Carboxylic acid

Organic Compound containing carboxylic group (-COOH) are called carboxylic acid.

Types:-

Aliphatic Carboxylic acid ($R-\overset{\overset{O}{\|}}{C}-OH$)

Aromatic carboxylic acid ($Ar-\overset{\overset{O}{\|}}{C}-OH$)

Aliphatic Carboxylic Acid:

Carboxylic acid in which -COOH is attached with hydrogen or alkyl group is called aliphatic carboxylic acid.

$$R-\overset{\overset{O}{\|}}{C}-OH$$

→ All mono-aliphatic carboxylic acid are fatty acid

- fatty acid → 1-carboxylic acid
- fatty acid → aliphatic chain (straight)

Aromatic Carboxylic Acid:

Carboxylic acid in which -COOH is attached with phenyl or aryl group is called Aromatic Carboxylic acid.

$$AR-\overset{\overset{O}{\|}}{C}-OH$$

→ Not fatty acid

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Nomenclature of alkonic acid

1- $H-\overset{\overset{O}{\|}}{C}-OH$

IUPAC: Methanoic acid

C.N: Formic acid

↳ formica = ant

2- $CH_3-\overset{\overset{O}{\|}}{C}-OH$

IUPAC: Ethanoic acid

C.N: Acetic acid

↳ Acetum = vinegar

3- $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

IUPAC: Propanoic acid

C.N: Propionic acid

↳ Protas = fat

4- $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

IUPAC: Butanoic acid

C.N: Butyric acid

↳ Butyrum = butter

5- $CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

IUPAC: Pentanoic acid

C.N: Valeric acid **Imp**

6- $CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$

IUPAC: 2-Methylpropanoic acid

C.N: β-Methylpropanoic acid

7- $CH_3-\underset{\underset{OH}{|}}{CH}-COOH$

IUPAC: 2-Hydroxypropanoicacid

C.N: Lactic acid **Imp**

8- $\overset{COOH}{\underset{COOH}{|}}$

IUPAC: 1,2-Ethanedioicacid

C.N: oxalicacid **Imp**

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9. $CH_2(COOH)_2$

IUPAC: Propane-1,3-dioic acid

C.N: Malonic acid Imp

10. $HOOC-CH_2-CH_2-COOH$

IUPAC: butane-1,4-dioic acid

C.N: Succinic acid Imp.

11. $HOOC-CH=CH-COOH$

IUPAC: 2-butene-1,4-dioic acid

C.N: Maleic acid Imp.

12. $HOOC-CH(OH)-CH(OH)-COOH$

IUPAC: 2,3-Dihydroxybutane-1,4 dioic acid

C.N: Tartaric acid Imp

13. $HOOC-CH_2-CH_2-CH_2-COOH$

IUPAC: Pentane-1,5-dioic acid

C.N: Glutaric acid

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14. $COOH-CH_2-CH_2-CH_2-CH_2-COOH$

IUPAC: hexane-1,6-dioic acid

C.N: Adipic acid Imp

15- C_6H_5-COOH

IUPAC: Benzoic acid

C.N: "

16. $C_6H_4-(COOH)_2$

IUPAC: Benzene-1,2-dicarboxylic acid

C.N: pthalic acid

17. $(C_6H_4)-(COOH)_2$

IUPAC: Benzene-1,4-Dicarboxylic acid

C.N: Terepthalic acid

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Physical properties

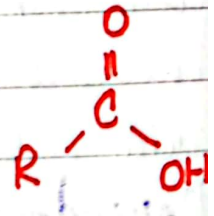
They are polar due to the presence of :-

C-OH , C=O

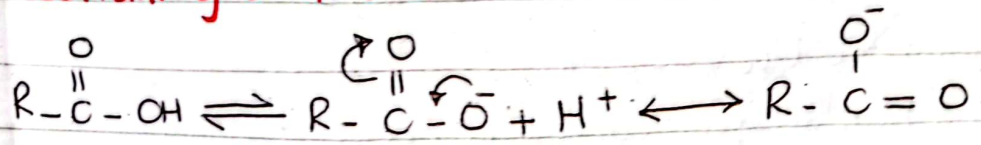
- They have high melting and high boiling point than analogous alkane.
- They have high solubility.
- Aliphatic carboxylic exists in liq state and Aromatic exists in solid state.

Structure

- The carboxyl group Carbon is sp^2-hybridized.
- Shape is somewhat Trigonal planar
- Angle b/w C=O is 120°, O-H is 104.5°.
- The hydroxy Oxygen has lone pair that is delocalized, making a resonating structure.



Resonating Structure :-



2 resonating structure

* carboxylate ion.

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Carboxylic acid is stable due to delocalization of (-) charge.

acidity

pKa amount of extend with which an electron donates a proton.

→ Carboxylic acid is way more Acidic than Alcohol.

Pka :-

pka value of COOH = 5

pka value of OH = 10-15

This shows that higher value of Pka leads to lower strength of acid. (OH)

Lower value of pka offers greater strength to acid. (COOH)

Dependence :-

Electron-Donating group :-

The electron-donating group decrease the acidic strength.

