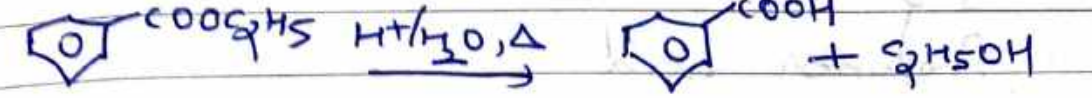
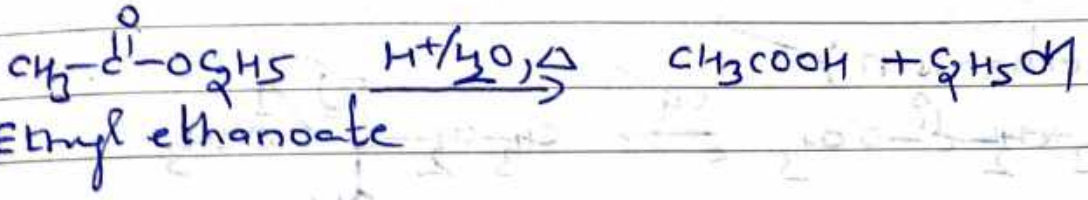
Carboxylic Acids (aromatic + aliphatic)

Preparation of Carboxylic Acids

1/ Acidic hydrolysis of esters

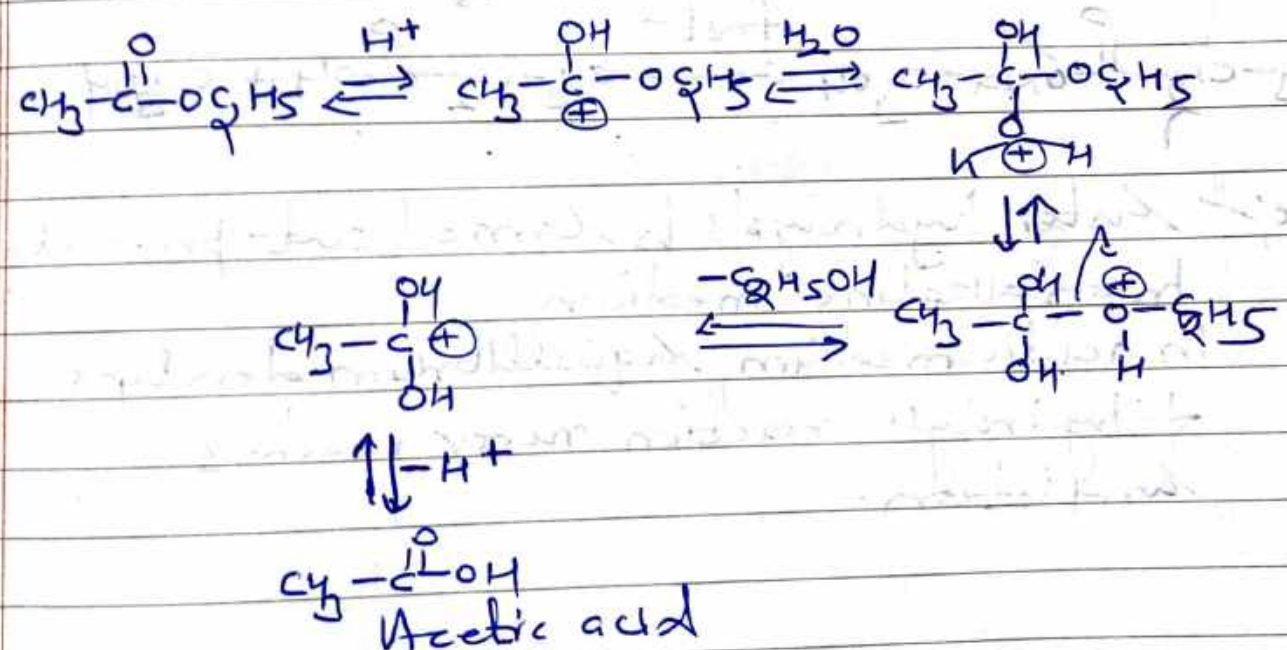
Hydrolysis of esters with mineral acids gives directly carboxylic acids.





