Short Answers and Questions

Q1: Write down the formula of the following?

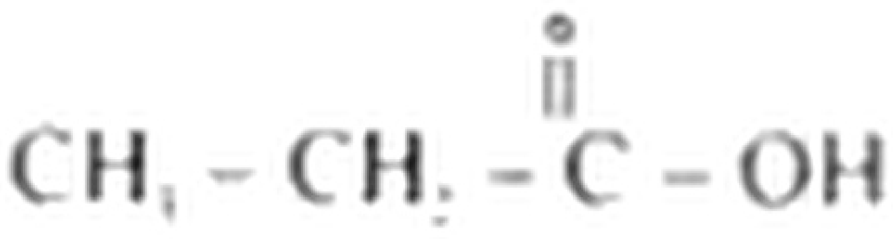
a) Succinic acid **b) Glutauic acid**

c) Adipic acid **d) Malomic acid**

e)Oxalic acid **f) Propionic acid**

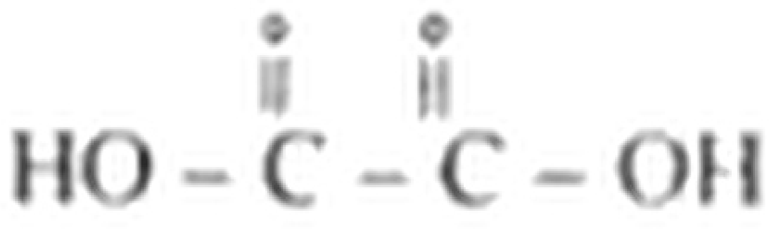
Answer

a) Propionic acid



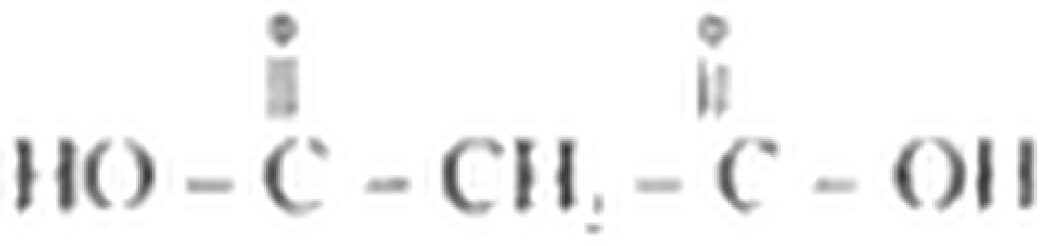
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

b) Oxalic acid



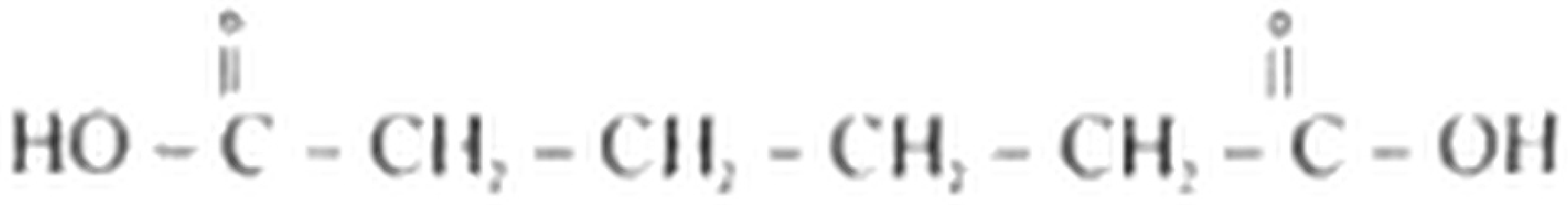
$HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$

c) Malonic acid



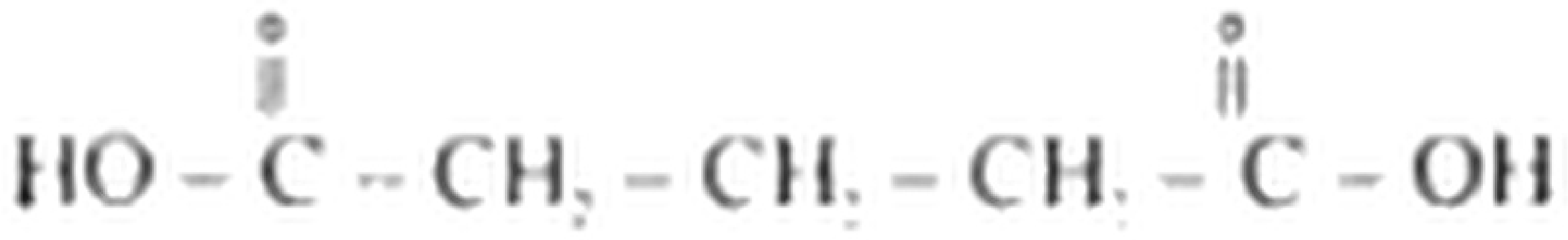
$HO-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OH$

d) Adipic acid



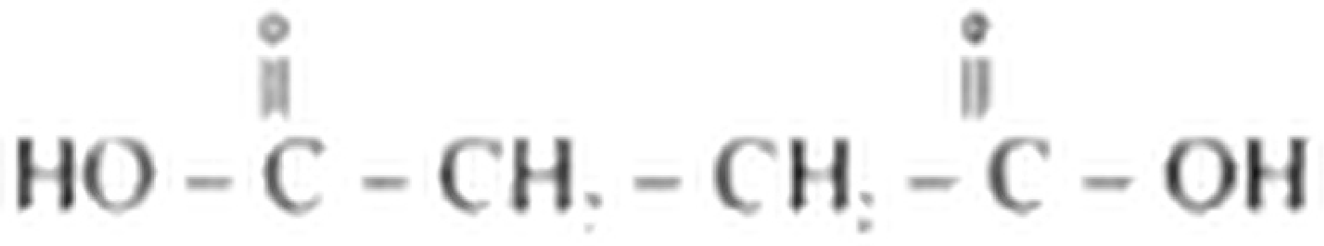
$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

e) Glutaric acid



$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

f) Succinic acid



$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$

Q2: Write down the physical properties of carboxylic acid.

Answer

The polar nature of both the O —H and C = O bonds, due to the electronegativity difference of the atoms results in the formation of strong hydrogen bonds with other carboxylic acid molecules or other H bonding system. The implications are:

1) High melting and boiling points compared to analyses alcohols.

2) High solubility in aqueous media.

3) Hydrogen bonded dimmers in gas phase and dimmers an aggerates in pure liquids.

Q3: Write down the structure and acidity of carboxylic acid?

Answer

The CO_2H units is plane and consistent with SP^2 hybridization and a resonance interaction of the lone pairs of the hydroxyl oxygen with that system of the carboxyl.

Acidity

Carboxylic acid and the most acidic simple organic compounds (PKa — 5).

But they are weak acids compared to acids like HCl or H_2SO_4.

Resonance stabilization of the carboxylate allows the negative change to be decolorized between the two electronegative oxygen atoms. Adjacent electron with drawing substituents increases the acidity by further stabilizing the carboxylate.

Q4: Write down the preparation of carboxylic acids.

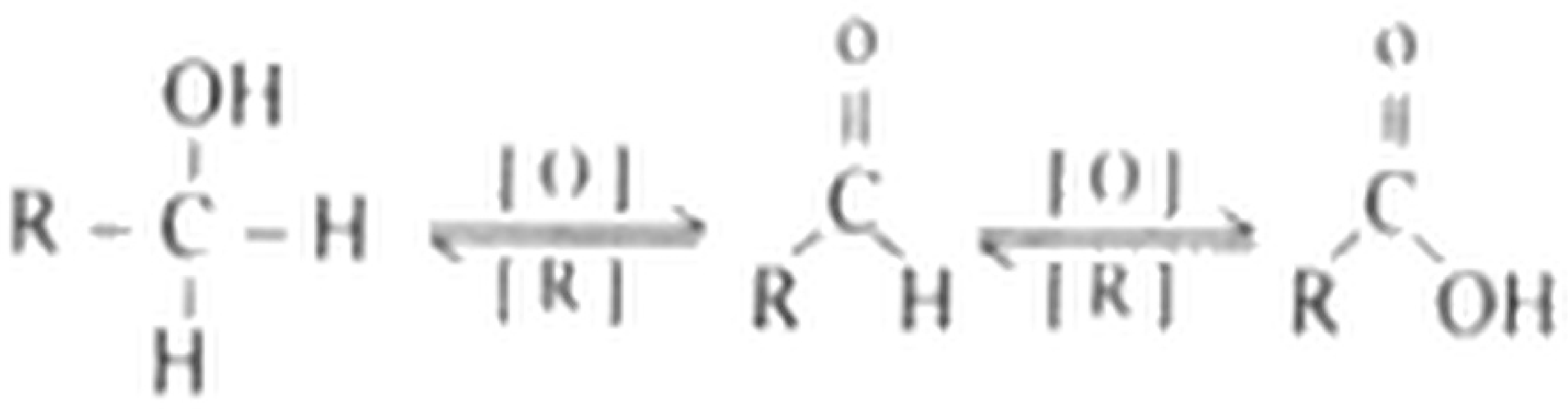
Answer

Carbonation of Grignard Reagents RMgX, by CO_2

$$RMgx + \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}} \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH$$