→ They push the e^- towards carboxyl group.

→ This increase electron-density.

→ Making harder for carboxylic acid to release its proton.

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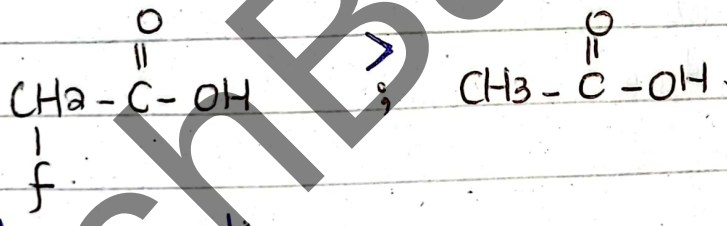
→ Furthermore, the negative charge on conjugate base (carboxylate ion) is less stabilized because extra electron charge density from electron-donating group makes neg charge more concentrated.

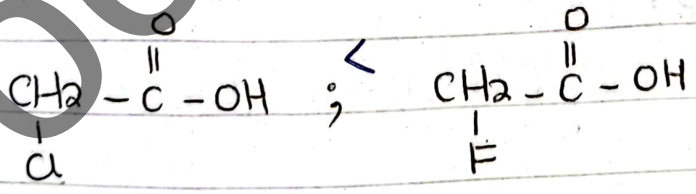
↳ more acidic.

Electron-withdrawing group :-

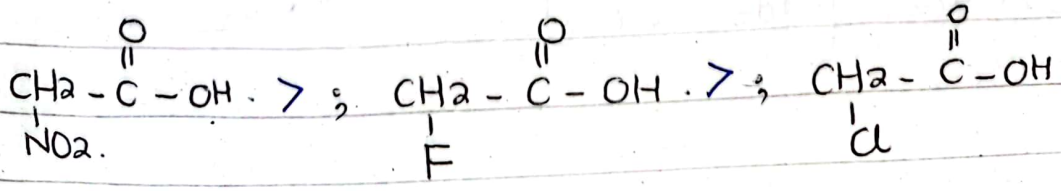
- Electron-withdrawing group increases the acidity of carboxylic acid by stabilizing the negative charge on the conjugate base.
- They pulls the electron density away from negative charged oxygen, stabilizing through inductive effect.
- Greater electron-negativity, closer to EWG.



↳ more acidic



↳ less acidic



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Order of with-drawing

$CN > NO_2 > SO_3H > COOH > CHO > COR_2 > COOR > NR_3 > NH_3 > F > Cl > Br > I$.

Order of donating group

$CH_3 > CONH_2 > NHR > NH_2 > OH > OR, SR$

Preparation

1) Grignard Reagent :-

$$CH_3\text{-}Mg\text{-}Br + \underset{\underset{O}{\|}}{\overset{O}{\|}}{C}{\underset{\|}{\overset{\|}{}}} \xrightarrow[\text{ether}]{\text{dry}} CH_3\text{-}\underset{\underset{O\overset{\oplus}{M}gBr}{|}}{\overset{O}{\|}}{C} \xrightarrow[H^+]{H\text{-}OH} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{Br}{\overset{OH}{Mg}}$$

ethanoic acid

Note:-

formic acid can't be Prepared by this method due to presence of min two Carbon.

2) Hydrolysis of Nitrile :

* Organic Compound containing $C \equiv N$ is called the Nitrile.

* Hydrolysis of an alkyl hanitrile on boiling with mineral acids fields $COOH$.

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$$R\text{-}C\equiv N + 2H_2O + HCl \xrightarrow{\Delta} R\text{-}COOH + NH_4Cl$$

$$CH_3\text{-}C\equiv N + 2H_2O + HCl \xrightarrow{\Delta} CH_3\text{-}COOH + NH_4Cl$$

ethane nitrile
ethyl cyanide

ethanoic acid

Convert methane to acetic acid?

1) $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$

2) $CH_3Cl + HCN \longrightarrow CH_3CN + HCl$

3) $CH_3CN + 2H_2O + HCl \longrightarrow CH_3\text{-}COOH + NH_4Cl$

3) Oxidation of primary alcohol: MDCAT

1°-alcohol is oxidized which convert into aldehyde & further oxidized into carboxylic acid.

2°-alcohol is oxidized into Ketone.

ter. alcohol is oxidized into alkene.

$$CH_3\text{-}\underset{OH}{CH_2} + [O] \xrightarrow[\Delta]{K_2Cr_2O_7,\ H_2SO_4} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + H_2O$$