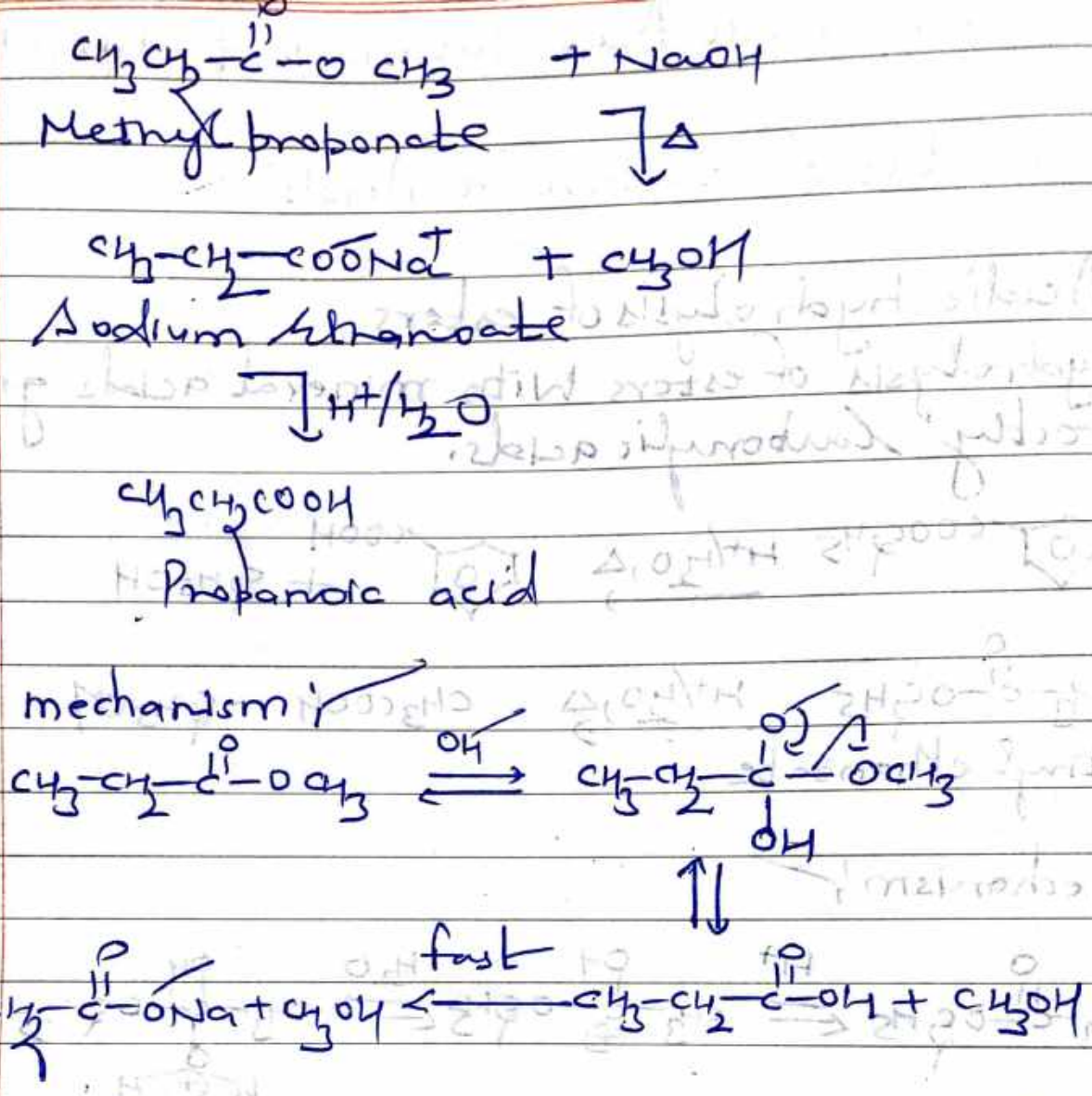
Ethyl ethanoate

mechanism:



2/ Alkaline hydrolysis of esters

Alkaline hydrolysis of esters gives carboxylate salts which upon subsequent acidification give the corresponding carboxylic acid.