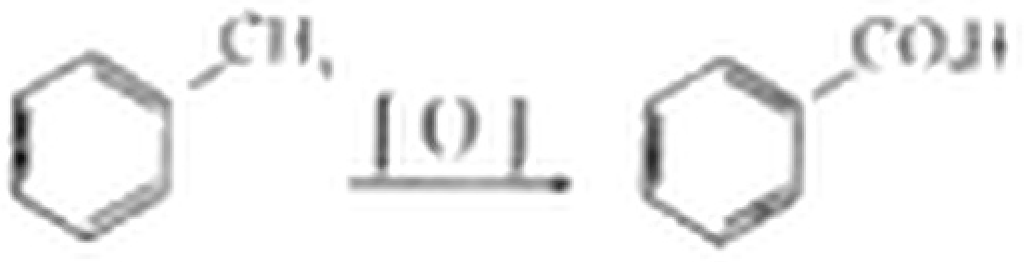
Hydrolysis of Nitriles

Oxidation of Primary alcohol



Oxidation of Aldehydes

Oxidation of Alkyl Benzenes



Q5: Write down the reaction of carboxylic acids? Carboxylic acids undergo the following types of reaction. ,

Answer

i) The reaction in which hydrogen atom of the carboxyl group in which hydrogen atom of the carboxyl group is involved (salt formation).

ii) The reaction in which OH group is replaced by another group. iii) The relational involving carboxyl group as.

Reaction involving H atom of the carboxylic group. Carboxylic acids are weaker acids than mineral acids. They furnish H when dissolved in HO.

Reaction with Bases

Carboxylic acid reacts with (NaOH, KOH) to form salts.

$$CH_3COOH + NaoH \longrightarrow CH_3COONa + H_2o$$

Reaction with carbonates and bicarbonates. Carboxylic acids decomposers carbonate and bicarbonate evolving carbon dioxide gas with effervescence.

$$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COONa + Co_2 + H_2o$$

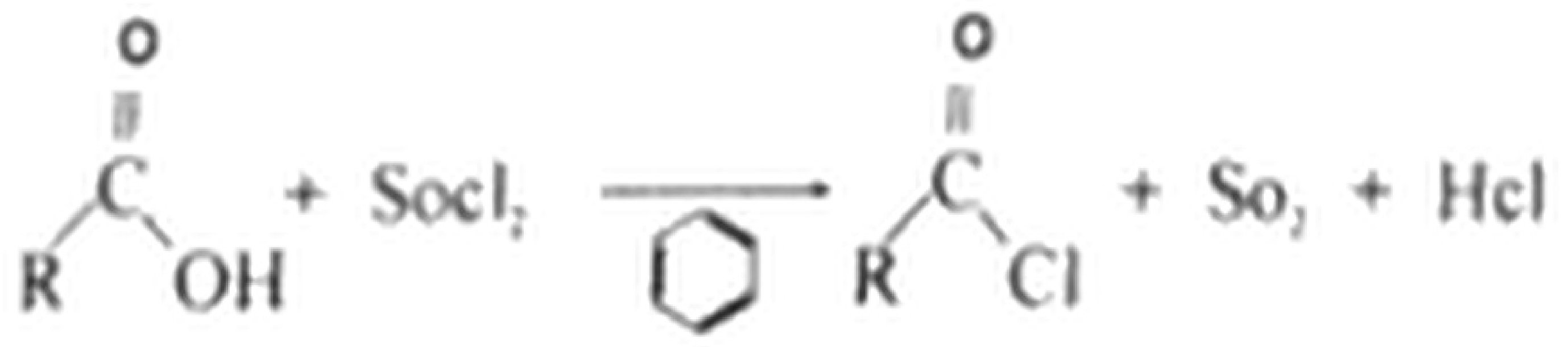
$$CH_3COOH + NaHco_3 \longrightarrow CH_3COONa + Co_2 + H_2o$$

Reaction with Metals

Carboxylic acids reaction with active metals such as Na, K, Ca, Mg etc to form their salts with evolution of hydrogen gas.

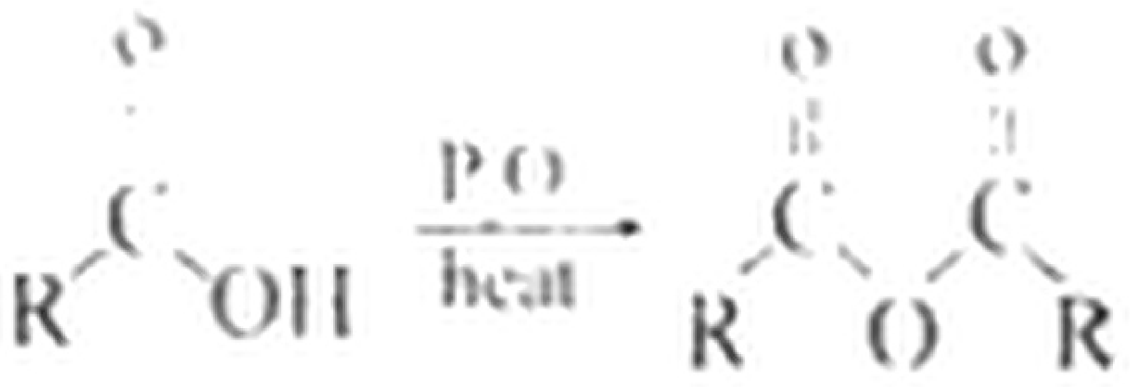
$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2o$$

Q6: Write down the preparation of Acyl chlorides.



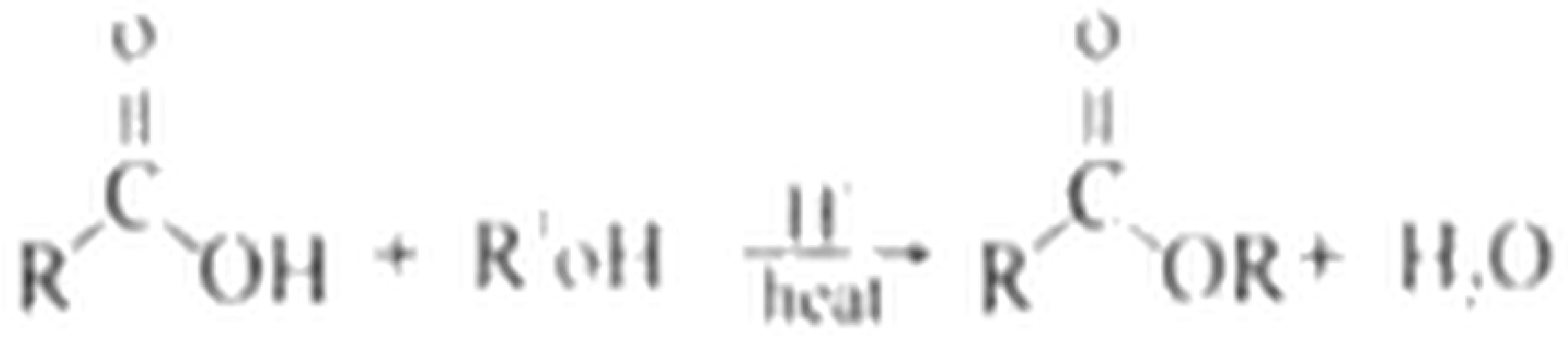
Answer

Acyl chlorides are prepared by treating the carboxylic acid with tlioxyl chloride SOC12 in the presence of a base. Acyl chlorides are by far the most commonly encountered of the acyl halides. Preparation of Acid Anlydides.



Preparation of Esters

This reaction is known as the Fisher esterification Esters au obtained by refluxing the pacent carboxylic acids with the appropriate alcohol with an acid catalyst.,



The equilibrium can be driven to completion by using an excess of either the alcohol or the carboxylic acid, or by removing the H20 as it forms. Esters can also be made from other carboxylic acid derivates, especially acyle halides and anlydides, by reacting them with the appropriate alcohol in the presence of a weak base. If a compound contains both hydrogen and carboxylic acid groups, then cyclic esters or lactomes can from via an intermolecular reaction. Reactions that from 5 or 6 membered rings are particularly favorable.