Ethyl alcohol:

ethanal

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}H + [O] \xrightarrow[\Delta]{K_2Cr_2O_7,\ H_2SO_4} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

ethanal

ethanoic acid

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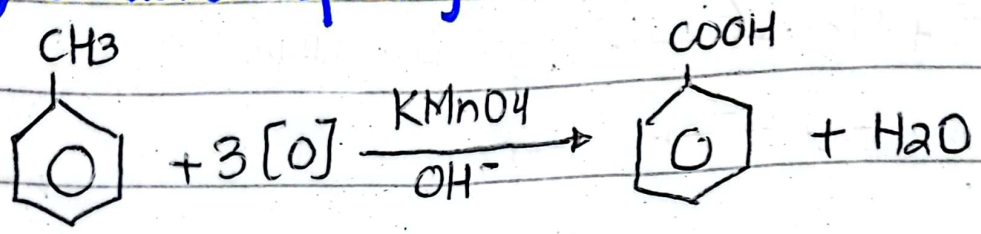
4) Oxidation of alkyl benzene:

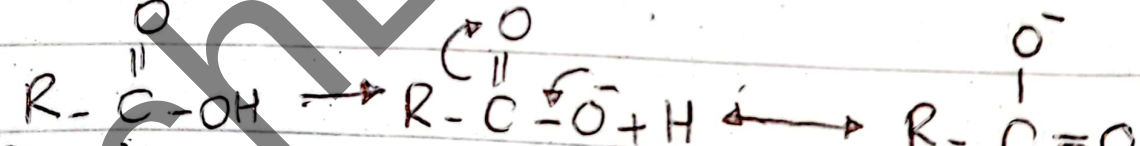


toluene — benzoic acid.

Reactivity

Carboxylic acids shows the chemistry of carboxylic acid as well as Hydroxyl group. Due to reason that these molecule are reactive due to presence of COOH group.

Resonating structure



Reactions:

a) Reactions involving H-atom.
b) Reactions in which OH group is present
c) Reaction involving COOH group.

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a) Reactions involving H-atom of Carboxyl group

1) Reaction with base :-

form salts.

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + NaOH \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-ONa + H_2O$$

ethanoic acid — sodium acetate.

Sodium salt of acetic acid

2) Reaction with Carbonates and Bicarbonates :-

evolves CO_2 with effervescence.

$$2CH_3-\overset{\overset{O}{\|}}{C}-OH + NaCO_3 \longrightarrow 2\,CH_3-\overset{\overset{O}{\|}}{C}-ONa + CO_2 + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + NaHCO_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONa + CO_2 + H_2O$$

3) Reaction with metals :

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + Na \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONa + 1/2\,H_2$$

Sodium acetate.

$$2CH_3-\overset{\overset{O}{\|}}{C}-OH + Ca \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O\diagdown\!\!\diagup Ca + H_2$$

$$CH_3-\overset{\overset{O}{\|}}{C}-O\diagup$$

calcium acetate

$$2CH_3-\overset{\overset{O}{\|}}{C}-OH + Mg \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O\diagdown\!\!\diagup Mg + H_2$$

$$CH_3-\overset{\overset{O}{\|}}{C}-O\diagup$$

Magnesium acetate.

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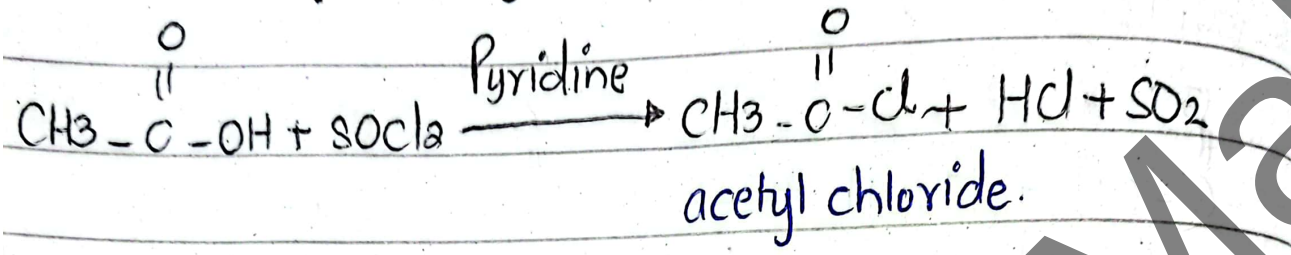
b) Reactions involving OH group

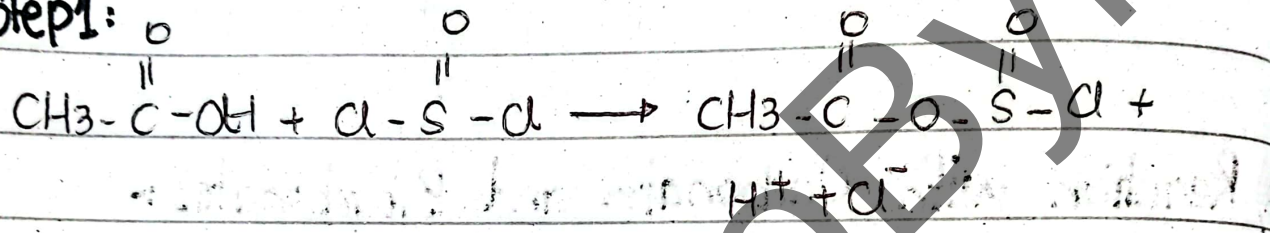
1) Reaction of thionyl chloride:



