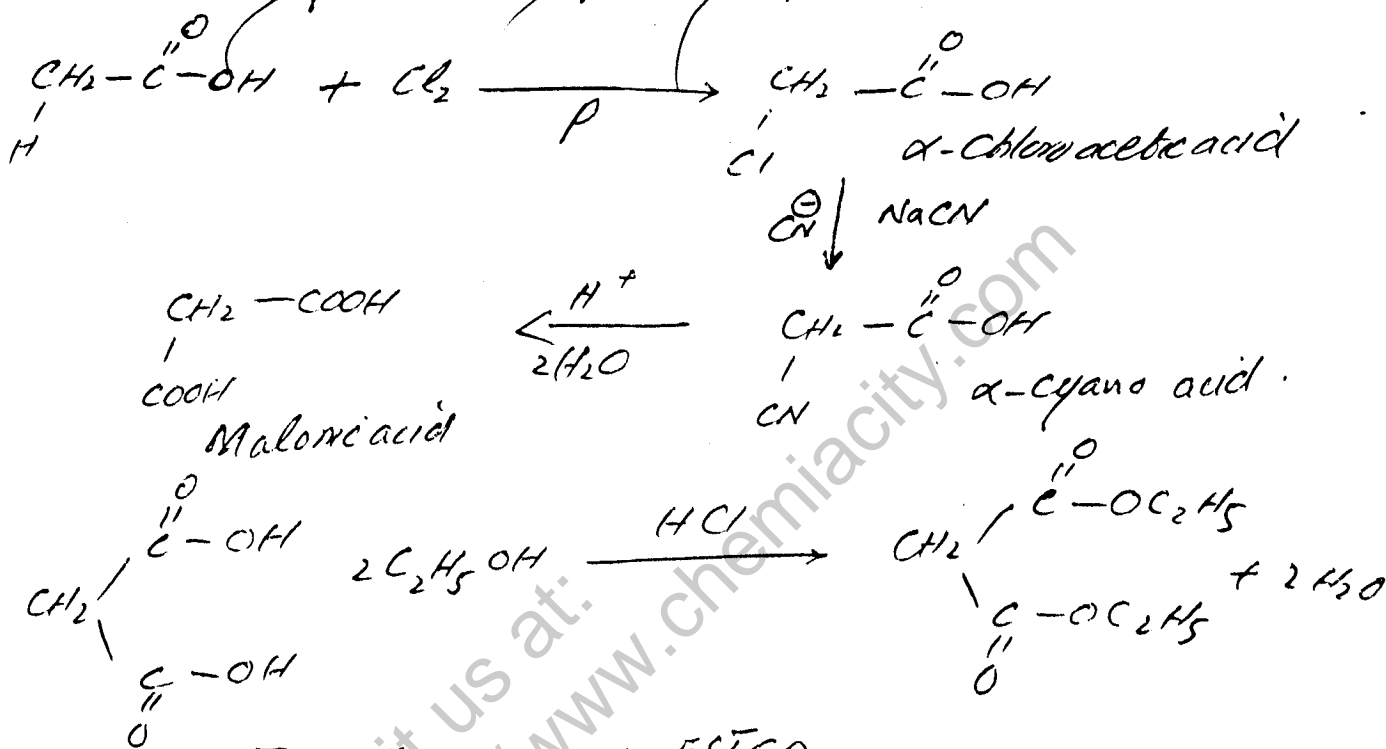


Q: WHAT IS MALONIC ESTER. HOW IS IT PREPARED? GIVE ITS SYNTHETIC APPLICATIONS?

Ans: Diethyl malonate is commonly called Malonic Ester. It is an ester of malonic (acid $\text{CH}_2(\text{COOH})_2$ (Propanedioic acid)), written as $\text{CH}_2(\text{COOC}_2\text{H}_5)_2$.

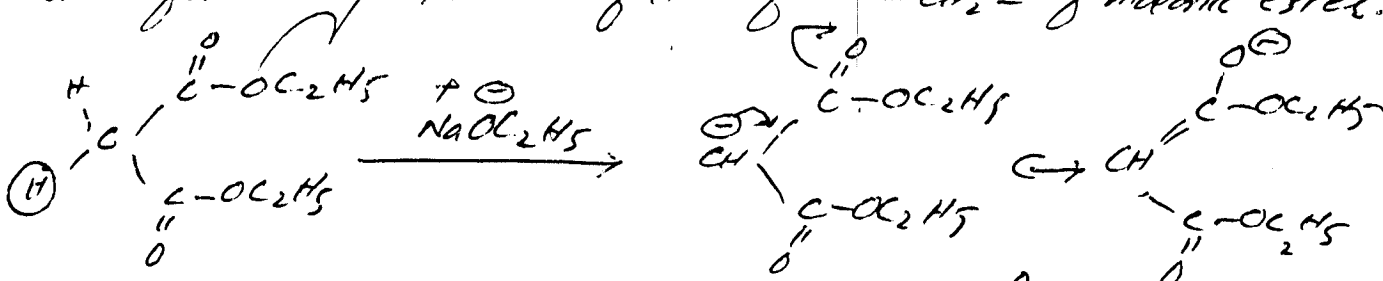
PREPARATION

It can be prepared from Acetic acid by Hell Volhard Zelinisky Reaction by following reaction scheme.



REACTIVITY OF MALONIC ESTER

Malonic ester is an active methylene compound. The $-\text{CH}_2-$ group of malonic ester is acidic. It can be explained on the basis of stability of anion formed by removal of H^+ from $-\text{CH}_2-$ of malonic ester.



This malonate anion is stabilized by resonance. Hence $-\text{CH}_2-$ is reasonably acidic. All the reactions of Malonic ester are due to this active methylene group. These reactions are catalyzed by strong base (NaOCl).

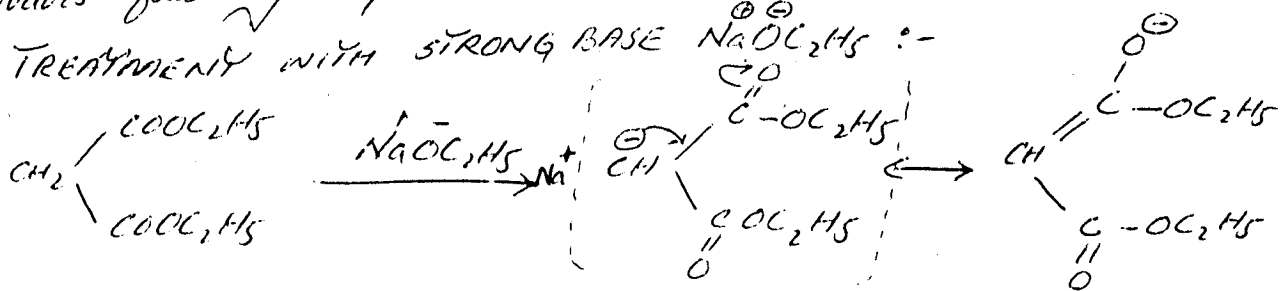
Synthetic Applications of Malonic Ester:-

Malonic ester is a very important organic compound used to prepare a number of other organic compounds especially, higher carboxylic acid, dicarboxylic acid, cyclic carboxylic acids etc. Let us discuss applications in detail.

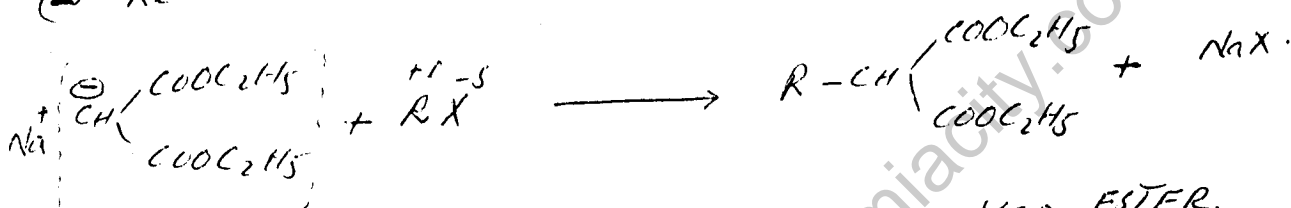
MONOALKYLATION OF MALONIC ESTER:- (HIGHER CARBOXYLIC ACID)

Malonic ester can be converted into higher carboxylic acids by alkylation followed by hydrolysis and decarboxylation. The reaction involves following steps.

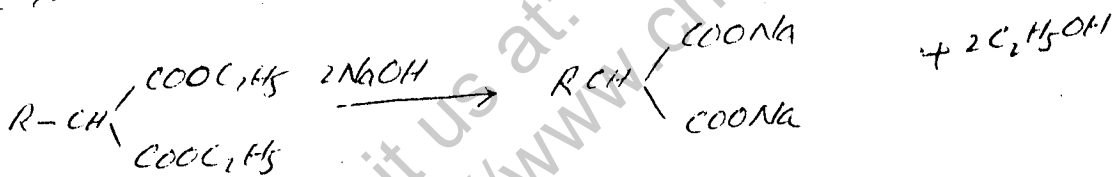
(1) TREATMENT WITH STRONG BASE NaOC_2H_5 :-



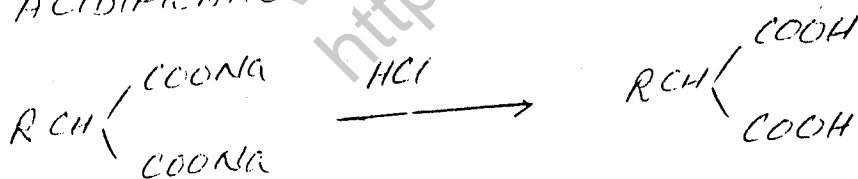
(2) REACTION WITH ALKYL HALIDE :-



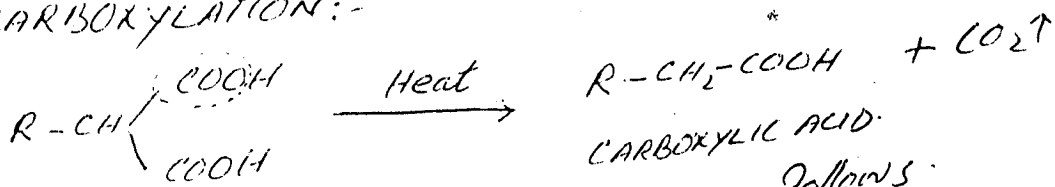
3:- BASE HYDROLYSIS OF MONOALKYLATED ESTER.



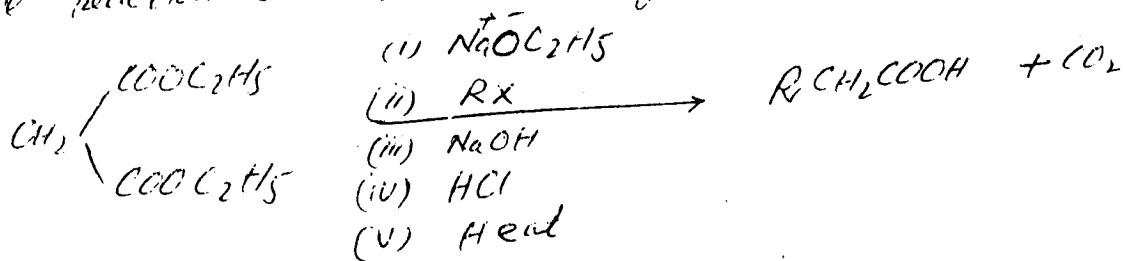
4:- ACIDIFICATION OF SODIUM SALT.