Q7: With mechanism for reaction for Acid catalyzed esterification. Answer

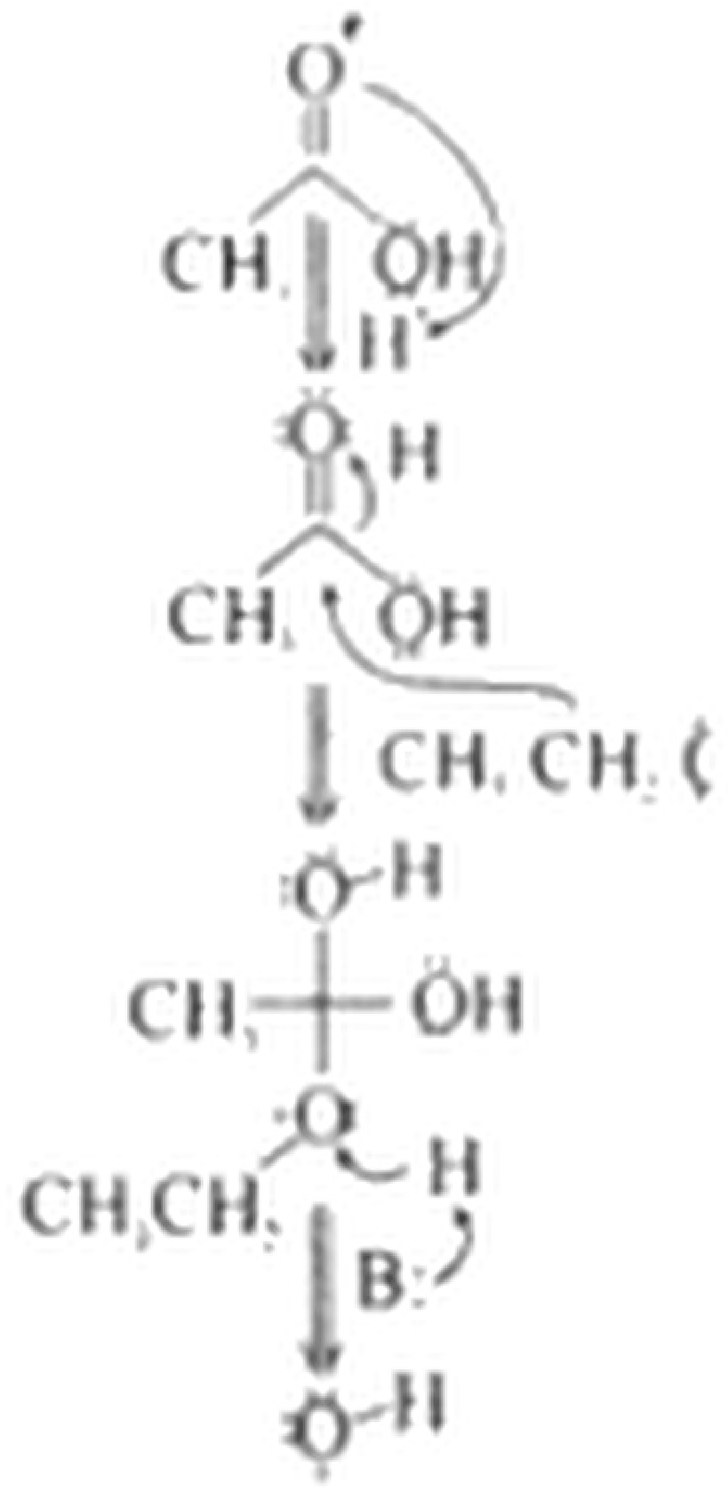
Step

Step 1

Protonation of carboxyl of acid group

Step 2

The alcohol O functions as the nucleophite and electrons moving towards the oxonium ioin, creating the tetrahedral intermediate.



Step 3

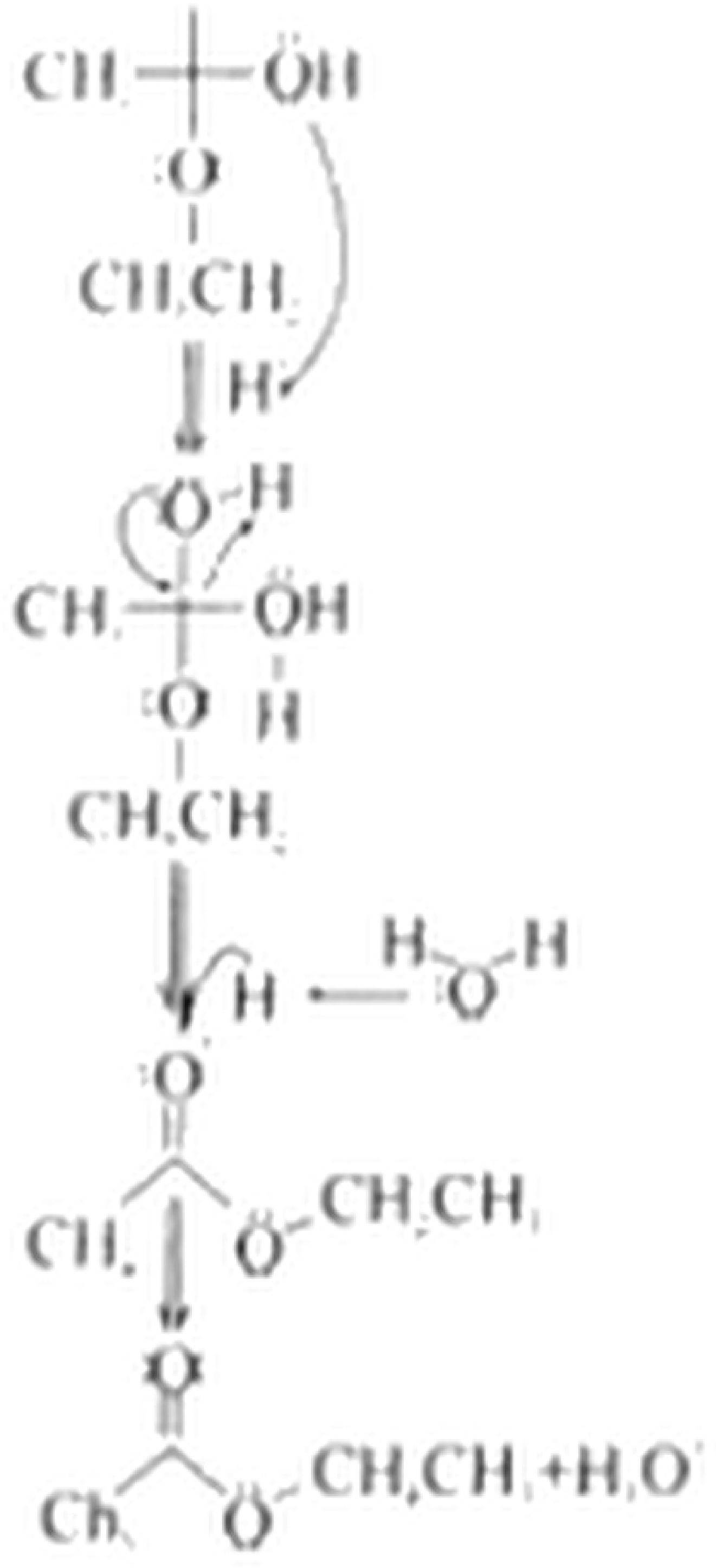
An acid/ base reaction Deprotonate the alcoholic oxygen.

Step 4

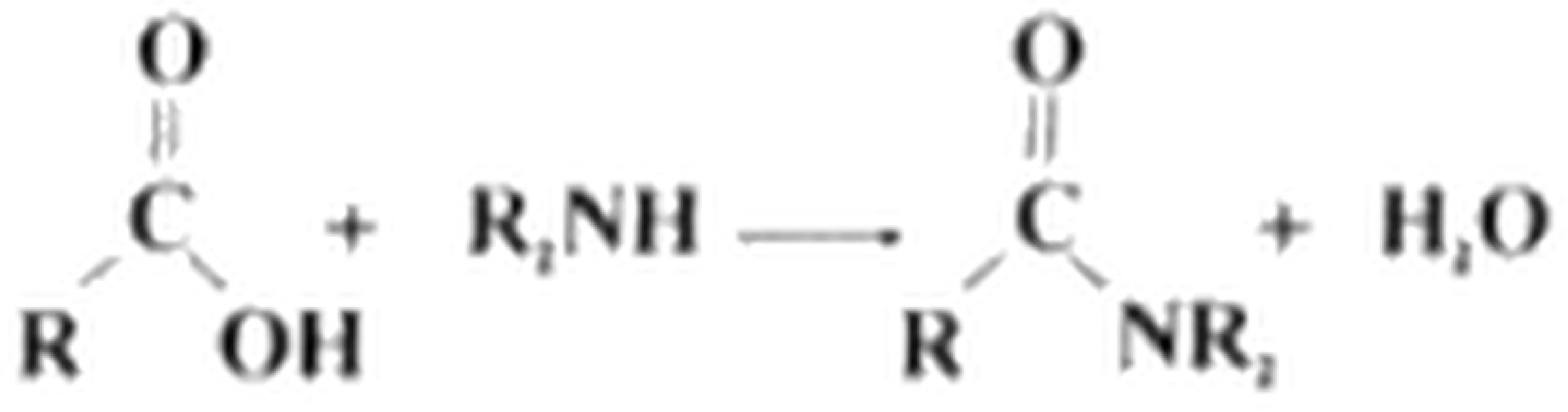
Acid base reaction in which OH leave and connect it into a good leaving group by protonation.

Step 5

The electrons of an adjacent oxygen to help "push out" the leaving group a neutral water molecule.