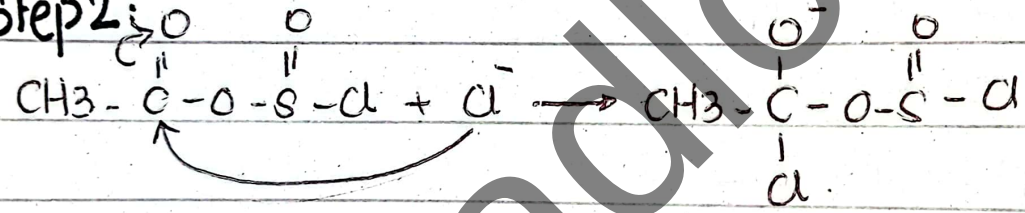
acetyl chloride.

mechanism:-

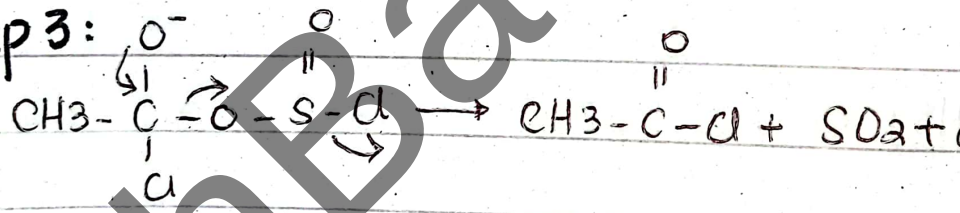
Step1:



Step2:

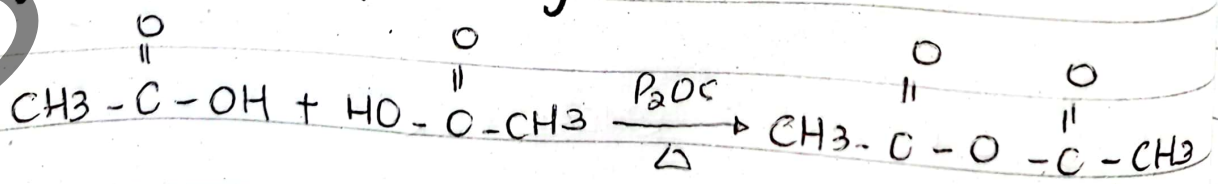


Step 3:



Step 4:

2) Dehydration of Carboxylic acid:



acetic anhydride

+ H_2O.

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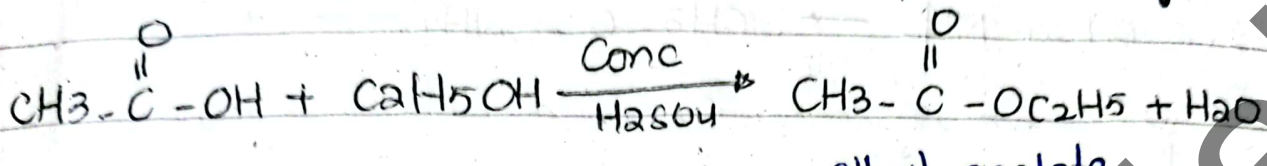
3) Reaction with alcohol / formation of ester / fisher esterfication / CT for confirmation of COOH

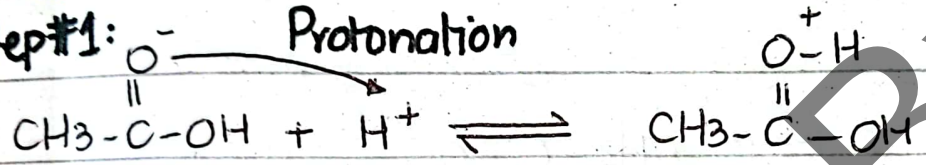


ethyl acetate

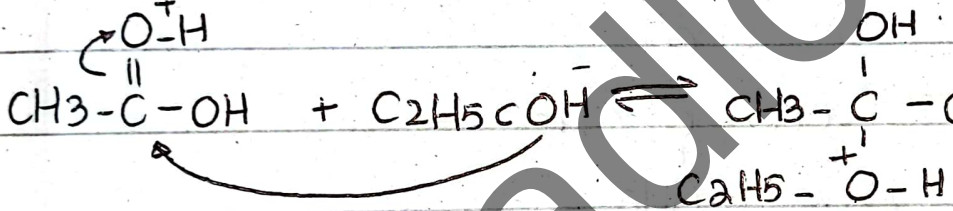
→ give fruity / fishy smell.