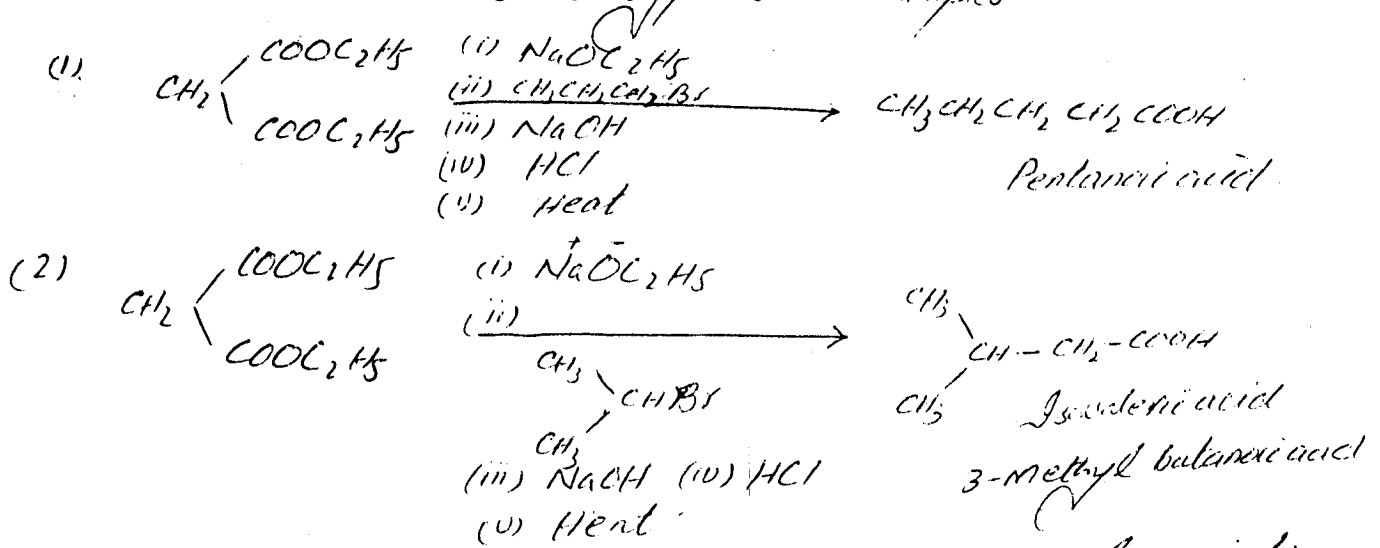
5:- DECARBOXYLATION:-



The reaction can be summarized as follows.

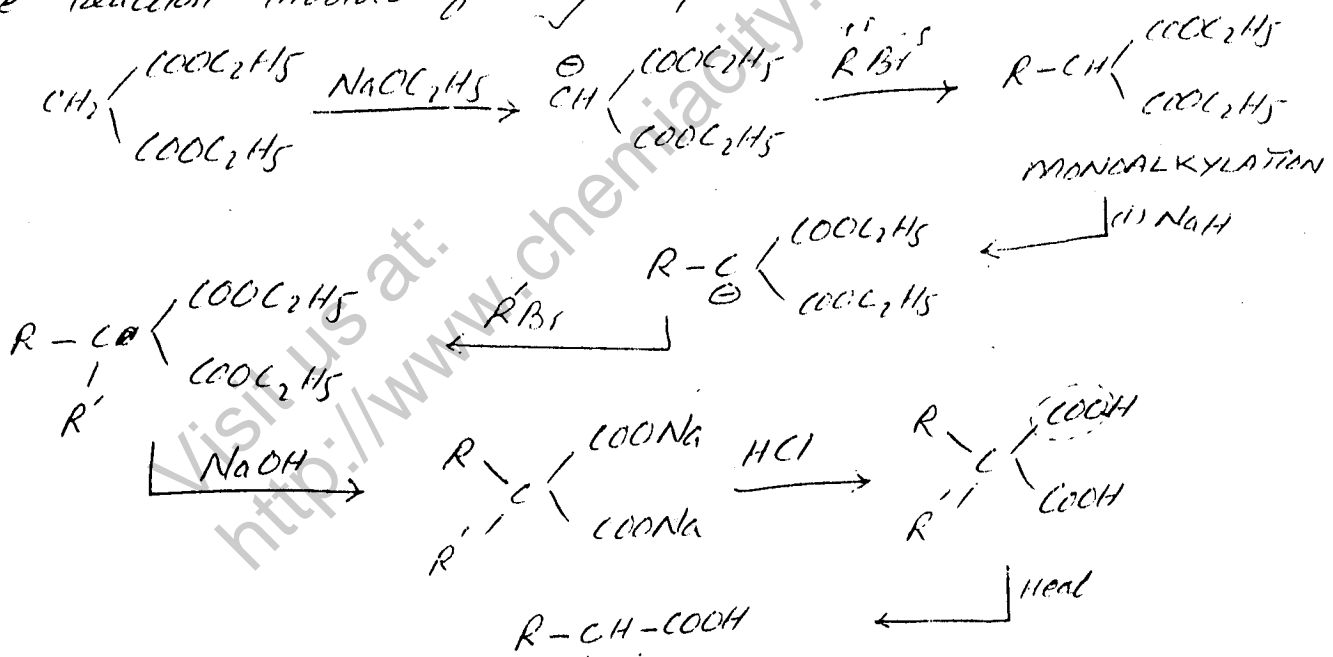


Let us consider some typical examples.

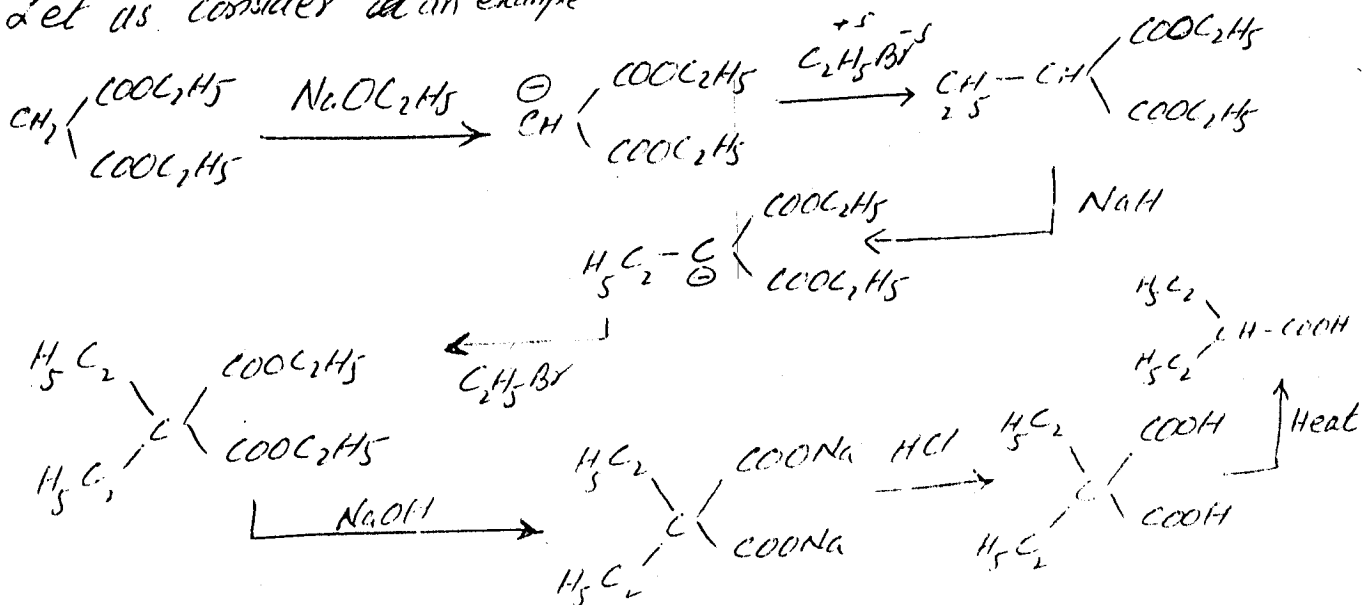


Note that two carbons of product carboxylic acids are contributed by malonic ester.

DIALKYLATION OF MALONIC ESTER:- The malonic ester can be dialkylated by replacing both hydrogens of methylene group one by one. A very strong base NaNH is used to remove second hydrogen. The reaction involves following steps.