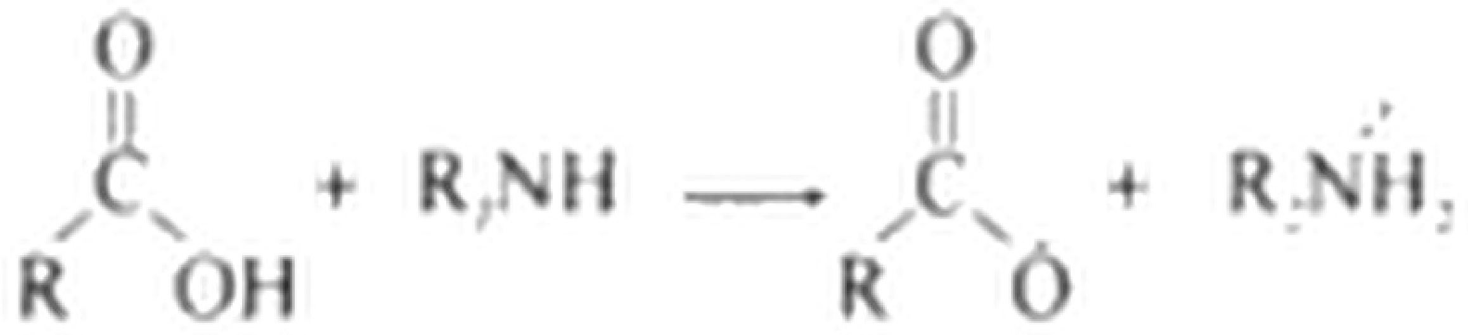
Q8: Write down the preparation of Amides.



$RCOOH + R_2NH \longrightarrow RCONR_2 + H_2O$

Answer

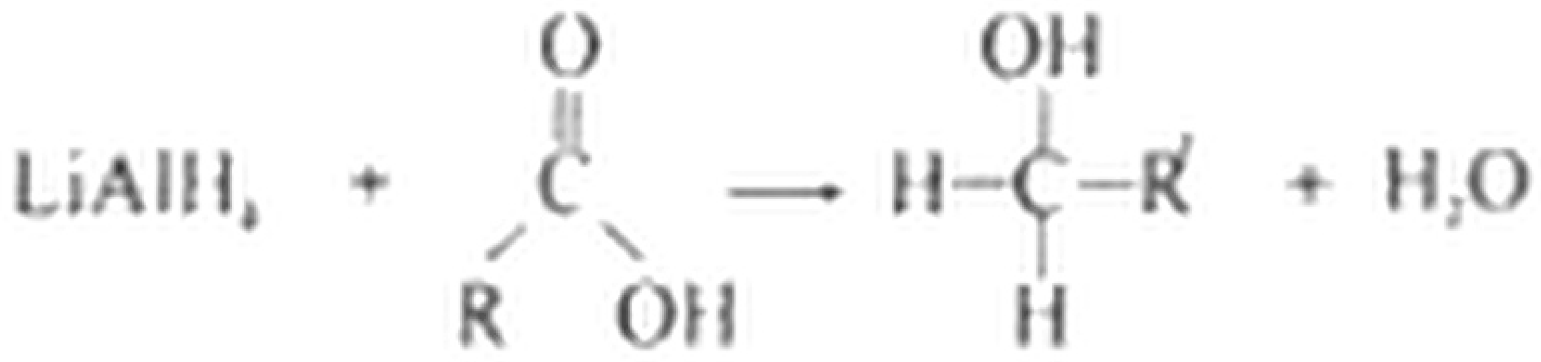
In general, it is not easy to prepare amides directly from the pacent carboxylic acid. The acid will protonate the amine preventing further, reactions since the carboxylate is a poor electrophile and the ammonium ion is not nucleophilic.



$RCOOH + R_2NH \longrightarrow RCOO + R_2NH_2$

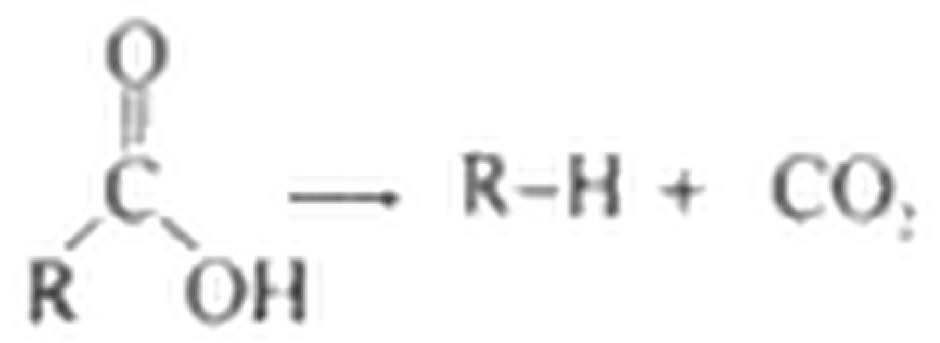
It is much easier to convert the carboxylic acid to the more reactive acyl chloride fist.

Reduction to Alcohols

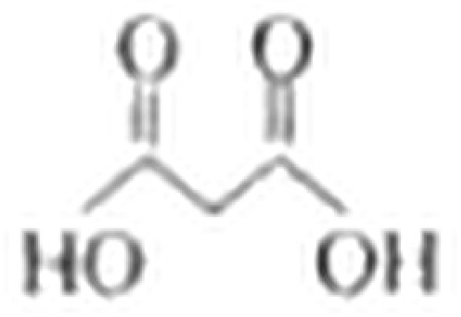


$LiAlH_4 + RCOOH \longrightarrow H\text{–}CH(OH)\text{–}R' + H_2O$

Carboxylic acid is less reactive to reduction by hydride than aldehydes, ketones, or esters. Carboxylic acids are reduced to primary alcohol. As a result of their low reactivity, carboxylic acid can only be reduced by LiALH4 not by the less reactive NaBH4 Decarboxylation.



Less of carbon dioxide is called decarboxylation. Simple carboxylic acids raxely undergo decarboxylation, Carboxylic acid with a carboxyl group at the 3 — (or P) position readily undergo thermal decarboxylation e.g. derivatives of matonic acid.



matonic acid

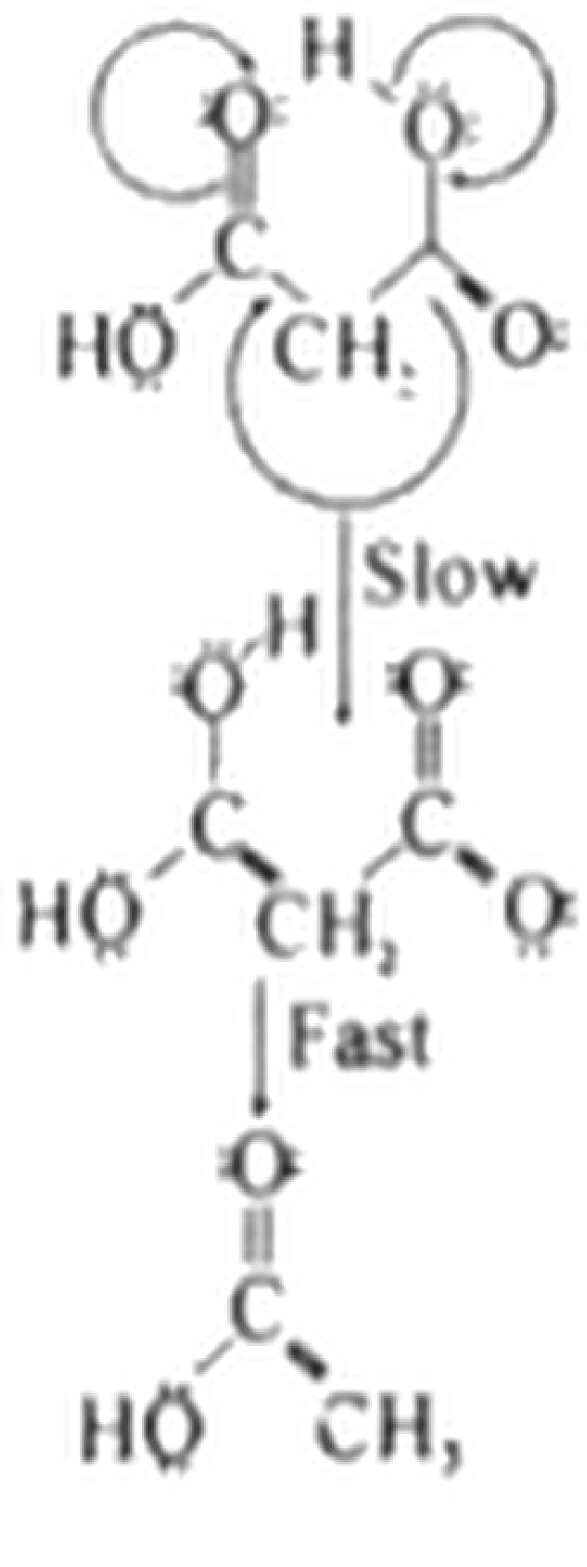
The reaction proceeds via a cyclic transition state guing an enol intermediate that tectomerizes to the carboxyl.

Decarboxylation

The protenation of the carboxyl, break the OH bond and form the bond, break the C — C and make the C = C. Note the concerted nature of this reaction and the cyclic transition state.