mechanism

Step #1: Protonation

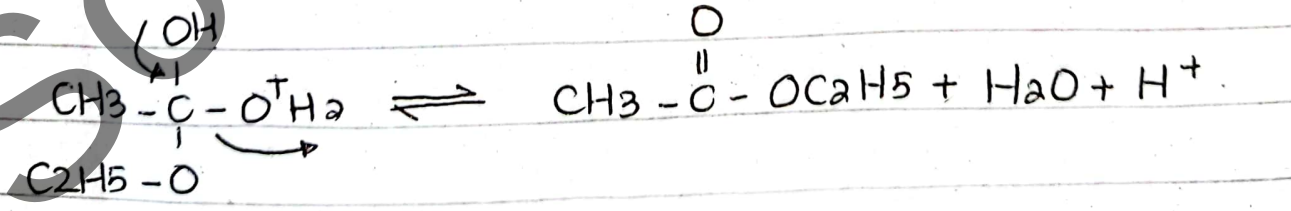


Step #2. attack of alcohol



Step #3 Rearrangement

Step #4 elimination of H_2O



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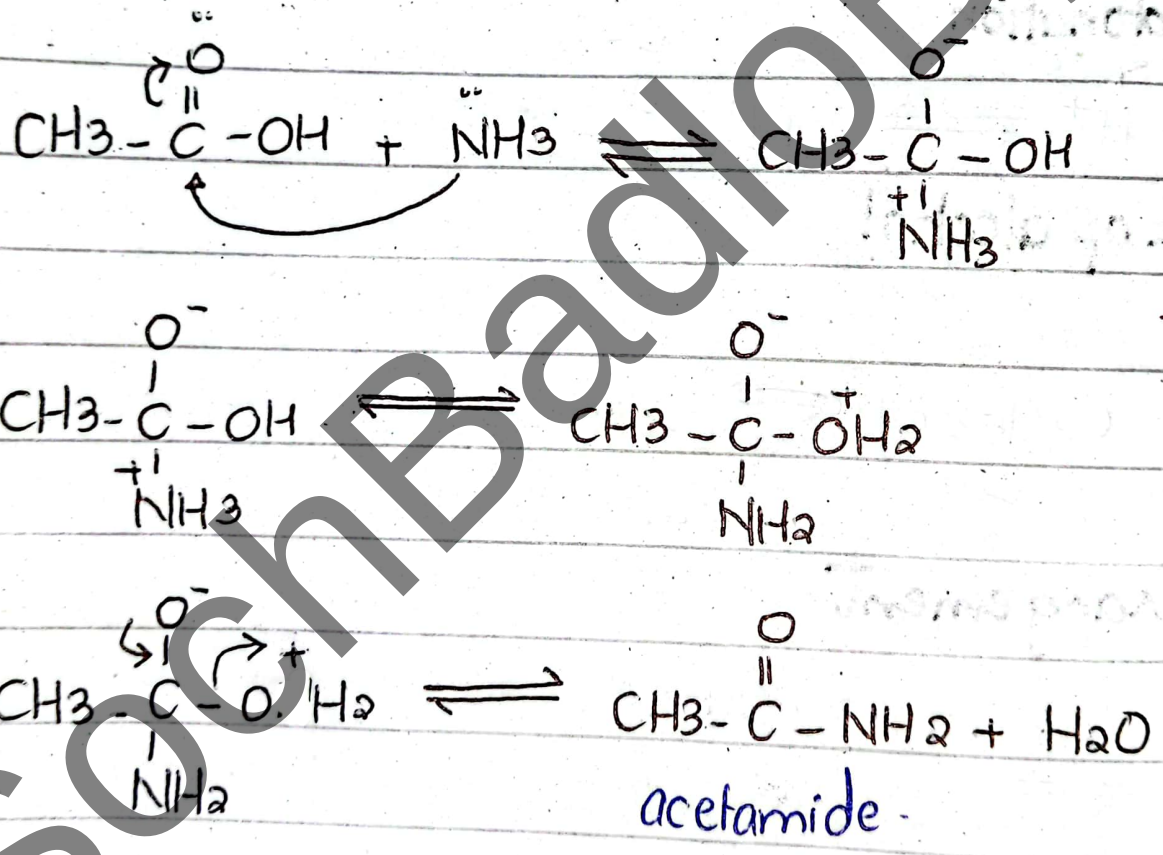
4) Reaction with NH_3

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + NH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONH_4 \xrightarrow{\Delta}$$

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$$

acetamide.

Mechanism:



acetamide.

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c) Reactions involving -COOH group

1) Partial reduction

Carboxylic acids are reduced to 1° alcohol.

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{ether}]{LiAlH_4} CH_3-CH_2-OH + H_2O$$

acetic acid / ethanoic acid → ethanol

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{ether}]{LiAlH_4} CH_3-CH_2-CH_2-OH + H_2O$$

propanoic acid → propanol

2) complete reduction of -COOH.

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + 6HI \xrightarrow[\Delta]{P(red)} CH_3-CH_3 + 2H_2O + 3I_2$$

ethanoic acid; HI: strong reducing agent; → ethane

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + 6HI \xrightarrow[\Delta]{P(red)} CH_3-CH_2-CH_3 + 3I_2 + 2H_2O$$

propanoic acid → (propane)

3) Decarboxylation :-

removal of CO_2.

reagent = Sodalime = NaOH + CaO(s)

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONa + H_2O$$

ethanoic acid → Sodium acetate.