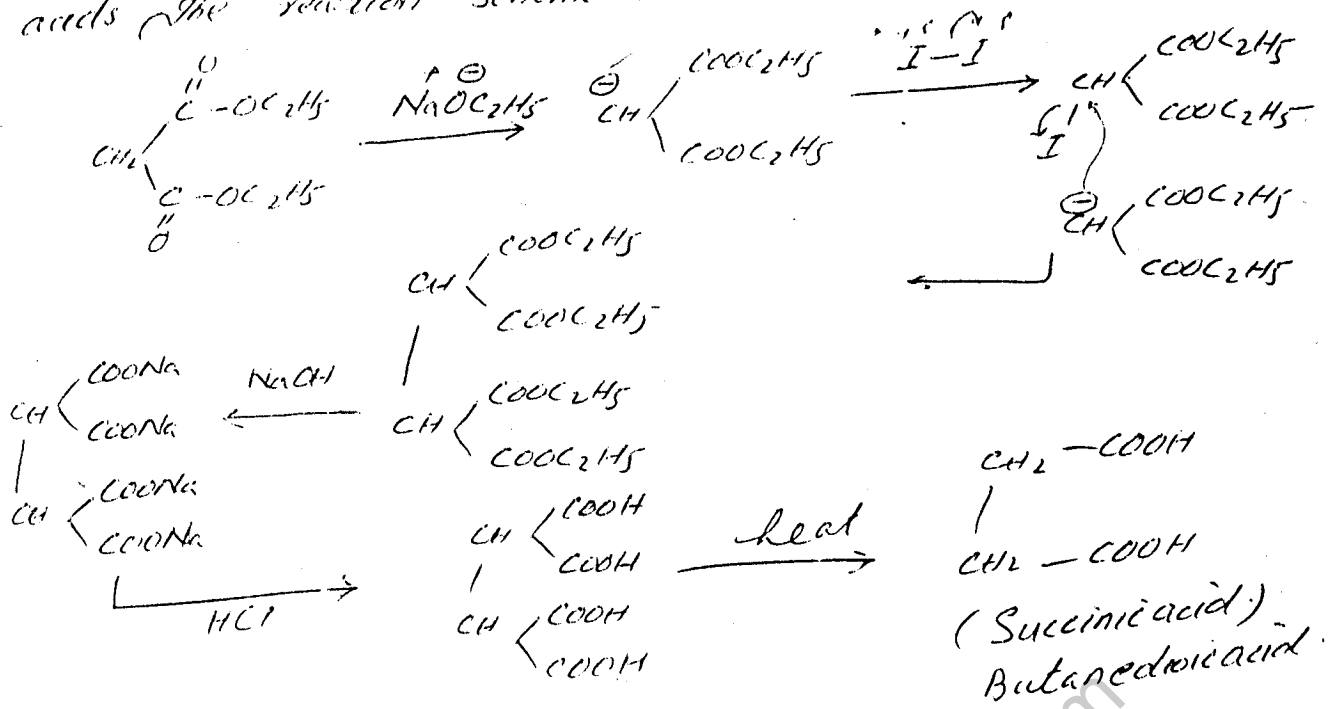


Let us consider an example



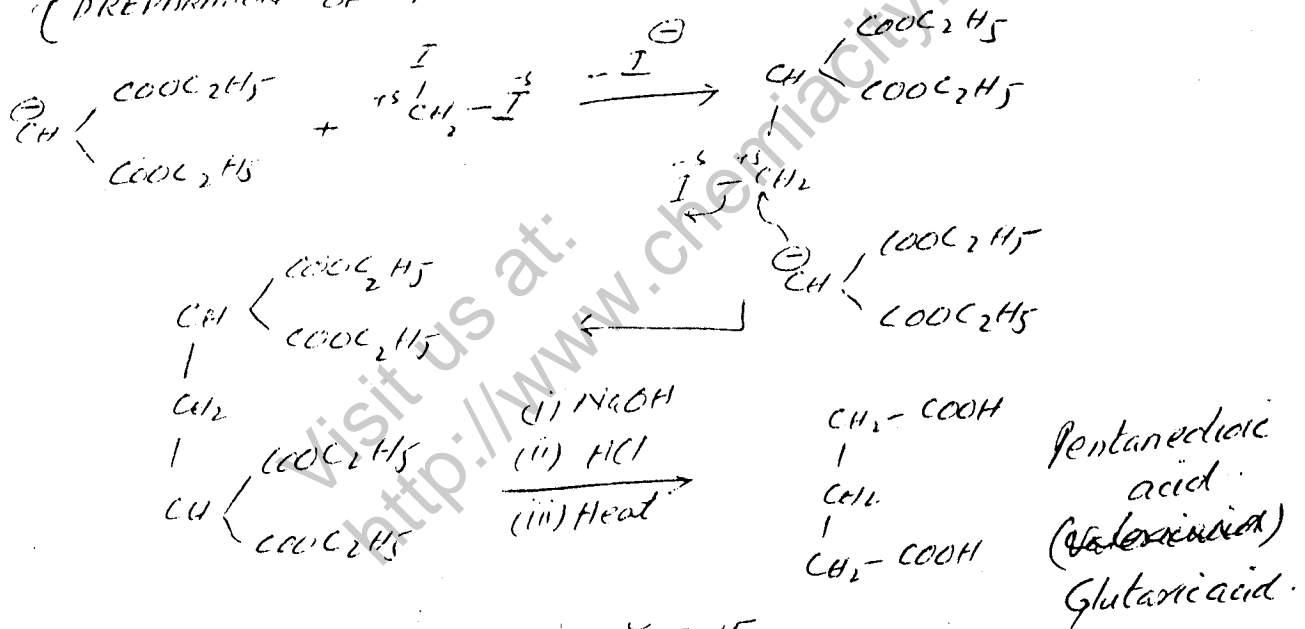
PREPARATION OF DICARBOXYLIC ACIDS:-(REACTION WITH I₂)

Malonic acid on reaction with I₂ in presence of NaOC₂H₅ followed by hydrolysis and decarboxylation produce dicarboxylic acids. The reaction scheme is shown below.

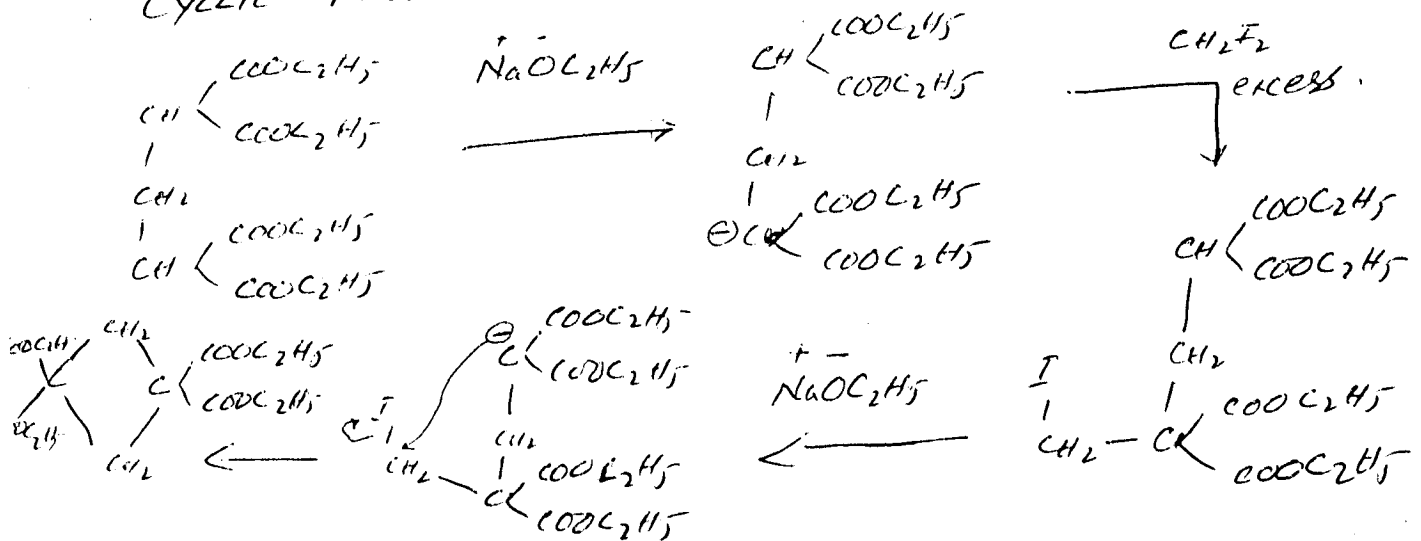


REACTION WITH DIODOMETHANE:-(CH₂I₂)

(PREPARATION OF PENTANEDIOIC ACID)

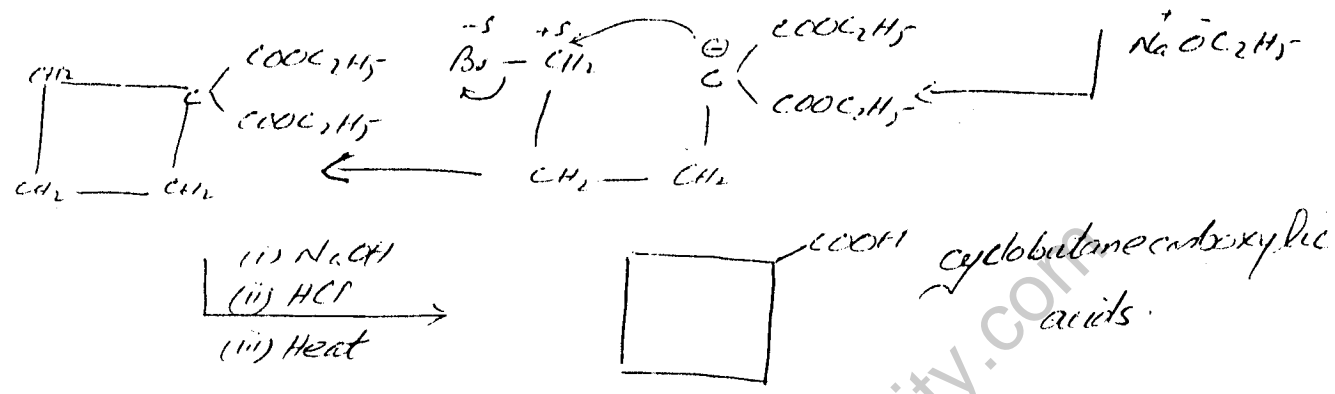


WITH EXCESS OF DIODOMETHANE
CYCLIC PRODUCTS ARE OBTAINED AS FOLLOWS.



(i) NaOH

-193-



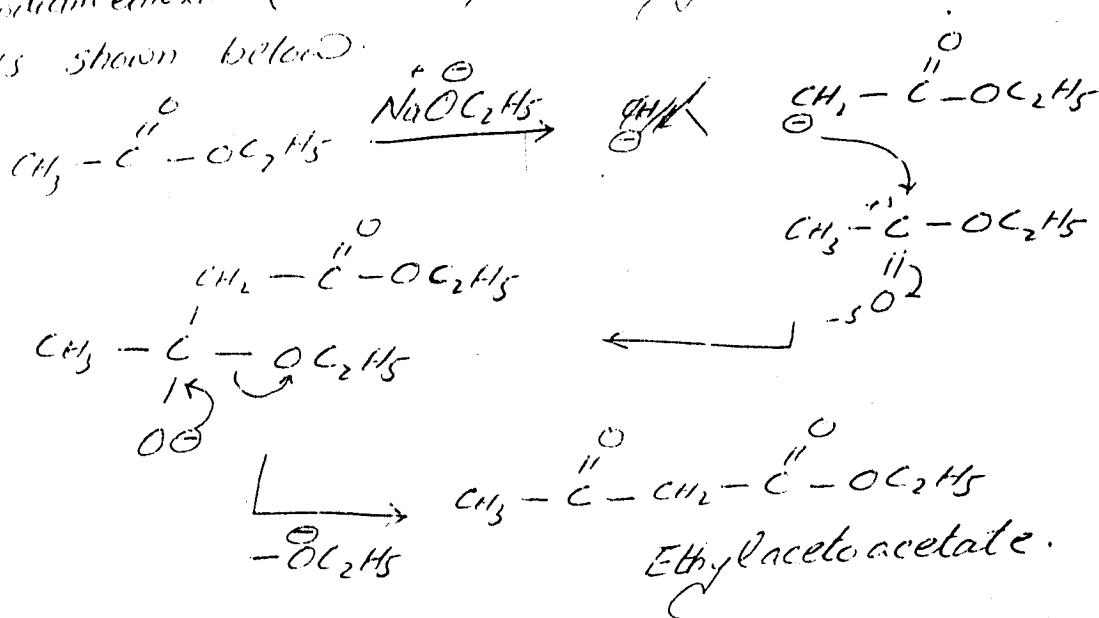
Thus malonic ester can be used to prepare:-

- (i) Higher carboxylic acids by monoalkylation and dialkylation.
- (ii) Dicarboxylic acids
- (iii) cyclic carboxylic acids.

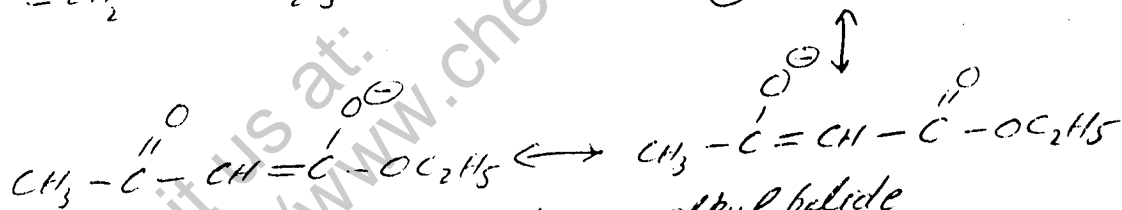
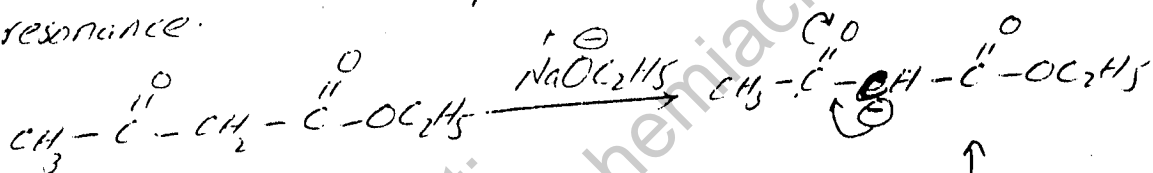
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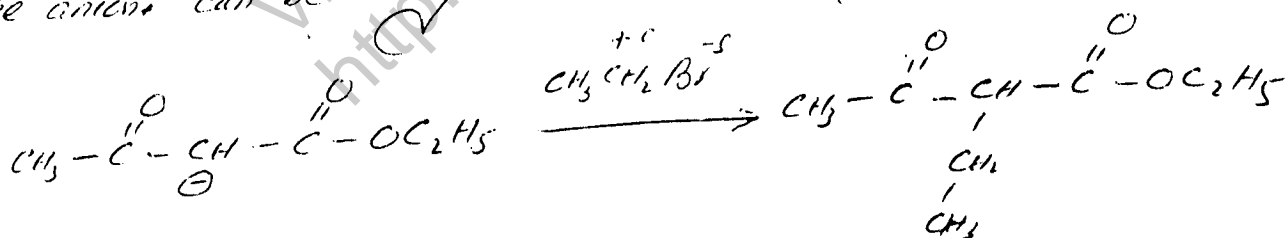
Preparation of Acetoacetic ester: $\text{CH}_3\text{-C}(=\text{O})\text{-CH}_2\text{-C}(=\text{O})\text{-OC}_2\text{H}_5$
 The ethyl acetoacetate (acetoacetic ester) can be prepared by Claisen condensation reaction of ethyl acetate in presence of sodium ethoxide (NaOC_2H_5) as strong base. The reaction scheme is shown below.