Note; Ester hydrolysis is carried out preferably in an alkaline medium.
In acidic medium, equillibrium develops & hydrolysis reaction never reaches completion.

Reaction Involving α-Carbon of Carboxylic Acids

α-Halogenation:

Hell-Volhard-Zelinsky Reaction:

When a carboxylic acid that contains α-hydrogen is treated with Cl_2 or Br_2, in the presence of phosphorous, the α-hydrogen atom are replaced by chlorine or bromine atoms. This rxn is known as Hell-Volhard Zelinsky Rxn (HVZ)

$$R-CH_2-COOH + Cl_2 \xrightarrow{P} R-\underset{Cl}{CH}-COOH + HCl$$

$$CH_3-CH_2-COOH + Br_2 \xrightarrow{P} CH_3-\underset{Br}{CH}-COOH + HBr$$

mechanism:

$$2P + 3Br_2 \longrightarrow 2PBr_3$$

$$3\,CH_3CH_2COOH + 2PBr_3 \longrightarrow 3\,CH_3CH_2\overset{O}{\overset{\|}{C}}-Br + H_3PO_3$$

Propanoyl bromide

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Br \rightleftharpoons CH_3-CH=\overset{OH}{C}-Br \xrightarrow[-HBr]{Br_2} CH_3-\underset{Br}{CH}-\overset{O}{\overset{\|}{C}}-Br$$

(keto) (enol)

2-Bromo-propanoyl bromide

$$\left.\begin{array}{l} \\ \\ \end{array}\right] + CH_3CH_2COOH$$

$$CH_3-\underset{Br}{CH}-\overset{O}{\overset{\|}{C}}-OH + CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Br$$

2-Bromopropanoic acid — Propanoyl bromide

Acid Derivatives :

I. Acid chlorides :

Preparation of acid chlorides from carboxylic acids :-

1. By rxn with Thionyl chloride ($SOCl_2$)

$$R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + HCl\uparrow + SO_2\uparrow$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + HCl + SO_2$$

2. By rxn with Phosphorous Trichloride (PCl_3)

$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + PCl_3 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$$

3. By rxn with Phosphorous Pentachloride (PCl_5)

$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \rightarrow CH_3CH_2-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

Chemical Properties :

$$R-\overset{O}{\overset{\|}{C}}-Cl + \ddot{N}H_3 \rightarrow R-\overset{O}{\overset{|}{C}}(-Cl)-\overset{\oplus}{N}H_3 \rightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + Cl^- + H^+ \text{ (from Advert)} \rightarrow HCl$$

Water, alcohols, ammonia are weak nucleophiles

chemical Rxn's

1) Hydrolysis

2) Alcoholysis

3) Ammonolysis

4) Rxn with Salts of Carboxylic Acids:

II Anhydrides

The compounds derived by loss of a water molecule b/w two molecules of a carboxylic acid are called Acid anhydrides

Preparation of Anhydrides:

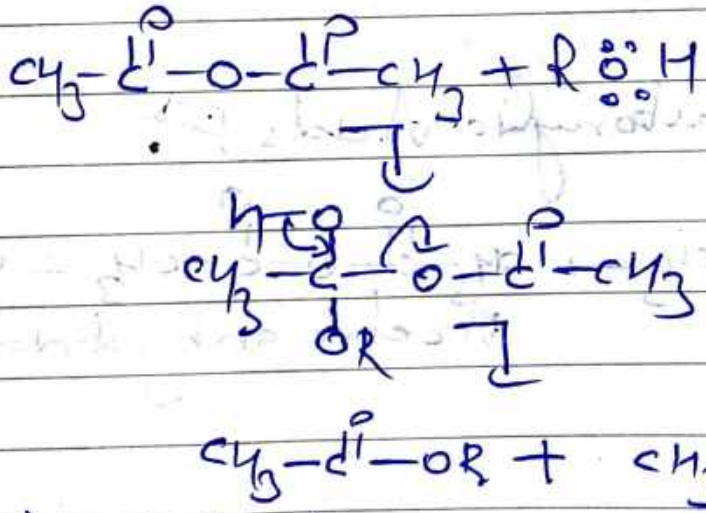
1) By rxn of carboxylic acid with acid Halide