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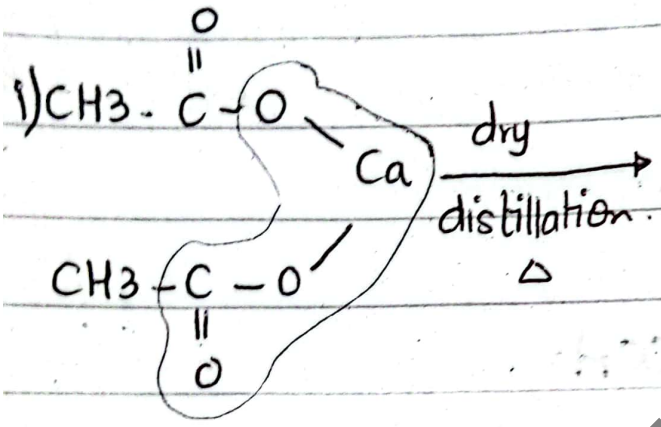
sodium acetate. methane. sodium carbonate.

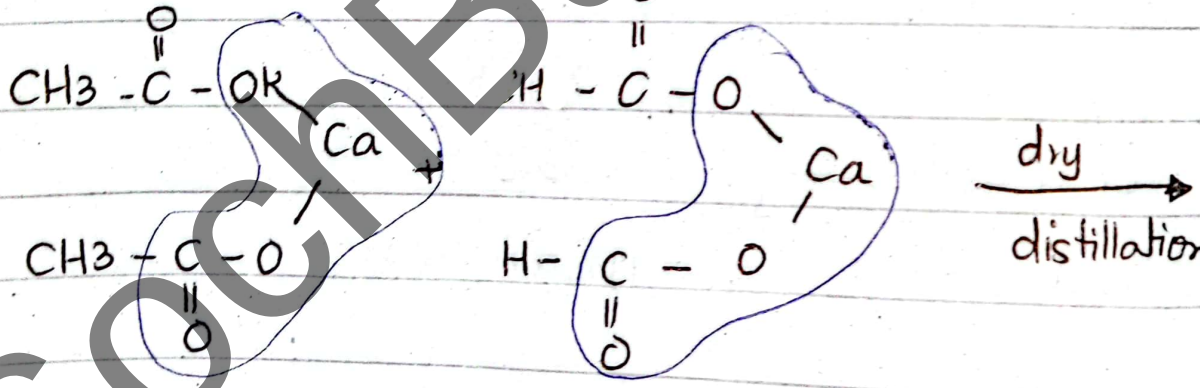
Dry distillation:



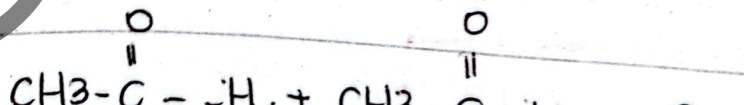
Calcium acetate.

acetone
propanone

formation of aldehyde:



calcium acetate. Calcimformate.



acetaldehyde / ethanal.

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reactivity order of derivatives

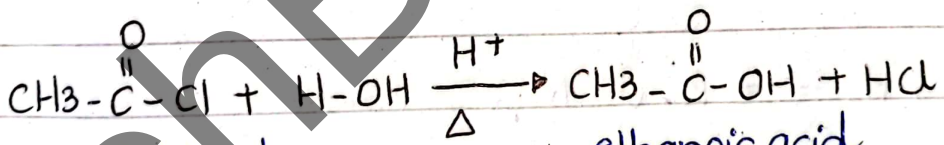
Acid halide > Acid anhydride > ester > carboxylic acid > amide.

reaction of derivatives

a) Reactions of Acid halide :

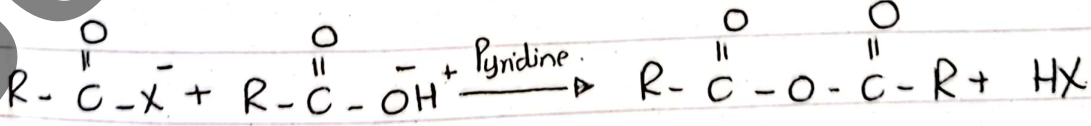
1) Hydrolysis , reaction of water :-

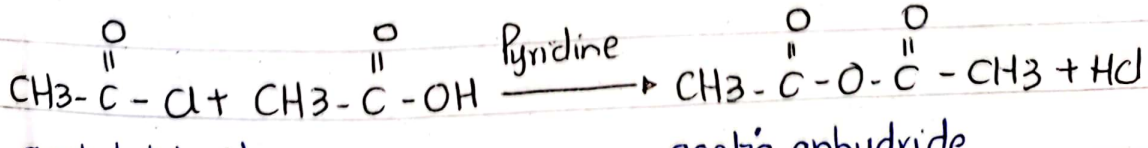
- acid chlorides reacts violently give -COOH.



Acetyl chloride — ethanoic acid

2) Rxn with -COOH.





acetyl chloride — acetic anhydride

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3) Rxn with alcohol.

catalyst H_2SO_4.

$$R-\overset{O}{\overset{\|}{C}}-X + R-OH \xrightarrow[\Delta]{H_2SO_4} R-\overset{O}{\overset{\|}{C}}-OR + HX$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3-OH \xrightarrow[\Delta]{H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + HCl$$

acetyl chloride. ethyl methanoate.