Step 2

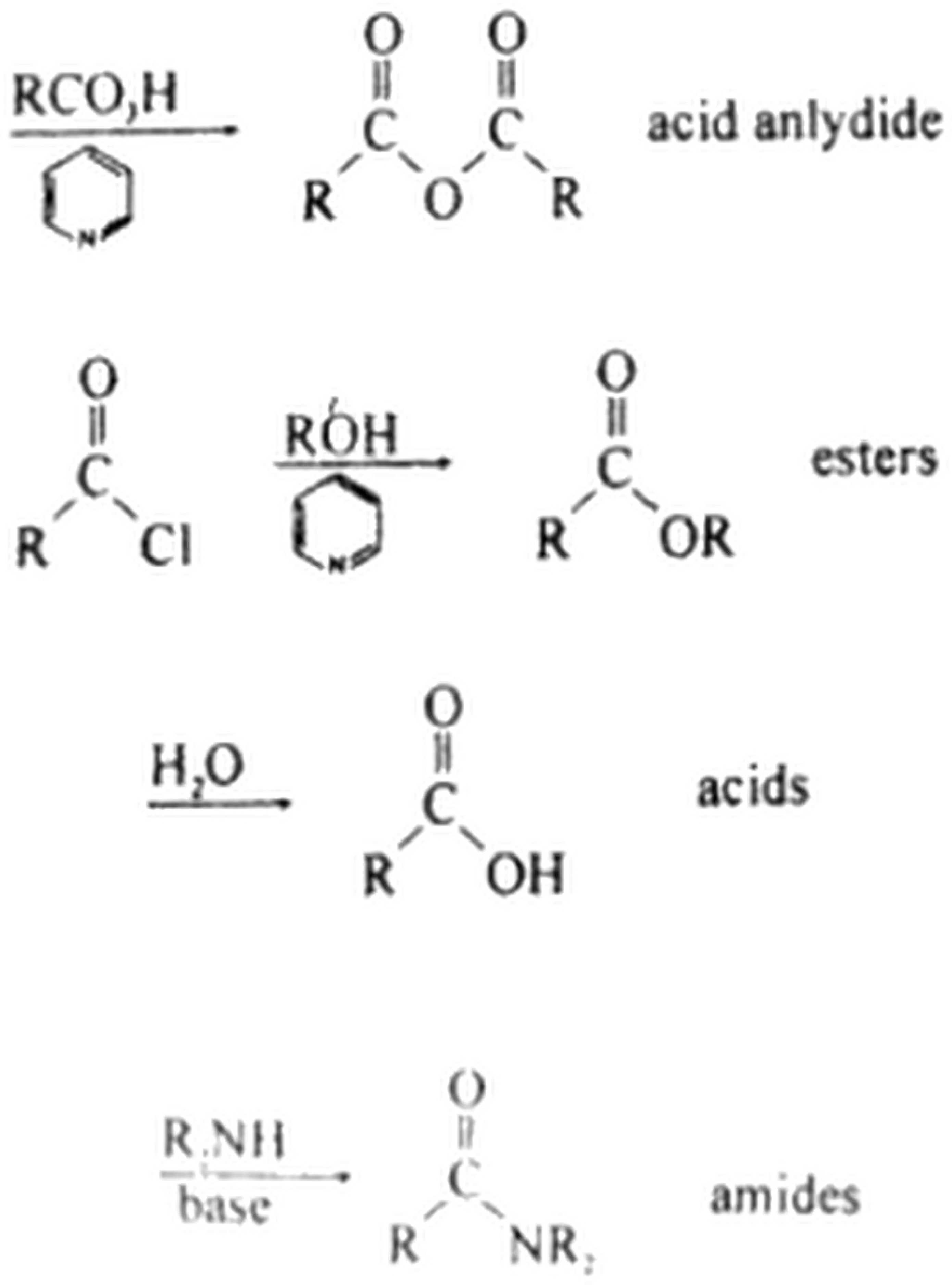
Tectomerization to the acid product.



Q9: Write down the Reactions of carboxylic Acid Derivates?

Answer

Interconversion of Acyl chlorides



Acyl chlorides are the most reactive of the carboxylic acid derivates and therefore can be readily converted into other carboxylic acid derivates.

They are sufficiently reactive that they react quite readily with cold water and hydrolyze to the carboxylic acid. The HCl by product is usually removed by adding a base such as pyridine or triethyl amine.

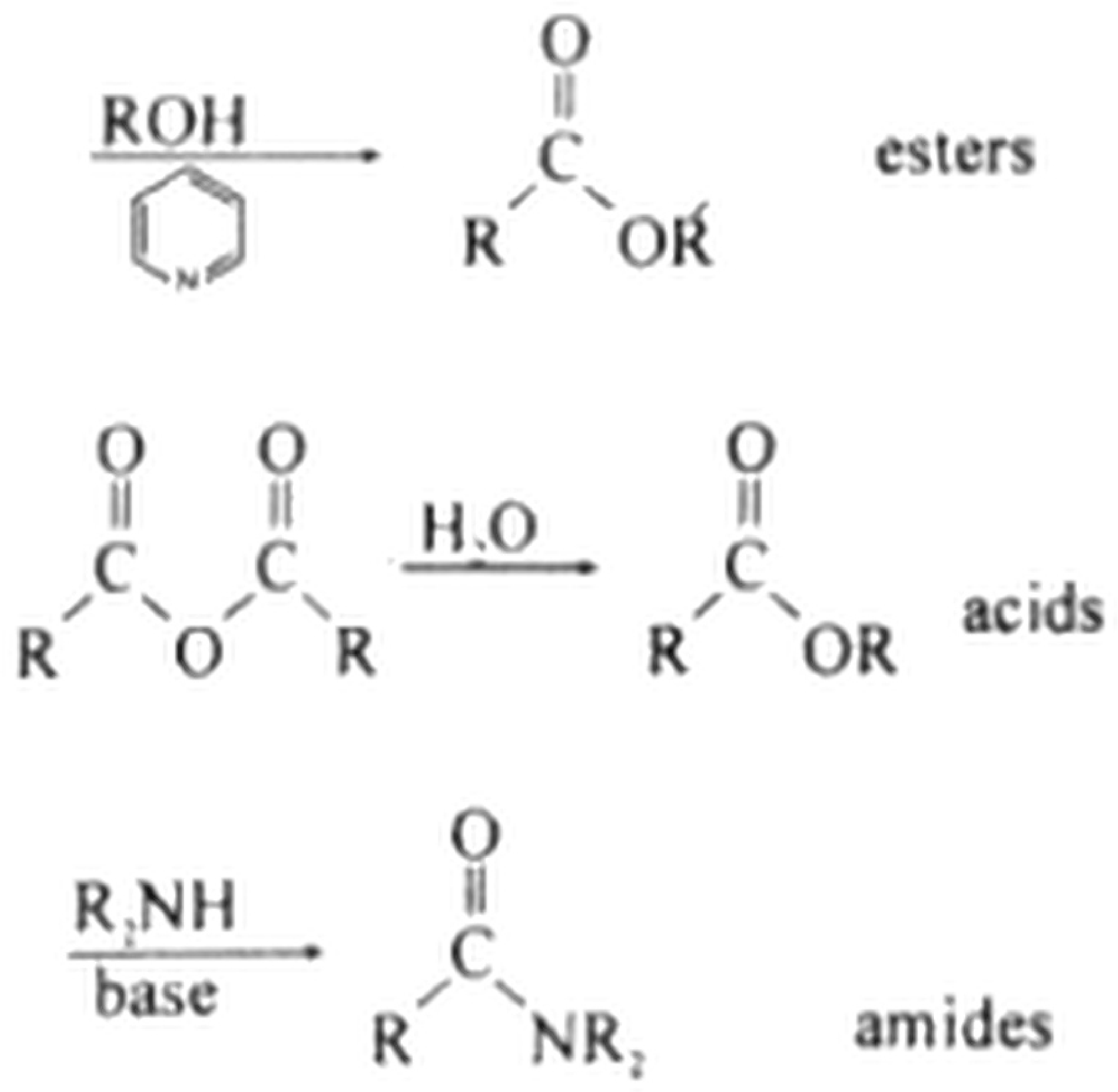
Friedel — crafts Acylation of Benzene

Overall transformation Ar — H to Ar — COR (Ketone). Named after Friedel craft who discovered the Reagent normally the acyle halide (usually RCOCl) with aluminium tuicltolide $AlCl_3$ a Lewis acid catalyst. The $AlCl_3$ enhances he electrophilicity of the acyl halide by complexing with the halide.

Electrophitic species the acyl cation or acylium ion (RCO+) formed by the removes of the halide by the Lewis acid catalyst. Friedel crafts reactions are limited to arnes as or more reactive than mono halobenzenes. Other sources of acylium can also be used as acid anhydrides with $AlCl_3$.