2) By rxn of acid halides with salt of carboxylic acid

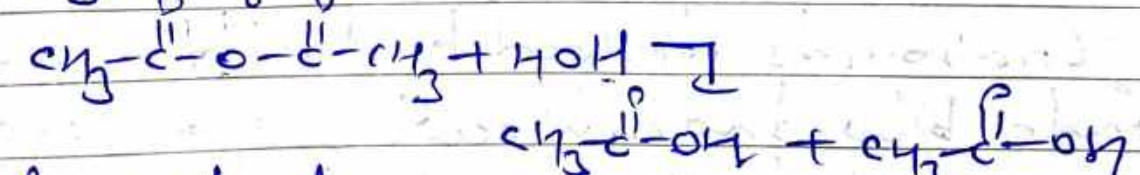
$CH_3COO^-Na^+ + CH_3COCl \rightarrow CH_3CO-O-COCH_3 + NaCl$

chemical properties

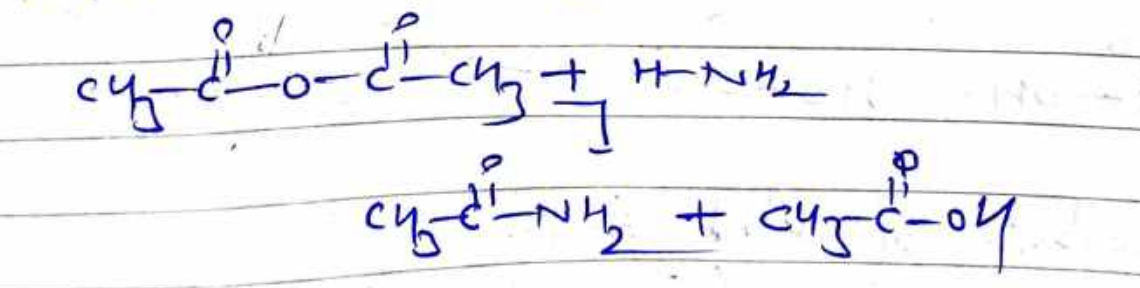
Anhydrides react with nucleophiles in the same way as acid chlorides. But since $-OCOR$ gp is not as electronegative as $-Cl$ atom, anhydrides are less reactive than acid chlorides



Hydrolysis

1) 

Rxn with Ammonia

2) 

III Amides

The derivatives of carboxylic acids in which the -OH function of the -COOH group has been replaced by $-NH_2$.

Preparation

1) By the action of Ammonia on Acid chlorides

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

Acetyl chloride

2) By Rxn of Anhydrides with Ammonia

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

3) By heating ammonium carboxylates

$$CH_3-\overset{O}{\overset{\|}{C}}-ONH_4^+ \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

Chemical Properties

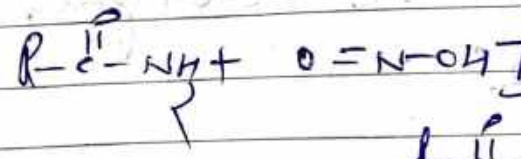
Amides are least reactive of the acid derivatives. They owe their chemical stability to resonance.