REACTIVITY OF ACETOACETIC ESTER: Acetoacetic ester is an active methylene compound. The hydrogen of $-\text{CH}_2-$ group can be removed as a proton and anion formed is stabilized by resonance.



The anion can be alkylated with an alkyl halide

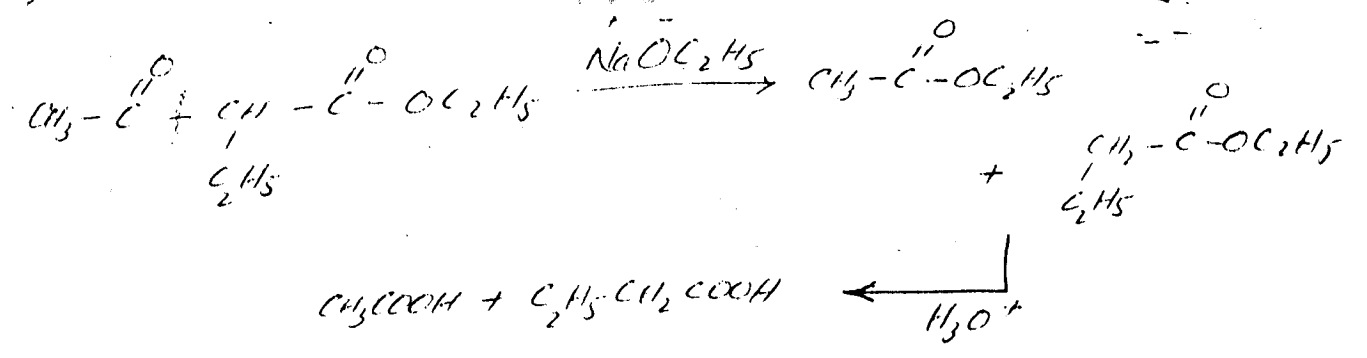


The alkylated product can undergo

(i) ACID CLEAVAGE

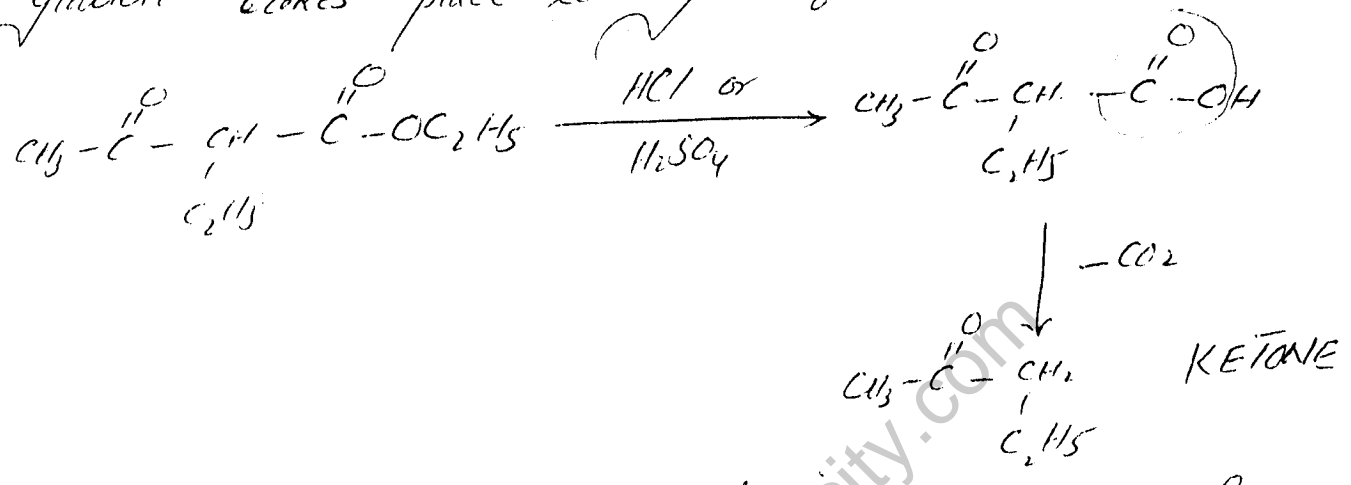
(ii) KETONIC CLEAVAGE.

ACID CLEAVAGE: The monoalkylated product is treated with a strong base such as NaOC_2H_5 . The product formed are hydrolyzed in presence of acid to form two carboxylic acid molecule. One of these is always acetic acid the other depend upon alkyl group introduced during monoalkylation.

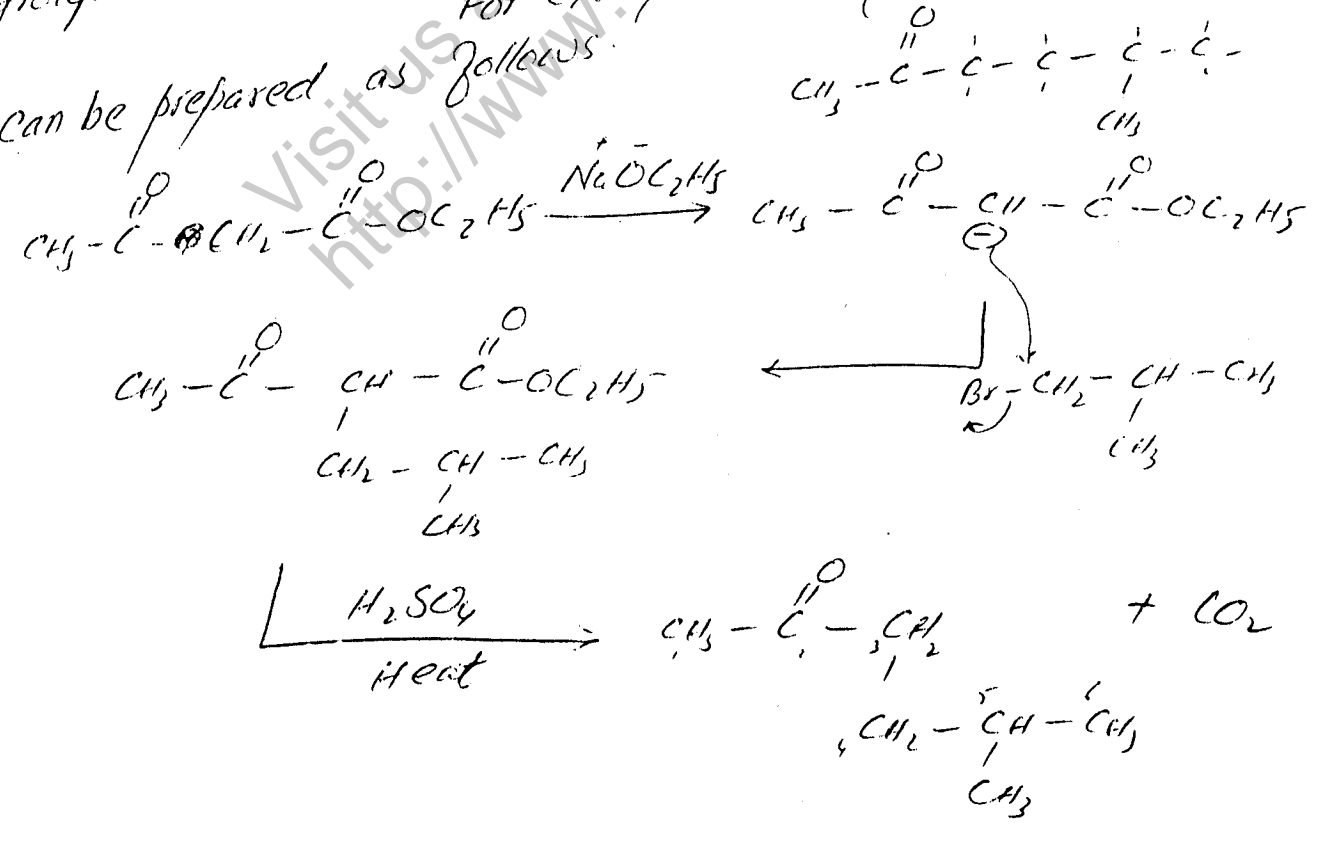


KETONIC CLEAVAGE:-

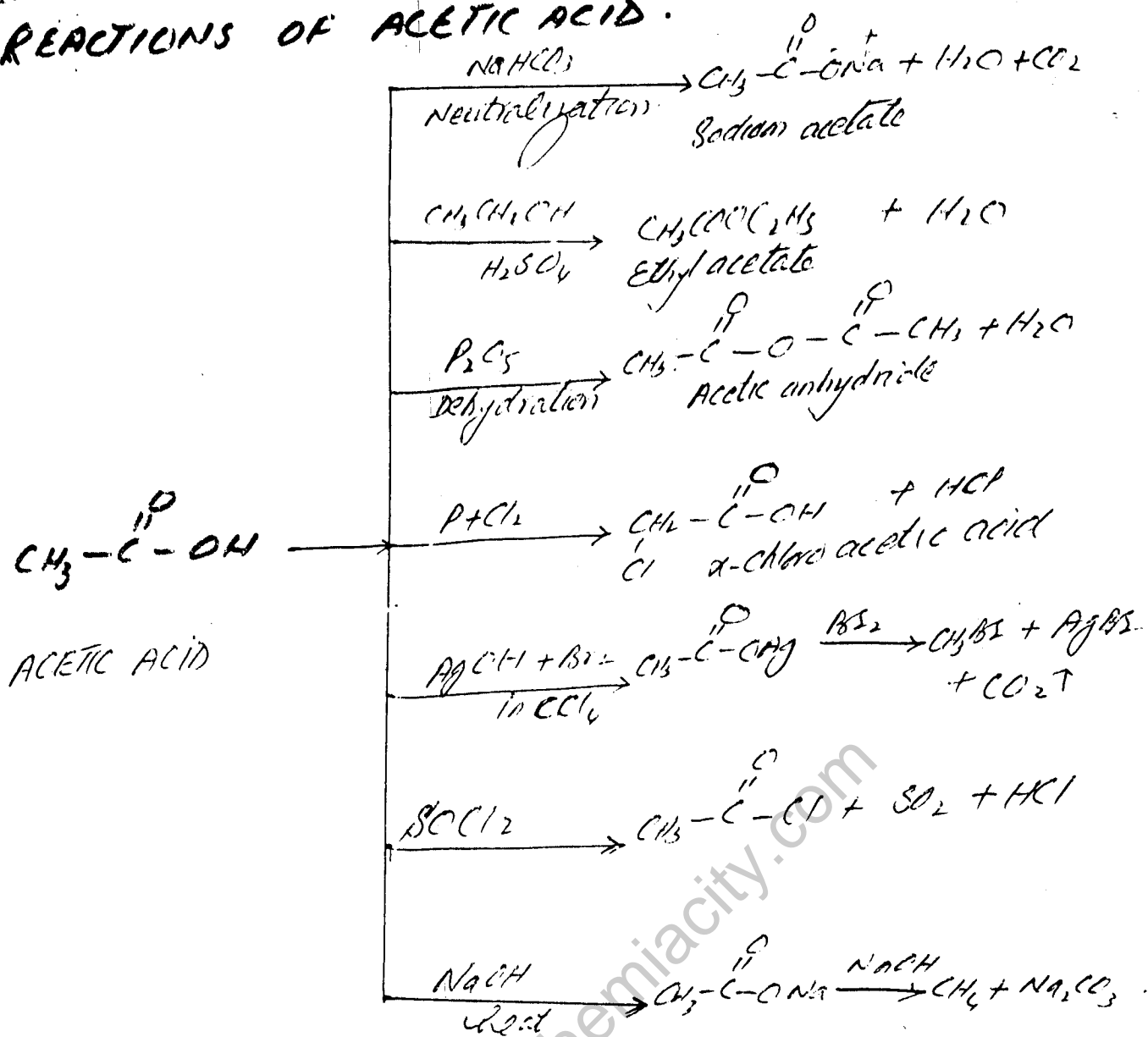
In ketric cleavage monoalkylated product is treated with sulphuric acid or HCl. The decarboxylation takes place leading to formation of a ketone