Reaction of Acid Anhydrides hydrolysis

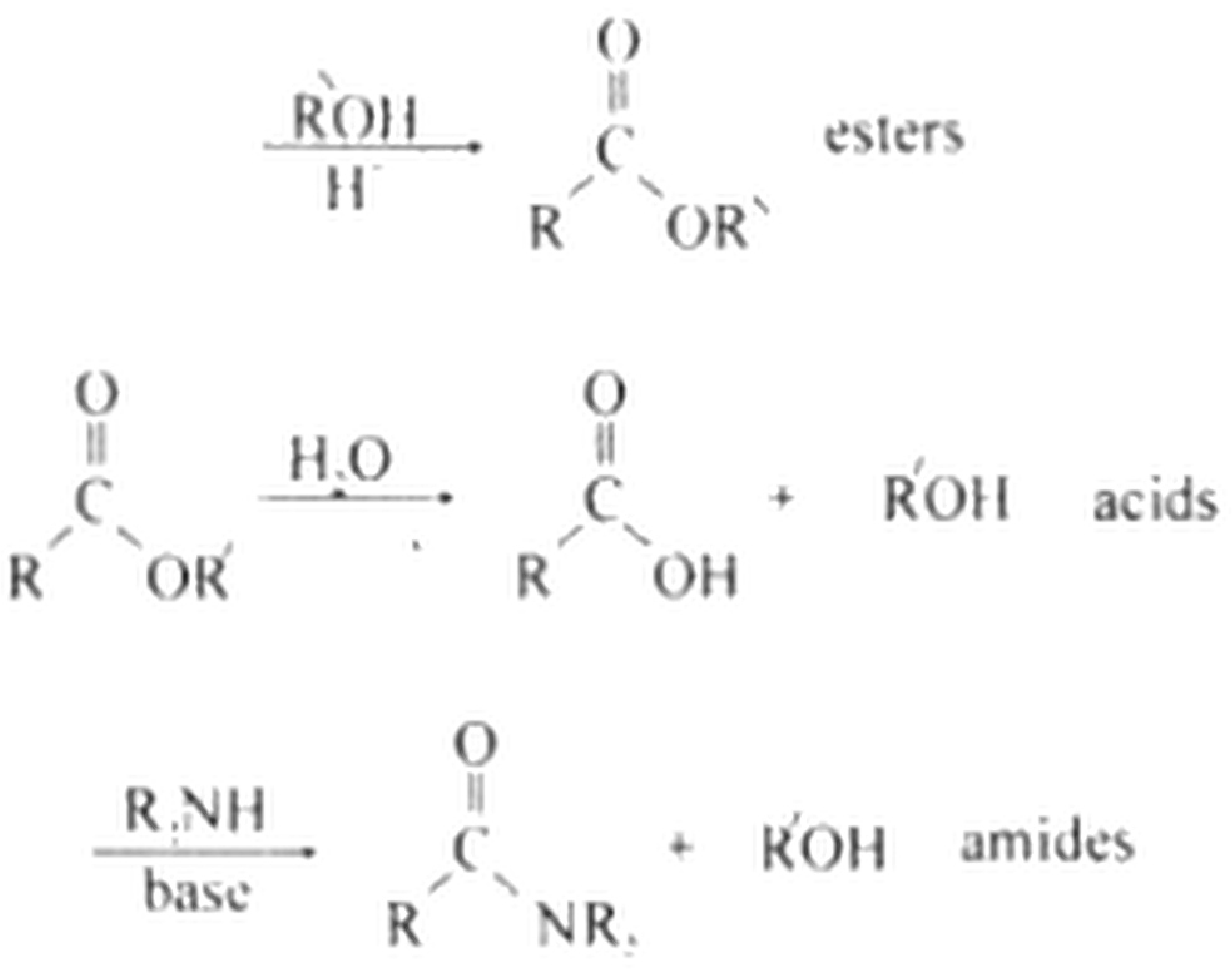
Interconversion Reaction of Acid anhydrides



Acid anhydrides are the second most reactive of the carboxylic acids derivates and can therefore be fairly readily converted into the other less reactive cathoxylic acid derivatives. A base in often added to neutralize the carboxylic acid by product that is formed.

Q10: Write down the reaction of Esters, hydrolysis, Reduction and with Grignard's reagent?

Answer

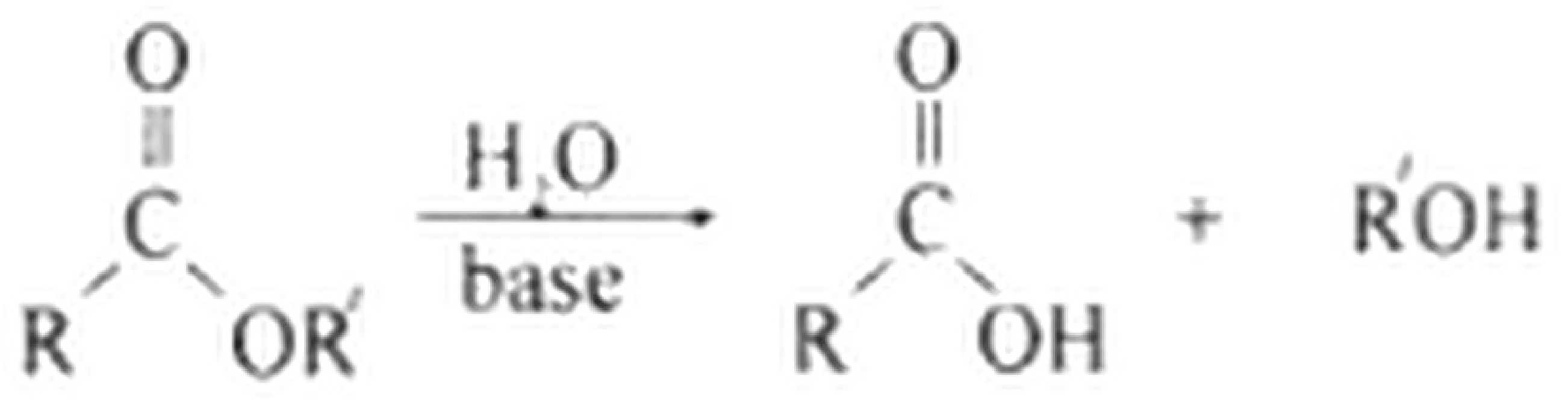


Esters can be converted into other esters the point carboxylic acid (hydrolysis) or amides.

Transebeatification heat with alcohol and acid catalyst Amide preparation heat with the amine, methyl or ethyl esters are the most reactive.

Q11: Write down the hydrolysis of Esters?

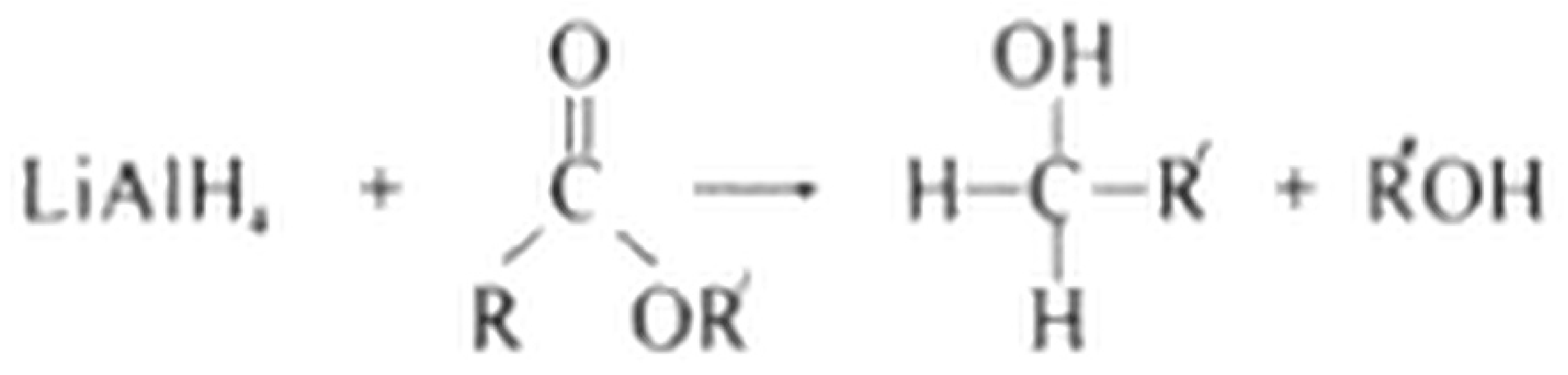
Answer



Carboxylic esters hydrolyze to the pacent carboxylic acid and an alcohol. Reagents aqueous acid (e.g. H_2SO_4) heat or aqueous NaOH heat known as saponification.

Q12: Write down the reduction of Esters?