4) Reaction with ammonia

$$R-\overset{O}{\overset{\|}{C}}-X + 2NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + NH_4X$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + 2NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + NH_4Cl$$

acetylchloride. amide.

and

$$R-\overset{O}{\overset{\|}{C}}-X + NH_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + NH_4X$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + HCl$$

acetyl chloride amide.

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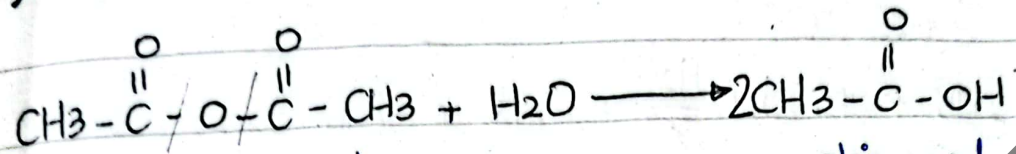
b) Reaction of acid anhydride :

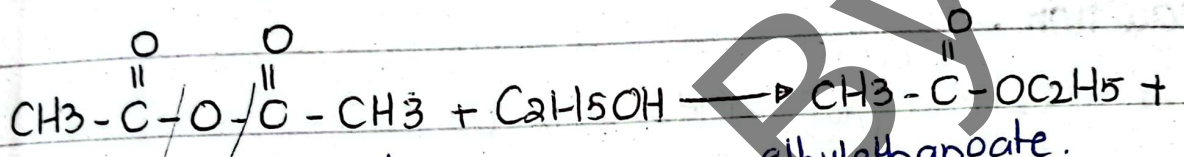
1) Hydrolysis / rxn with water.



acetic anhydride

acetic acid.

2) Alcoholysis

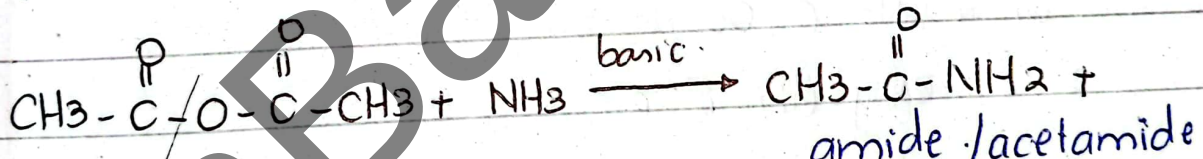


acetic anhydride.

ethylethanoate.

acetic acid.

3) Rxn with ammonia

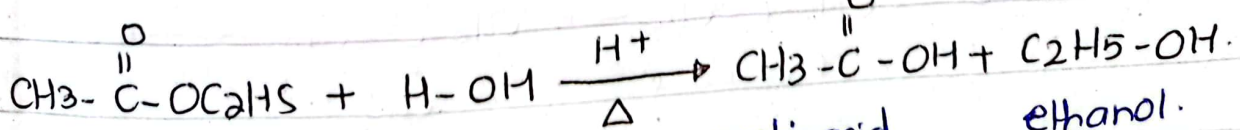


amide /acetamide

acetic acid.

c) Reaction of esters :

1) Hydrolysis / rxn with water (acidic)



ethylacetate.

acetic acid

ethanol.

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Basic Hydrolysis / Saponification:

alkalide salt of COOH = soap

$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + NaOH \xrightarrow[\Delta]{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-ONa + C_2H_5-OH$$

sodium salt of ethanoate.
sodium acetate
(Soap).

Reduction.

$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\text{dry ether}]{LiAlH_4} 2CH_3-CH_2-OH$$

ethyl ethanoate. ethanol.

Reaction with Grignard Reagent.

$$\bullet CH_3-Mg-Br + CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\text{ether}]{\text{dry}} CH_3-\overset{O-MgBr}{\overset{|}{C}}(CH_3)-OC_2H_5$$

ethyl ethanoate.

$$\bullet CH_3-\overset{O-MgBr}{\overset{|}{C}}(CH_3)-OC_2H_5 \xrightarrow[H^+]{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + C_2H_5OH + Mg\overset{Br}{\underset{OH}{}}$$

acetanone.

$$\bullet CH_3-Mg-Br + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-\overset{O-MgBr}{\overset{|}{C}}(CH_3)-CH_3 \xrightarrow[H^+]{H-OH} CH_3-\overset{CH_3}{\overset{|}{C}}(CH_3)-OH + Mg\overset{Br}{\underset{OH}{}}$$

Propanone.

Ter-Butanol.

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d) Reaction of amide :

1) Hydrolysis .

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H-OH \xrightarrow[H^+]{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3$$

acetamide — acetic acid

2) Reduction :

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2$$

acetamide. — Amino ethane.

e) Reaction of Nitrile :

1) Hydrolysis :

$$CH_3-C\equiv N + H-OH \xrightarrow[\Delta]{H^+} CH_3-\overset{O}{\overset{\|}{C}}-NH_2$$

Methyl nitrile — acetamide.