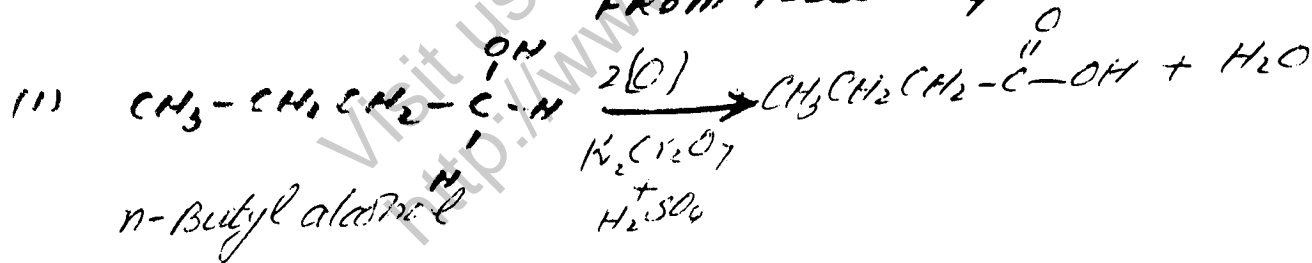
Acetoacetic ester is mostly used in ketone formation. The ketone formed has a methyl group on one side. For example 5-Methyl-2-hexanone can be prepared as follows.



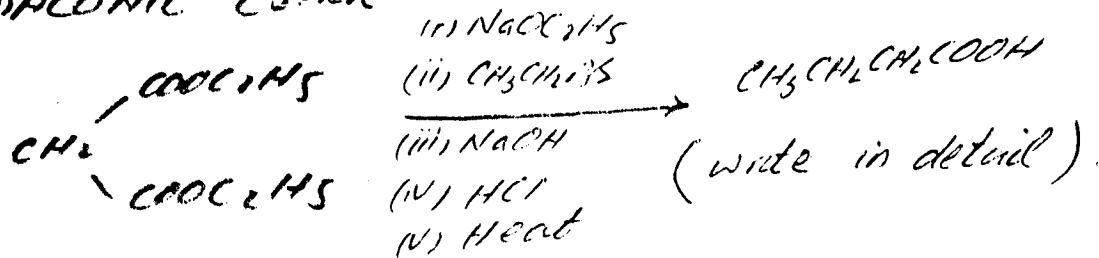
REACTIONS OF ACETIC ACID.



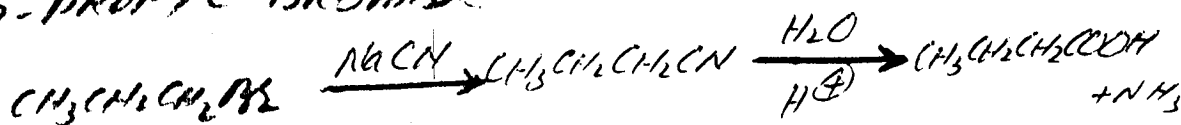
Q NO: 3:- HOW WILL YOU PREPARE BUTYRIC ACID FROM FOLLOWING



(ii) MALONIC ESTER.



(iii) n-PROPYL BROMIDE



Q. WHAT ARE ACID DERIVATIVES? DISCUSS METHODS OF PREPARATION OF ACID DERIVATIVES?

Ans: The chemical compounds which on hydrolysis produce carboxylic acids are called ACID DERIVATIVES. The most common acid derivatives are:

- (i) ESTERS (ii) AMIDES (iii) ACID HALIDES
- (iv) ACID ANHYDRIDES.

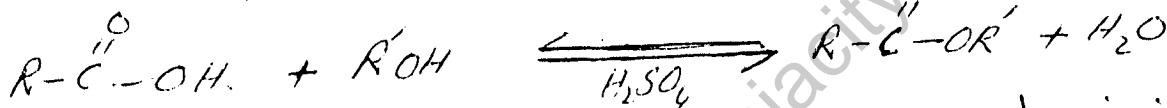
Keeping in view above definition of acid derivatives ^{alkyl} nitrils are also included in acid derivatives, but these will not be discussed here.

:- "METHODS OF PREPARATION:-"

Preparation of Esters:-

Esters can be prepared by following general methods.

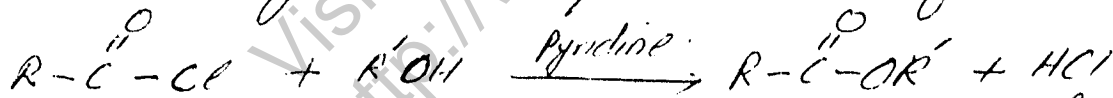
ESTERIFICATION REACTION:- Carboxylic acids can be converted into esters by reaction with alcohol in presence of acid catalyst.



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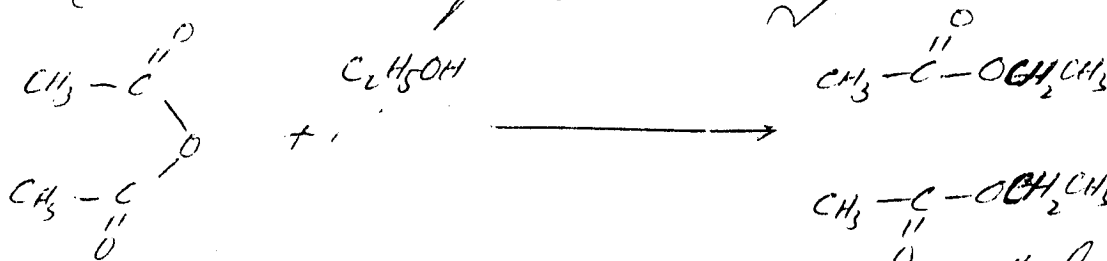
The reaction is reversible

FROM ACID HALIDES:- Acid halides react with alcohols to form esters in presence of pyridine. This reaction gives better yield as compared to esterification of acid.



FROM ANHYDRIDES:-

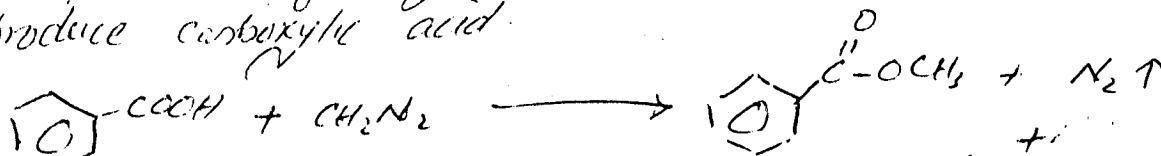
Acid anhydrides on alcoholysis produce ester. The reaction requires no catalyst



FROM DIAZOMETHANE AND CARBOXYLIC ACID

Ethylacetate

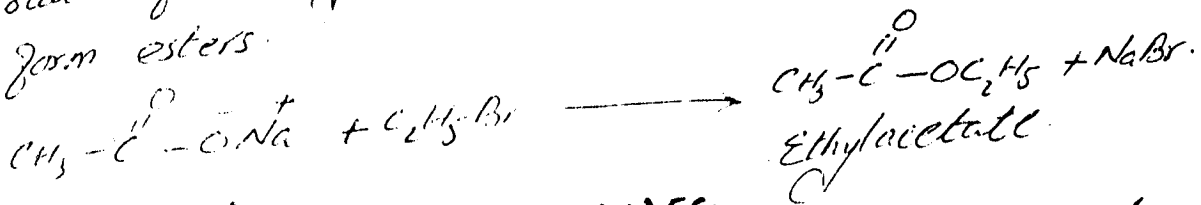
Ethereal solution of diazomethane reacts with carboxylic acid to produce carboxylic acid.



The reaction is used to prepare methyl esters.

ALKYL HALIDES & SALTS OF CARBOXYLIC ACID:-

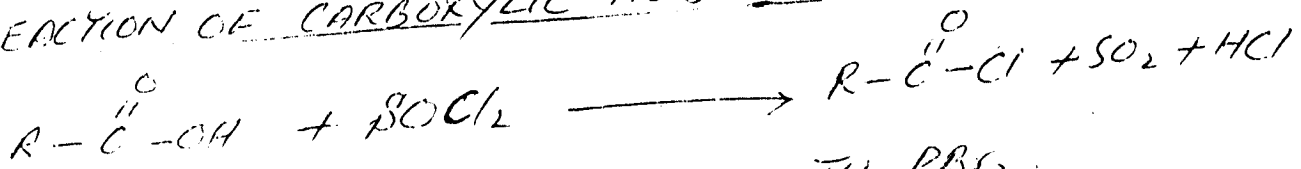
The salts of carboxylic acids react with alkyl halides to form esters.



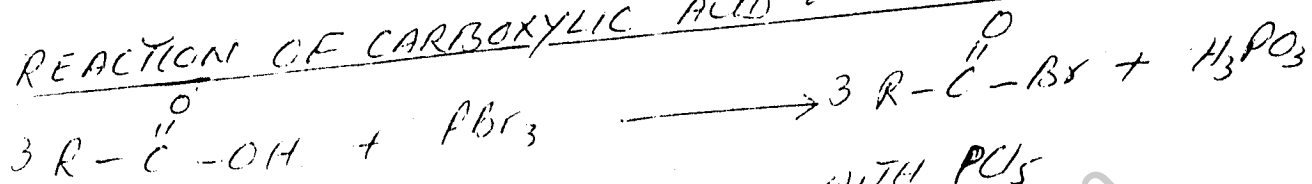
PREPARATION OF ACID HALIDES:-

The acid halides may be prepared by following reactions

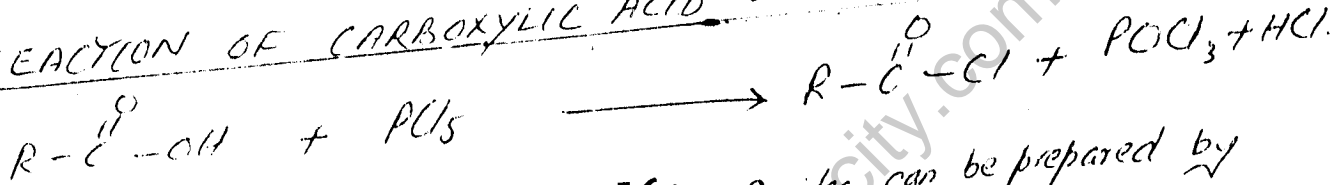
REACTION OF CARBOXYLIC ACID WITH SOCl_2 .



REACTION OF CARBOXYLIC ACID WITH PBr_3 .

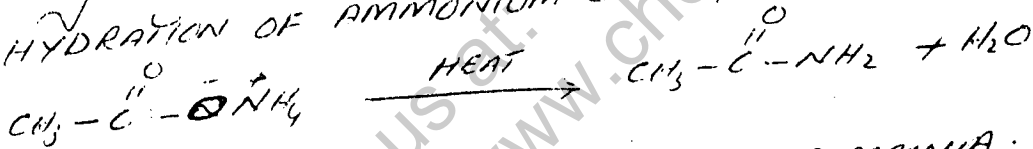


REACTION OF CARBOXYLIC ACID WITH PCl_5 .