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \longleftrightarrow R-\overset{O^-}{C}=NH_2^+$$

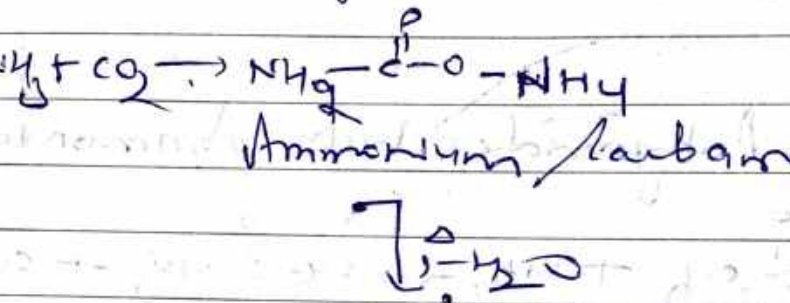
Reactions

1) $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{acid}]{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-OH + NH_4Cl$

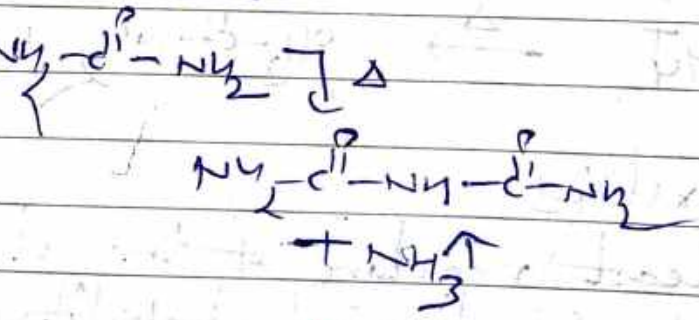
2) Reaction With Nitrous Acid ($NaNO_2 + HCl$)



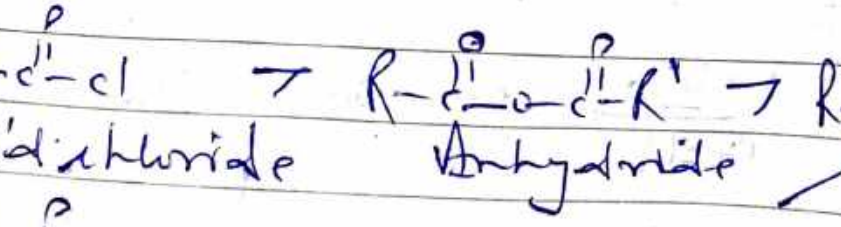
Urea
→ World's process
→ Commercial Synthesis



Biuret test



Comparative Reactivity of Acid Derivatives:
The relative reactivities of different acid derivatives towards nucleophilic substitution are as follows:



Amides are least reactive of all acid derivatives because of delocalization which reduces the electrophilicity of carbon of $CONH_2$. The electron releasing -OR gp in esters decreases the electrophilicity of carbon of $(-C^{\delta+}-OR)$. In acid chlorides the highly electronegative chlorine increases the electrophilicity of carbon of $(-C^{\delta+}-Cl)$, thereby making it most reactive.

Esters

When carboxylic acids are heated with alcohols or phenols in presence of conc. H_2SO_4 or Dry HCl gas (Fischer - Speier Esterification) esters are formed. The rxn is reversible in nature & is known as Esterification