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3$$

2) Reduction .

$$R-C\equiv N \xrightarrow{LiAlH_4} R-CH_2-NH_2$$

$$CH_3-C\equiv N \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2$$

amine.

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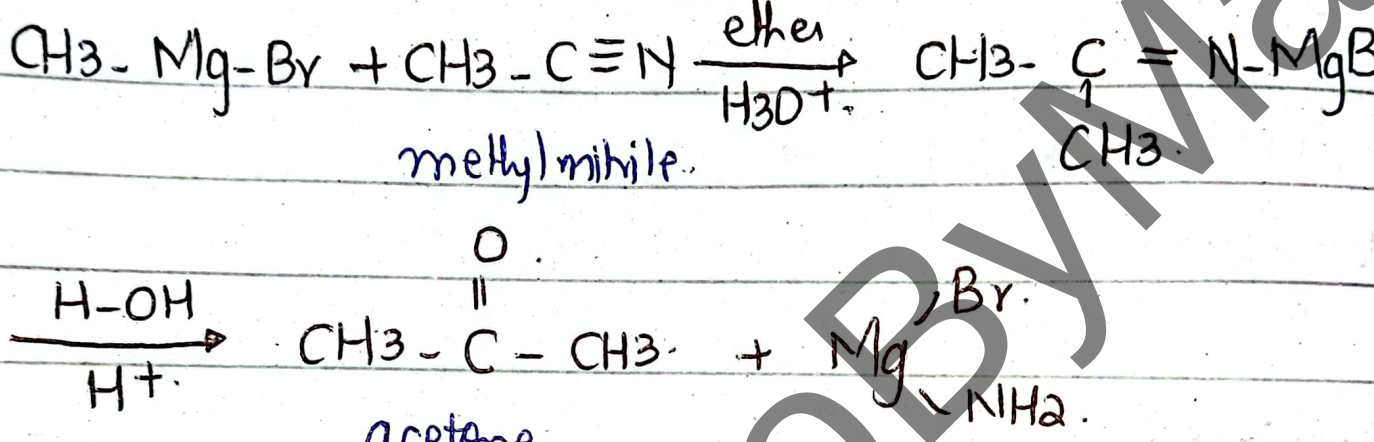
3) with grignord



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SOS

Q What are fatty acids?

Fatty acids consists of long hydrocarbon chain. At the end of the hydrocarbon chains, there's a carboxyl group giving it acidic property. But here's the condition not all carboxylic acids are fatty acids, only mono-aliphatic carboxylic acids are fatty acids.

Q Which is following given below is the strongest carboxylic acids?

a) Methanoic acid b) Ethanoic acid c) Propanoic acid.

Methanoic acid is the strongest among these.

→ Methanoic acid commonly known as formic acid has hydrogen atom directly attached to the carboxyl group, which does not donate electrons.

→ It has no weak alkyl electron-donating group that will reduce its acidity.

→ The formate ion ($HCOO^-$) is stable. The neg charge is delocalized on oxygen atoms, making it stronger acid.

→ Pka value is very small 3.75.

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Q Why fluoroacetic acid is stronger than chloroacetic acid?

Fluroacetic acid is stronger than the chloroacetic acid due to the inductive effect of the substituent group attached to acetic acid molecule.

→ Flourine being more electronegative, with-draws the e⁻s more powerfully than the chlorine.

→ The inductive effect of flourine is stronger than that of chlorine.

→ It stabilizes the conjugate base more effectively by delocalizing the neg charge.

Q. Why it's necessary to use either acidic or basic conditions for hydrolysis of nitriles.

Hydrolysis of nitriles to produce carboxylic acids or amides requires either acidic or basic conditions due to the nature of nitrile functional group.

acidic condition:

The acidic environment catalyzes the hydrolysis by stabilizing intermediates and transition states, facilitating the reaction.

Basic condition:

The basic environment stabilizes the neg charge intermediates and transition state, promoting the reaction.

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Q/ What happens when calcium acetate is heated?

When calcium acetate is heated, it undergoes the thermal decomposition to produce calcium carbonate and ~~acetate~~ acetone.

$$Ca(CH_3COO)_2 \xrightarrow[\text{dry distillation}]{\text{heat}} CH_3COCH_3 + CaCO_3$$

calcium acetate. (acetone or propanone) (calcium carbonate).

Q. Give some methods for preparing esters.

There are sophisticated method for the preparation of esters.

- Fischer esterfication.
- acyl chloride.
- acid anhydride.
- Steglich esterification (COOH + R-OH).

Q Convert acetic acid to :-

a) acetone:

- $2CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + 2H_2O$
- $(CH_3COO)_2Ca \longrightarrow CH_3COCH_3 + CaCO_3$

b) ethanol:

- $CH_3COOH \xrightarrow{LiAlH_4} CH_3-CH_2-OH$.

c) Methane:

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$.

$CH_3COONa + NaOH \xrightarrow{\Delta CaO} CH_4 + Na_2CO_3$.

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d) acetate :

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$.

e) acetyl chloride :

$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + HCl + SO_2$.

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