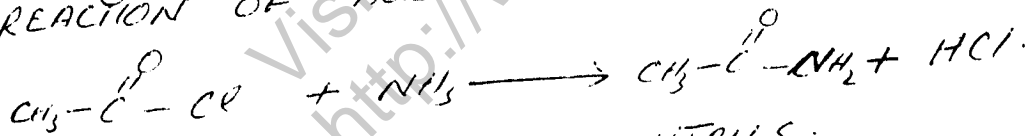


PREPARATION OF AMIDES:- Amides can be prepared by following reactions.

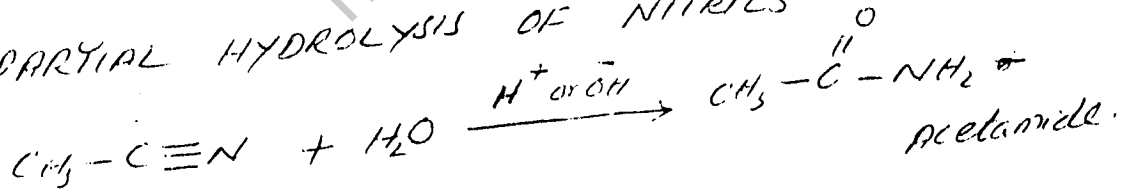
(1) DEHYDRATION OF AMMONIUM CARBOXYLATE:-



(2) REACTION OF ACID HALIDE WITH AMMONIA.

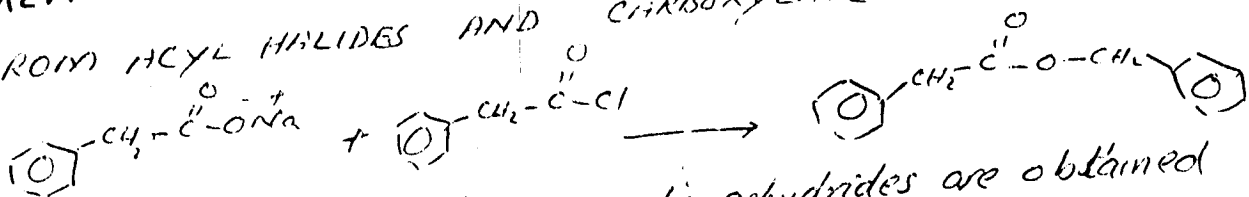


(3) PARTIAL HYDROLYSIS OF NITRILES.

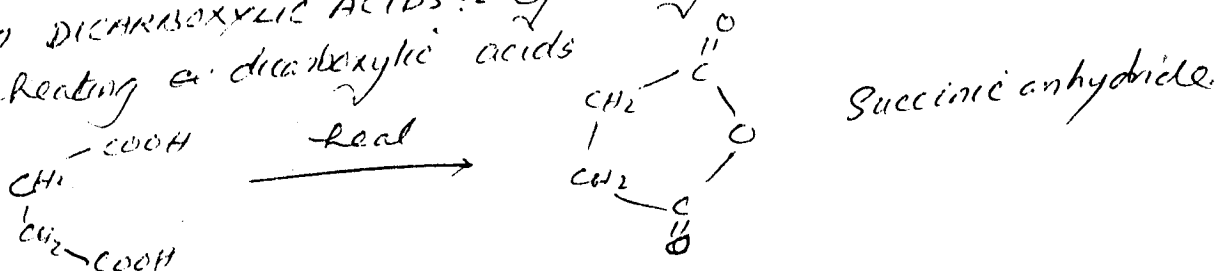


PREPARATION OF ACID ANHYDRIDES:-

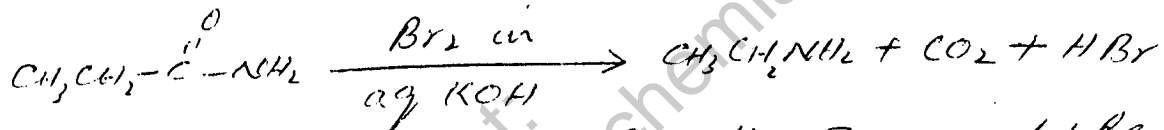
FROM ACYL HALIDES AND CARBOXYLATE SALTS.



FROM DICARBOXYLIC ACIDS:- Cyclic anhydrides are obtained by heating a dicarboxylic acid

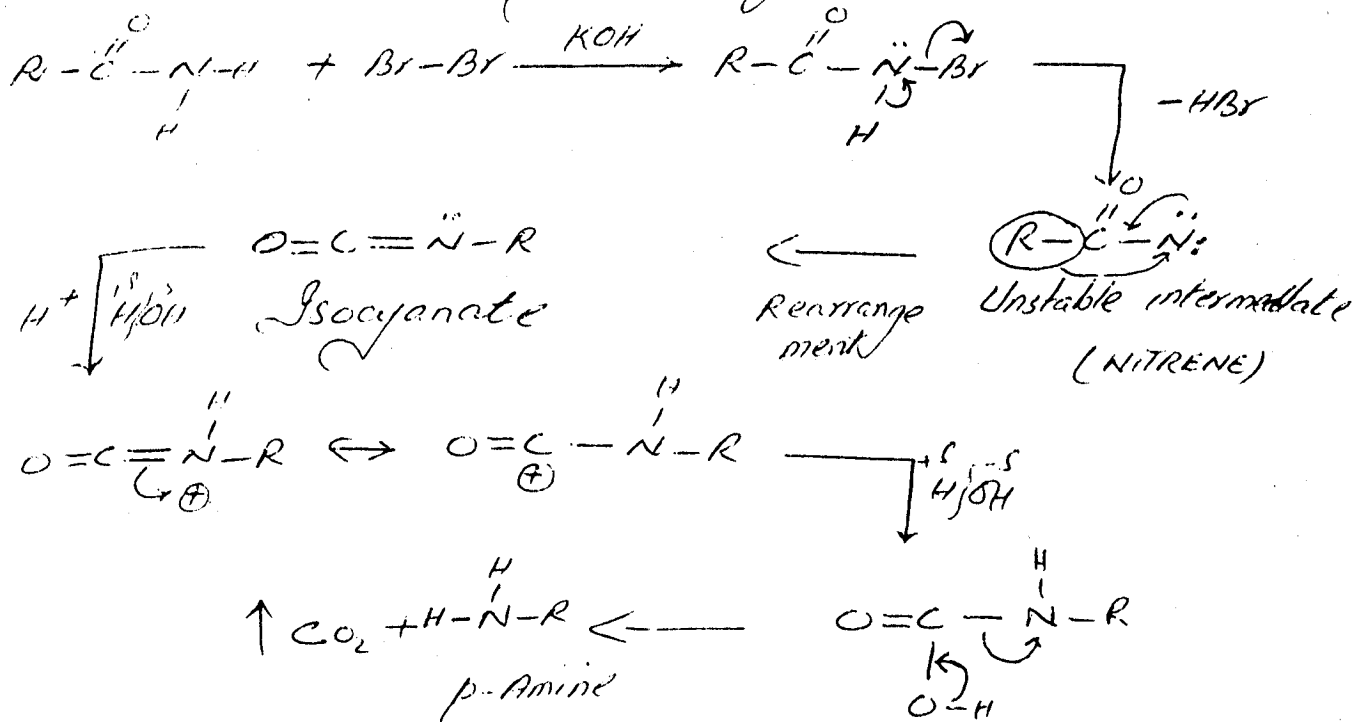


(ii) **HOFMANN BROMAMIDE REACTION**:- When an amide is treated with Br_2 and aqueous KOH , it forms an amine containing one carbon atom less than those in amide. This reaction is called **HOFMANN BROMAMIDE REACTION**.



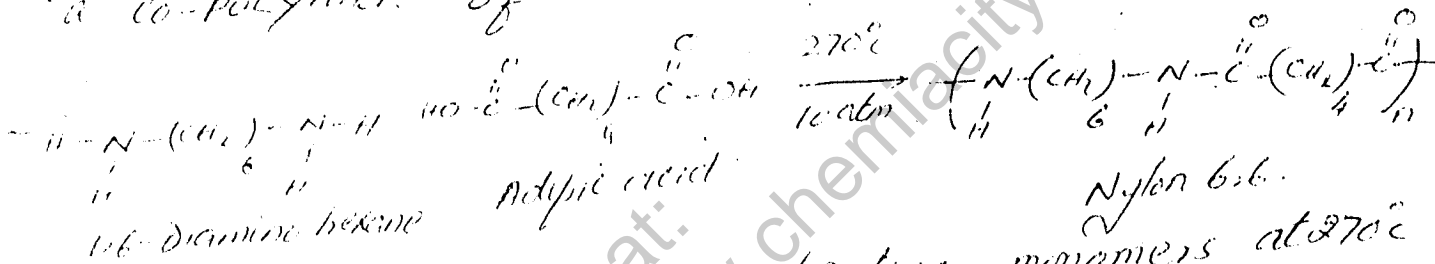
The reaction proceeds through formation of an unstable intermediate which rearranges to give Alkyl isocyanate

The reaction proceeds through following mechanism:



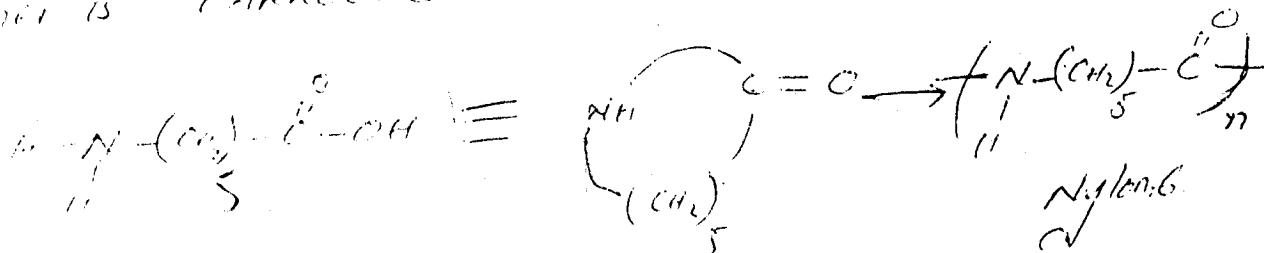
POLYAMIDES:- Polyamides are important commercial polymers

The most important polyamide is called Nylon 6,6. It is a co-polymer of 1,6-diamine hexane and adipic acid.