Answer



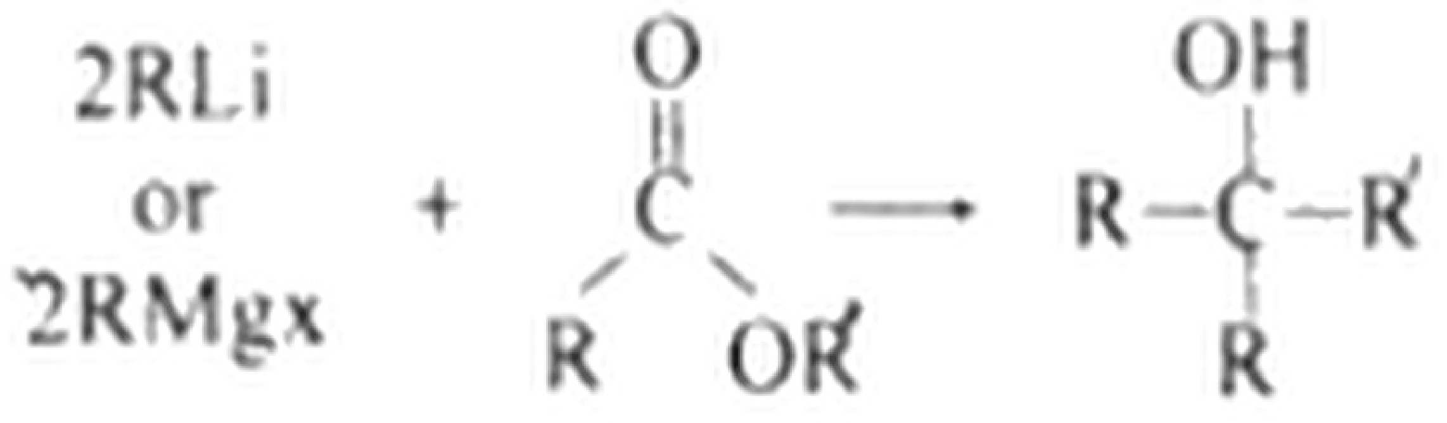
Carboxlic esters are reduced give 2 alcohols one form the alcohol portion of the ester and a I alcohol from the reduction of the carboxylate portion.

Esters are less reactive toward No than aldehydes or ketones.

They can only be reduced by $LiAlH_4$ and not by the less reactive $NaBH_4$.

Q13: Write down the reaction of RLi and Mgx with esters.

Answer



Carboxylic acid esters RC02R"react with 2 equivalents of organolithium or geignaed reagents to give tertiary alcohols. The tertiary alcohol that result contain 2 identical alhyl groups.

The reaction proceeds via a ketone intermediate which then reacts with second equivalent of the organometallic reagents. Since the Ketone is more reactive than the ester, the reaction cannot be used as a preparation of ketones. The mechanisms is an example of the reactive system type.

Q14: Write down the mechanism of the acids catalyzed hydrolysis of amides.

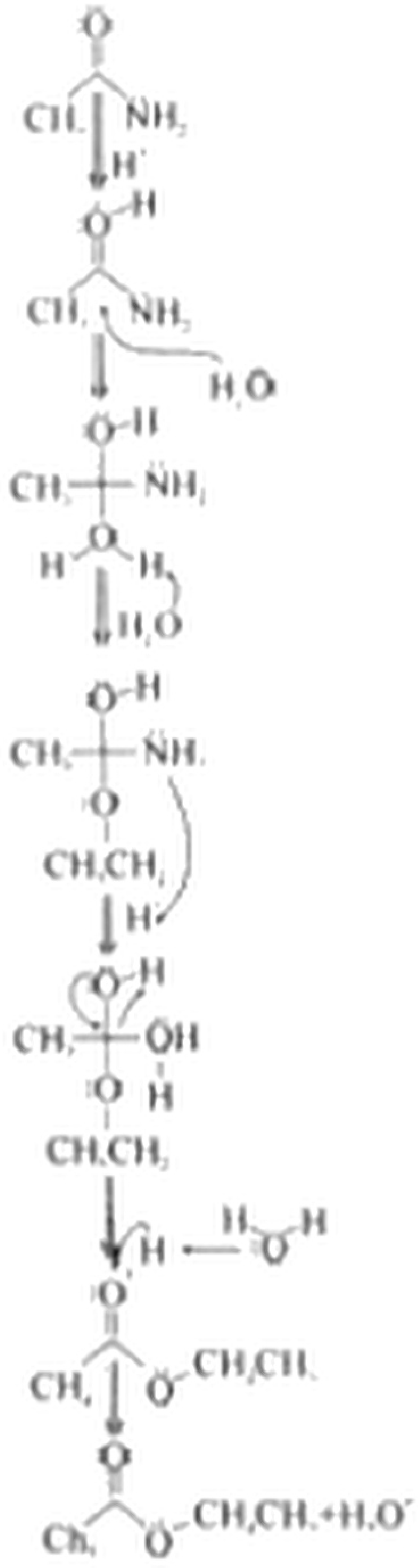
Answer

Step I

An acid/ base reaction sincere only have a weak nucleophite and a poor electrophile CHI NH, we need to activate the ester. Protonation of the amide carboxyl makes it more electrophitic.

Step 2

The H_2O O functions as the nucleophite attacking the electrophitic C in the C = O with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.



Step 3

An acid/ base reaction. Deprotonate the oxygen that came from the H_2O molecule.

Step 4

An acid base reaction needs to make the NH_2 leave but need to convert it into a good leaving group first by protonation

Step 5

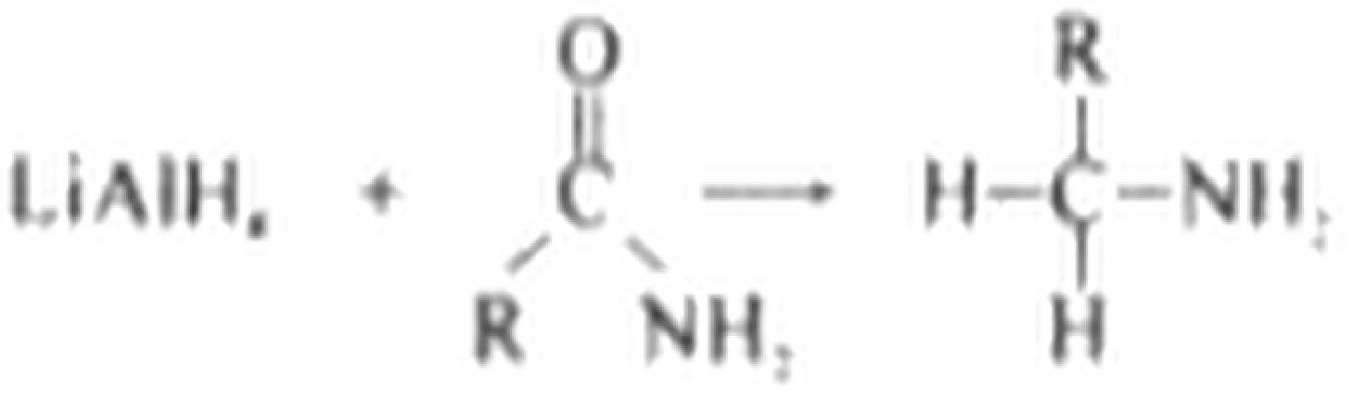
Use the electrons of an adjacent to help push out the leaving group a neutral ammonia molecule.

Step 6

An acid/ base reaction Deprotonation of the oxonium ion reacts the carboxyl in the carboxylic acid produced and regenerates the acid catalyst.

Q15: Write down the reduction of Amides.