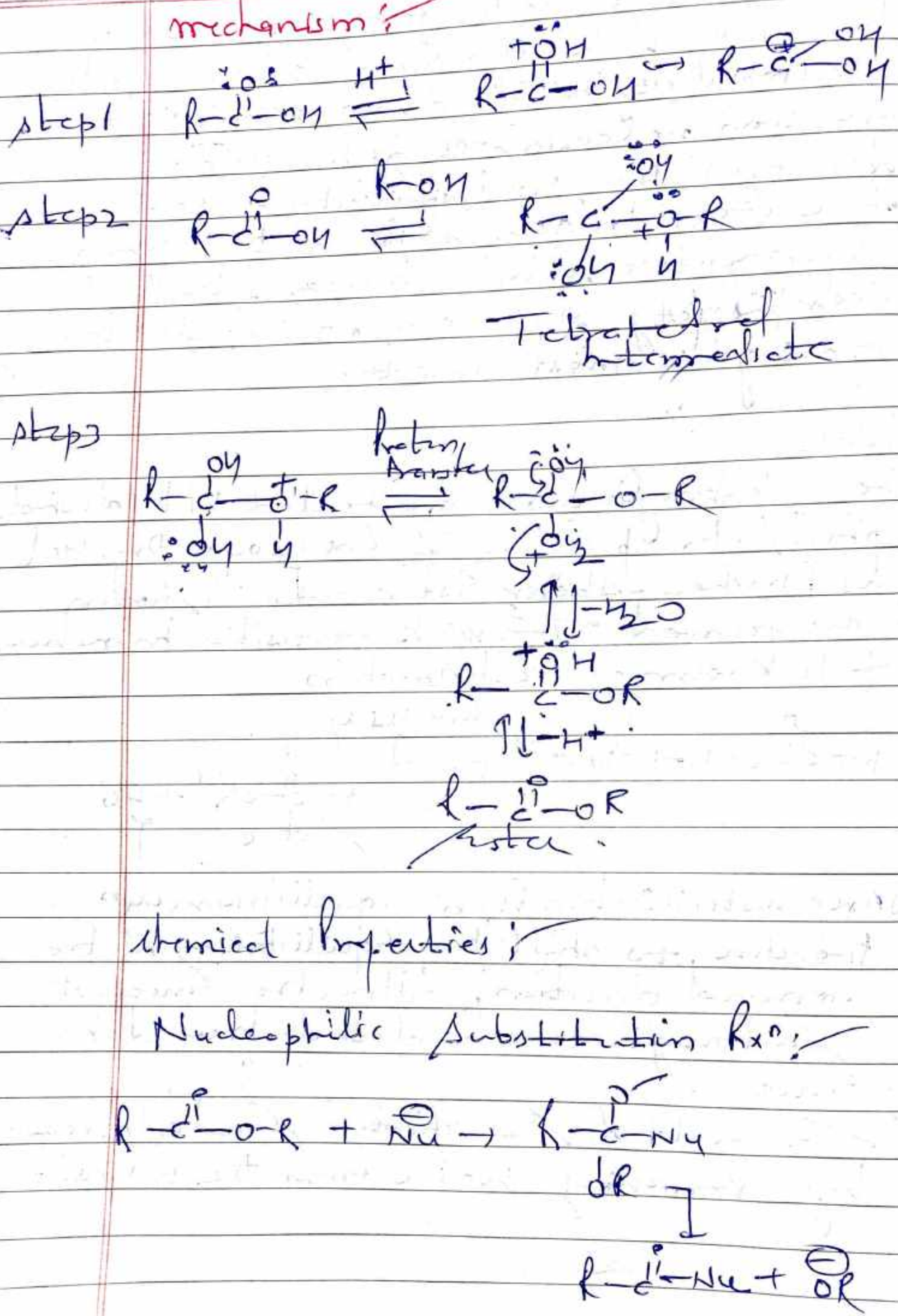
$$R-\overset{O}{\overset{\|}{C}}-O-H + HOR' \xrightleftharpoons{\text{conc. } H_2SO_4} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

Ester

→ Since esterification is an equilibrium rxn, therefore, to shift the equilibrium in the forward direction, either the excess of carboxylic acid or alcohol is used in excess.

→ The yield of esterification can be increased by removing water from the rxn mixture

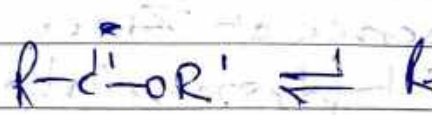
mechanism:



Chemical Properties:

Nucleophilic Substitution Rx°:

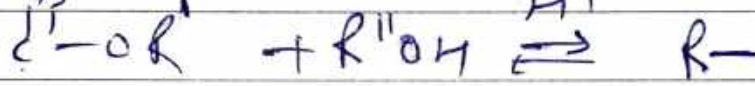
Esters undergo nucleophilic reactions less readily than do acid halides or anhydrides. This is attributed to resonance effect -