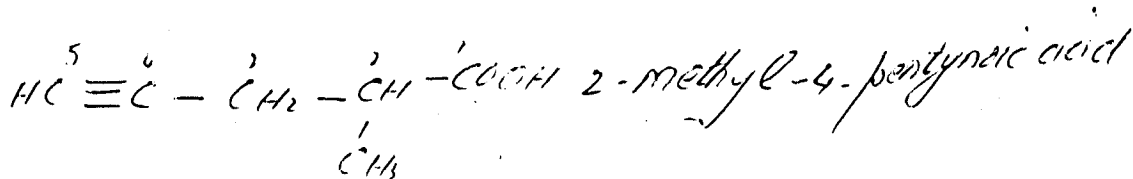
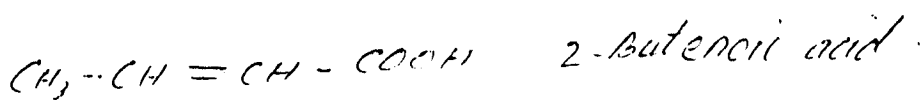
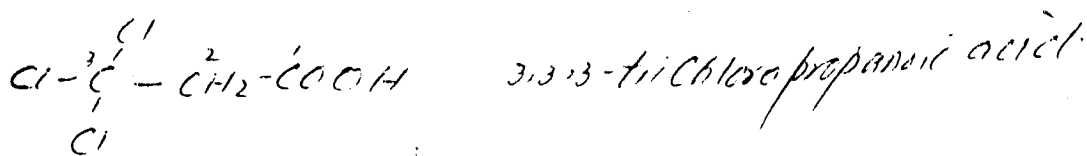
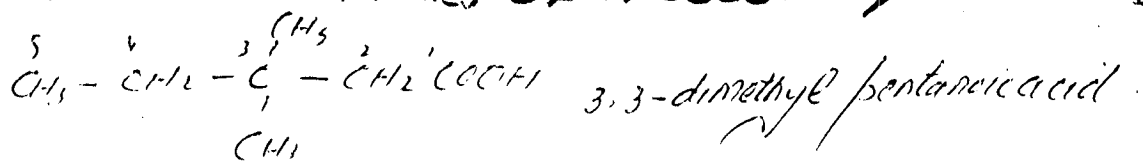
The polymer is formed by heating monomers at 270°C under a pressure of 10 atmosphere

Another important polymer is Nylon 6. This is polymer of 6-aminohexanoic acid (the actual monomer is CAPROLACTAM)



CARBOXYLIC ACIDS

QNO: - 1: - WRITE NAMES OF FOLLOWING COMPOUNDS.

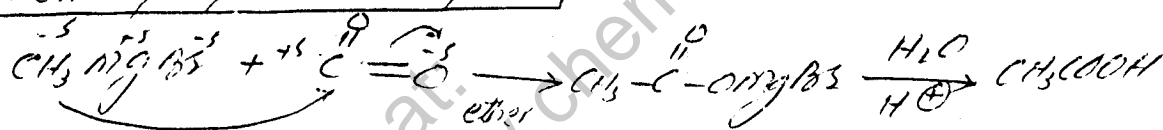


QNO: 2: - HOW ACETIC ACID IS PREPARED IN LABORATORY.

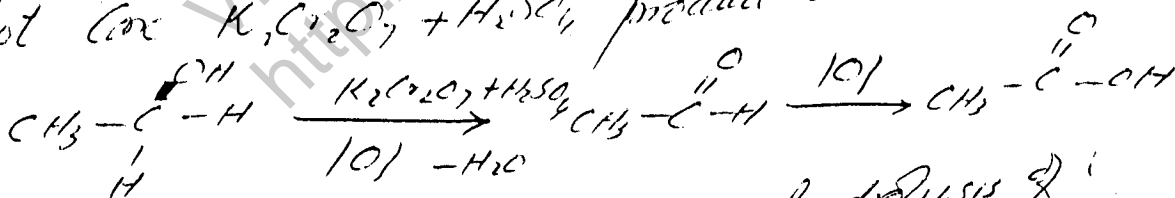
ANS: - ACETIC ACID PREPARATION: -

Acetic acid can be prepared in lab. by following methods.

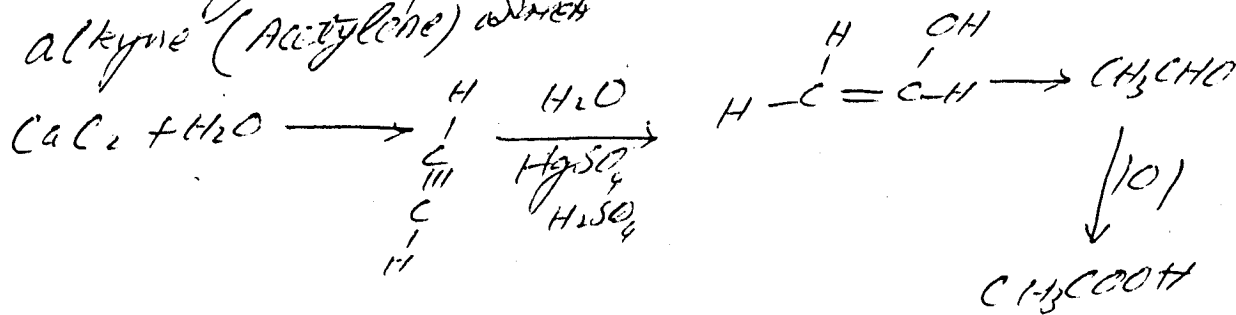
(i) FROM GRIGNARD REAGENT



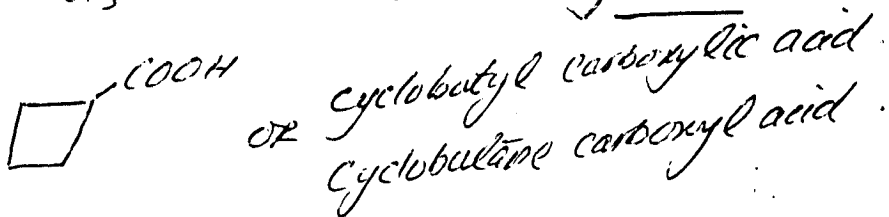
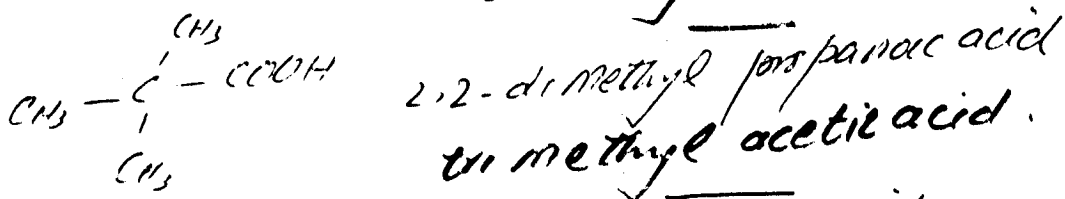
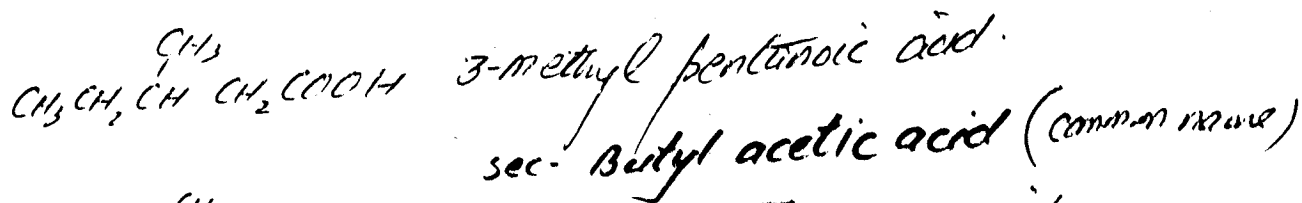
(2) OXIDATION OF ALCOHOL Ethanol on oxidation with hot conc $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ produce acetic acid.



(3) Acetaldehyde is prepared by hydrolysis of alkyne (Acetylene) which

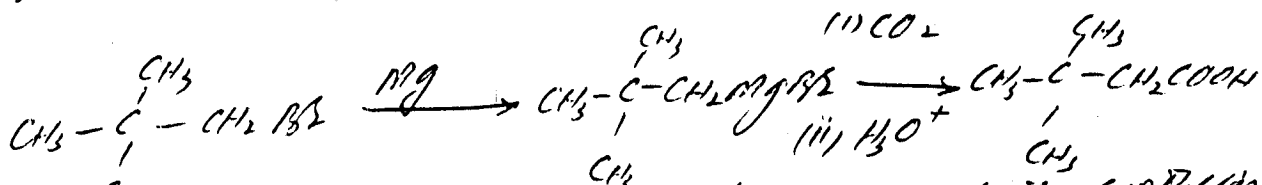
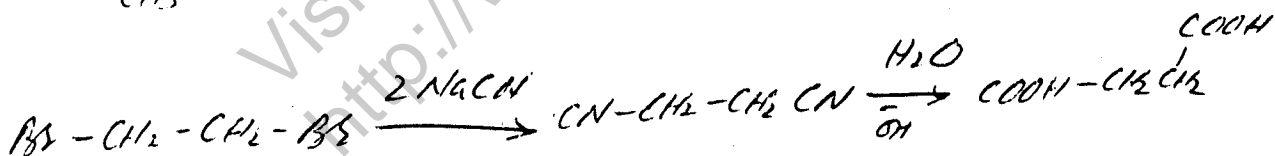
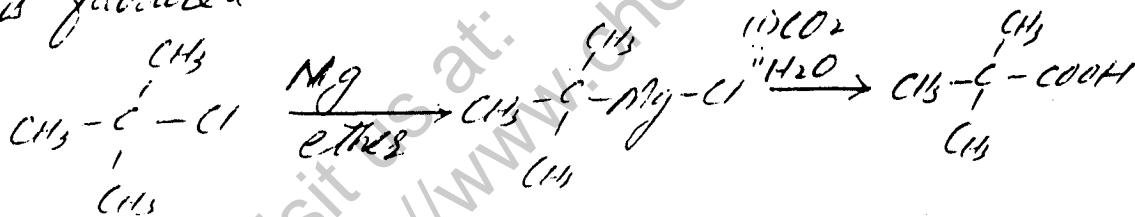


Q NO:- 5 WRITE NAMES OF FOLLOWING.

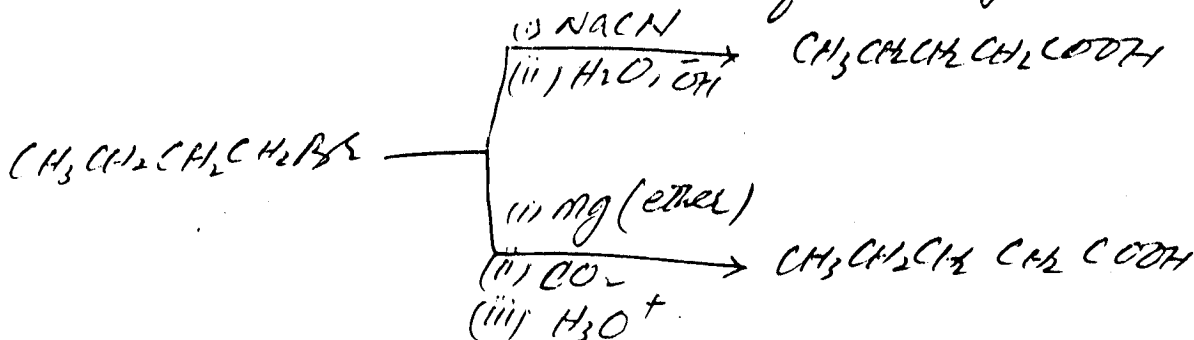


Q NO:- 6 :- CONVERSION OF ALKYL HALIDES INTO CARBOXYLIC ACIDS

Alkyl halides can be converted into carboxylic acid by nitril synthesis or via G.R. Nitril synthesis is not useful for ter. alkyl halides because it may produce elimination product as well. Thus for ter. alkyl halides the G.R. synthesis is preferred. For dialkyls Nitril synthesis is favoured.

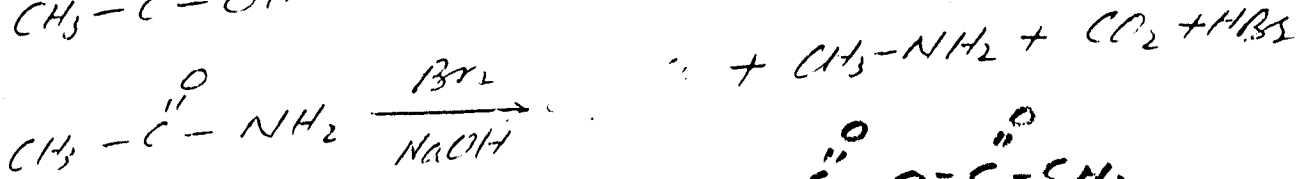
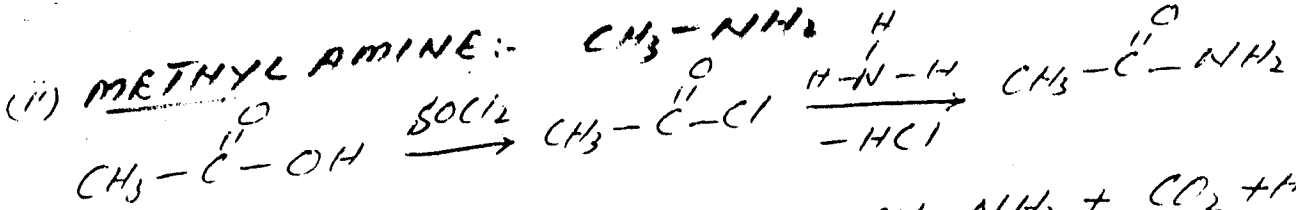
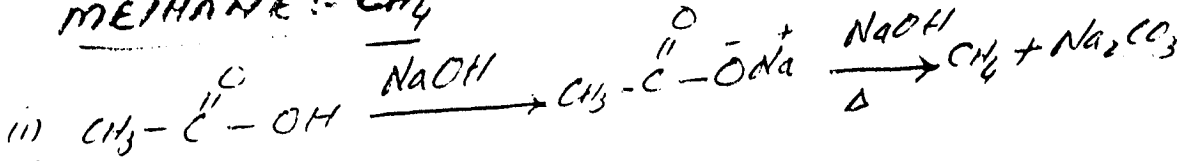


(Note G.R. is preferred because nitril synthesis will have chances of rearrangement).

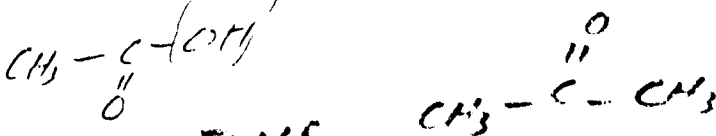
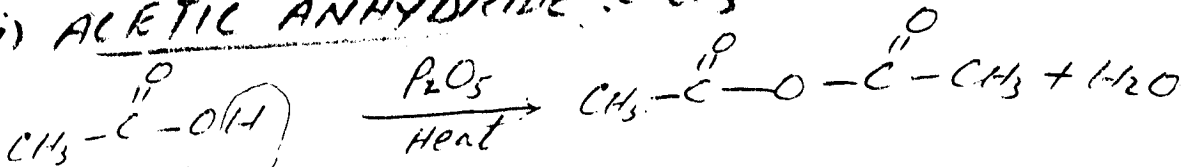


Q NO:- 8:- HOW WILL YOU CONVERT ACETIC ACID INTO FOLLOWING.

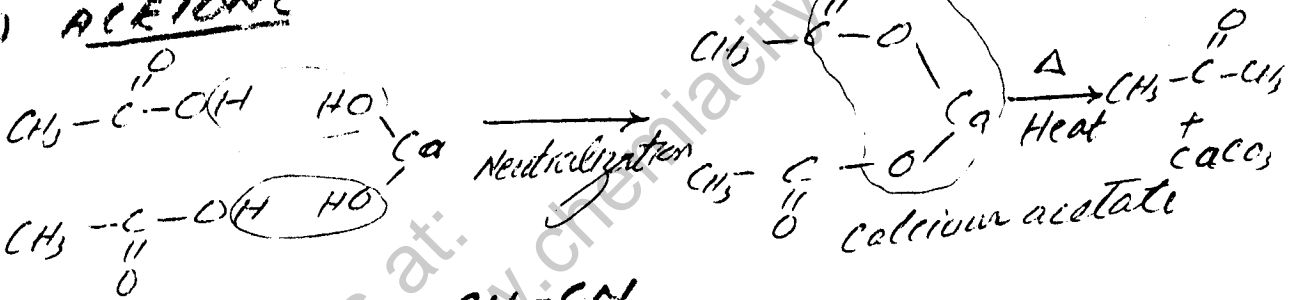
METHANE:- CH₄



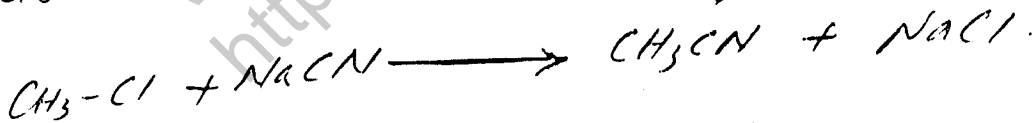
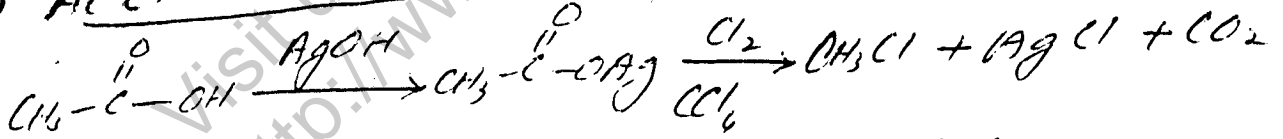
(iii) ACETIC ANHYDRIDE:- CH₃-C(=O)-O-C(=O)-CH₃



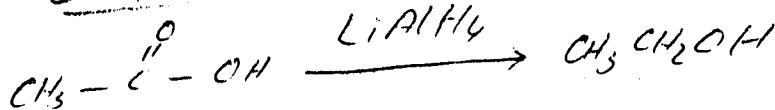
(iv) ACETONE



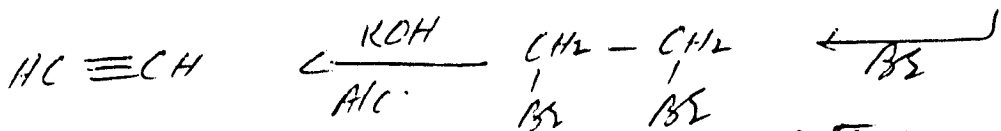
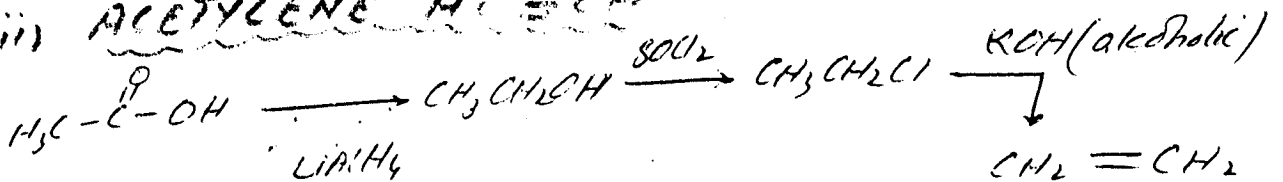
(v) ACETONITRIL CH₃-CN



(vi) ETHYL ALCOHOL CH₃CH₂OH



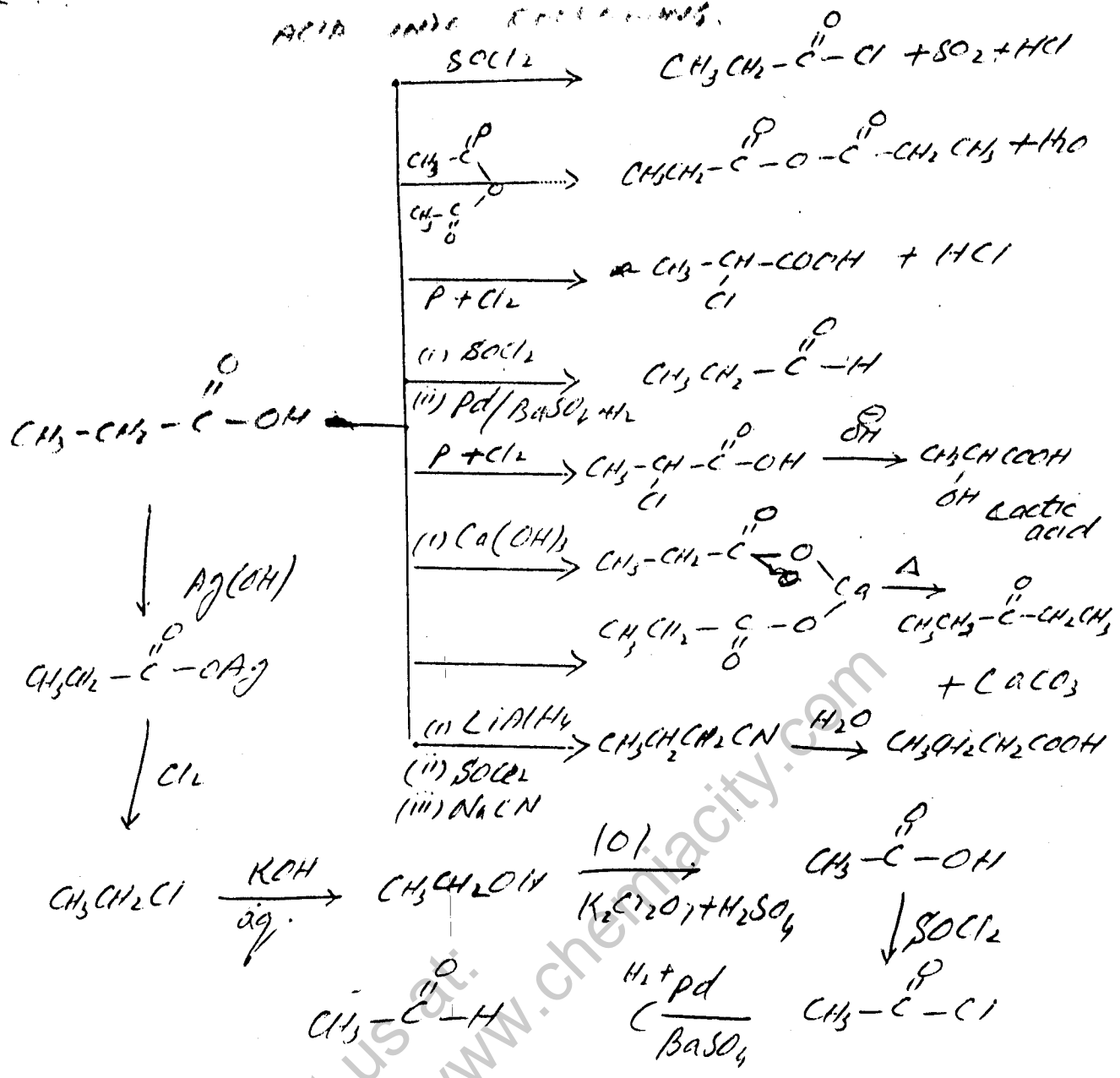
(vii) ACETYLENE HC≡CH



(viii) FOR MALONIC ESTER see your notes.

Q. NO. 10. HOW WILL YOU PREPARE PROPRIONIC ACID FROM FOLLOWING

ACID FROM FOLLOWING



Q NO. 10. WRITE STRUCTURES OF FOLLOWING

- (i) α -BROMOPROPIONITRI: $CH_3-\underset{Br}{CH}-CN$
- (ii) isopropyl butyrate: $CH_3CH_2CH_2-C(=O)-O-\underset{CH_3}{CH}-CH_3$
- (iii) N,N-dimethyl Formamide: $H-\overset{O}{\parallel}C-N(CH_3)_2$
- (iv) Ethyl Propionic Anhydride: $CH_3CH_2-C(=O)-O-C(=O)-CH_2CH_3$
- (v) Acetonitrile: CH_3-CN
- (vi) Butyryl bromide: $CH_3CH_2CH_2-C(=O)Br$