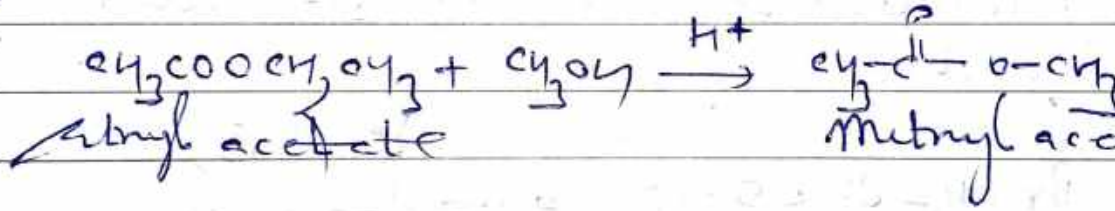
Chemical properties

Transesterification

Ester of an alcohol can react with another lower alcohol in the presence of a mineral acid to give the ester of second alcohol.

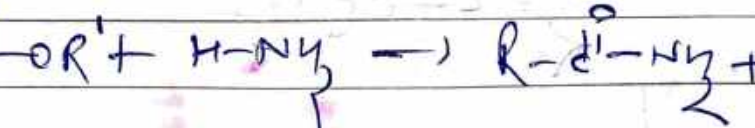


Eg:-



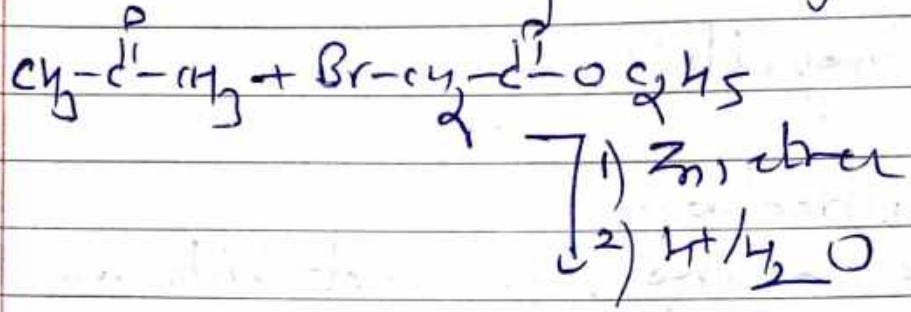
Methyl acetate.

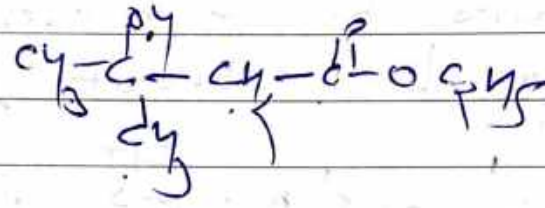
→ Rxn with Ammonia



Reformatsky Reaction

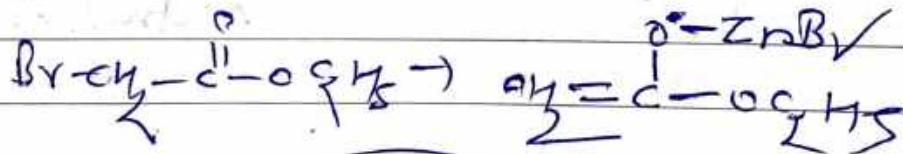
This involves the treatment of an aldehyde or ketone with α-bromo ester in the presence of Zinc.
The product is β-hydroxy ester.





Mechanism

1) formation of Zinc salt of enol of ester



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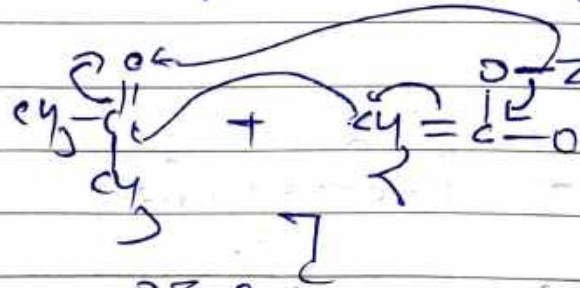

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