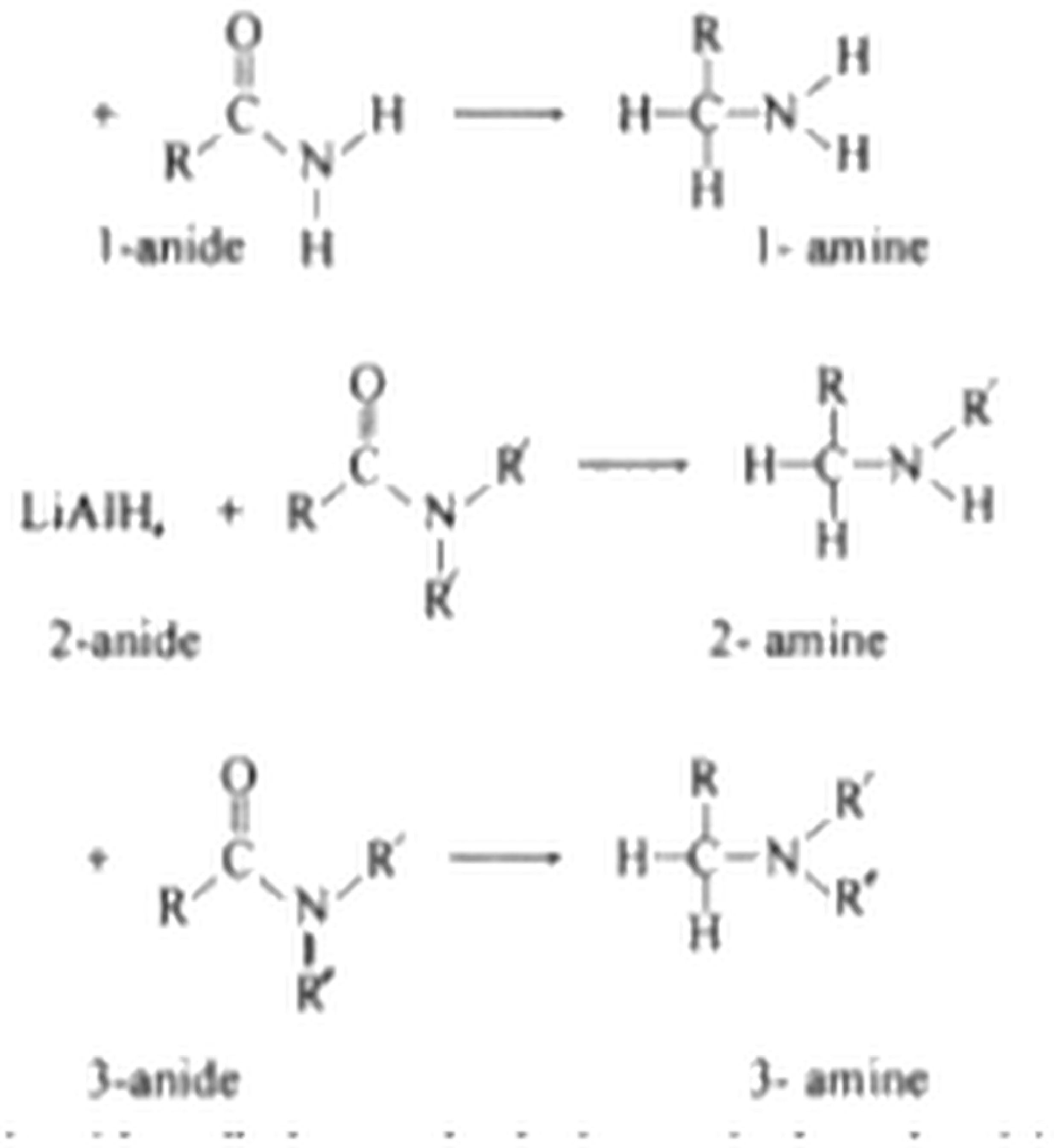
Answer



Amides $RCONR_2$ can be reduced to the amino RCH_3NR_2 by conversion of the C = O to - CH2.

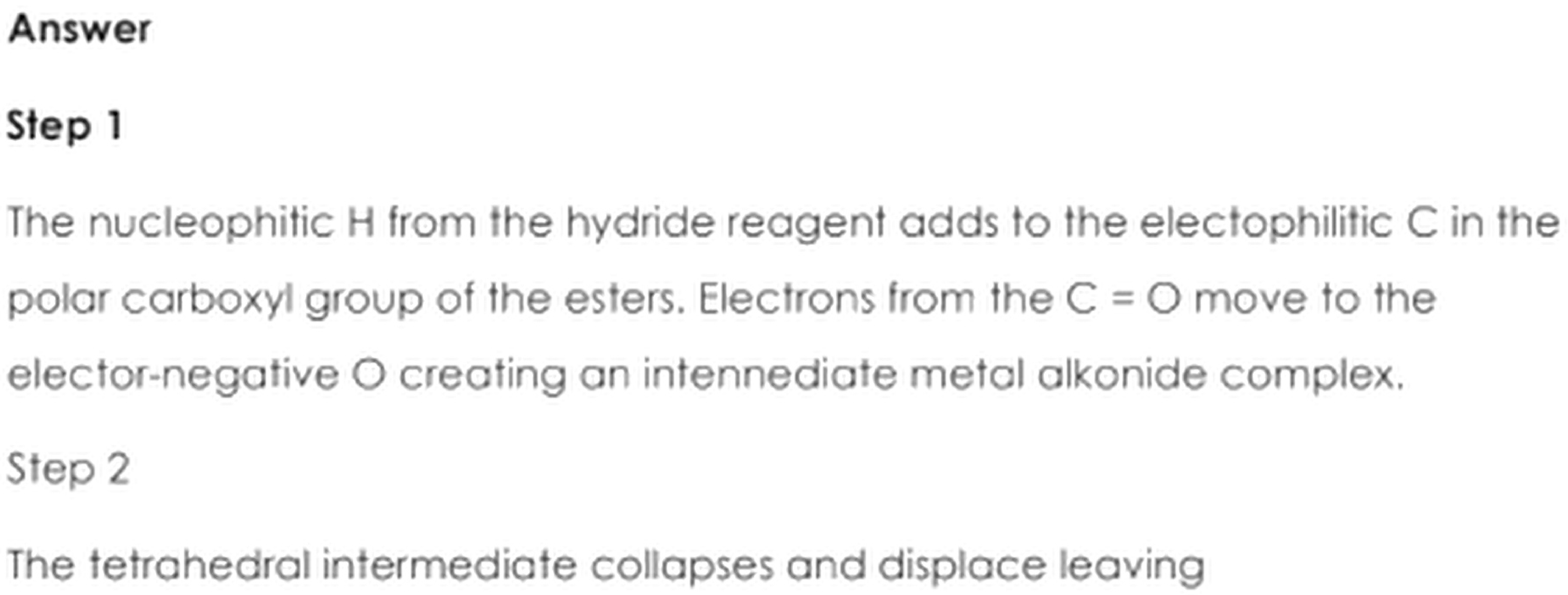
Amides can be reduced by $LiAlH_4$ but Not the less reactive $NaBH_4$.

This reaction is different to that of other C = O compounds which reduce to alcohols. The nature of the amine obtained depends on the substituents present on the original amide look at the N substituents in the following



R.R' or R" may be either alkyl or acyl substituents in the potential mechanisms with O System note that it is an O system that leaves. This is consistuent with O system being better leaving groups that the less electronegative N systems.

Q16: Write down the reaction of $LiAlH_4$ with an amide.



Answer

Step 1

The nucleophitic H from the hydride reagent adds to the electophilitic C in the polar carboxyl group of the esters. Electrons from the C = O move to the elector-negative O creating an intennediate metal alkonide complex.

Step 2

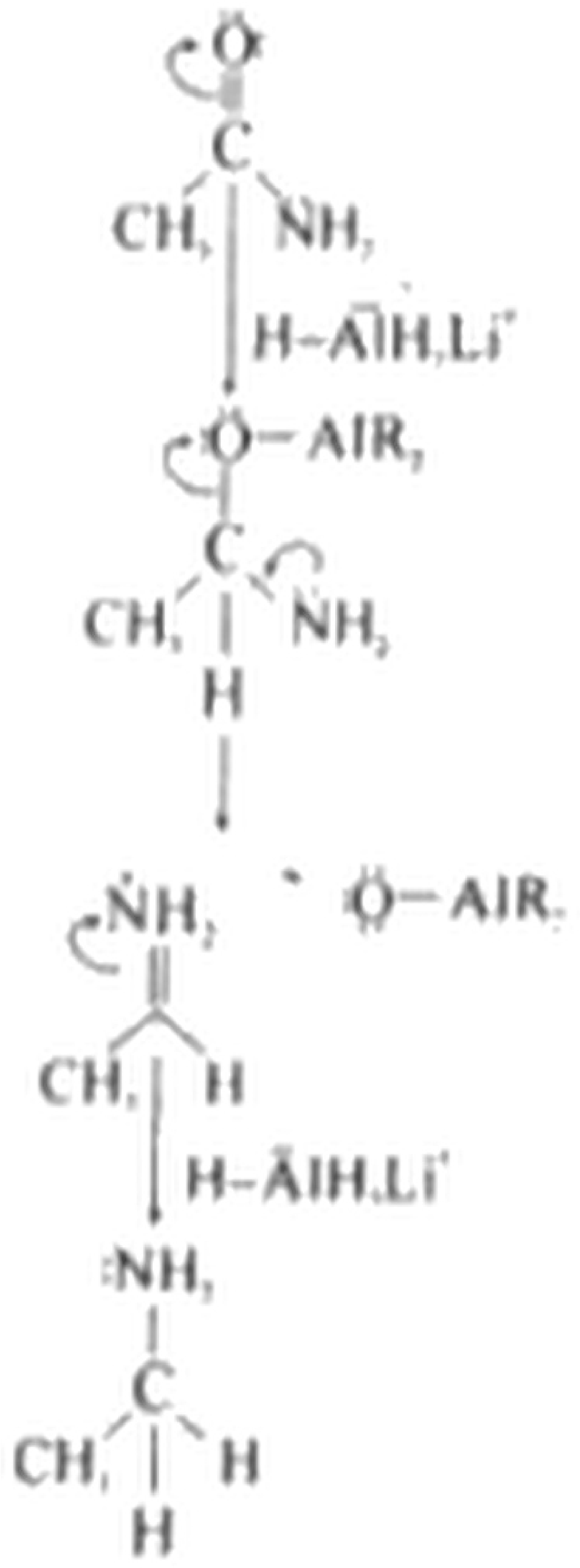
The tetrahedral intermediate collapses and displace leaving group thus produces a highly reactive imminium ion an

intemediate.

Step 3

Rapid reduction by the nucleophitic H from the hydride reagent as it adds to the electrophilic C en the iminium system

electrons from the C = N move to the cationic N neutralizingc the charge create amine product.



Q17: Write down the mechanisms of the acid catalyzed hydrolysis of nitrides.

Answer

Step 1

An acid/ base reaction.

Since we only a weak nucleophile so active the nitrile, protonation make it more electophitic.

Step 2

The water O functions as the nucleophile attacking the electrophilic C in the CN with the electons moving towards the positive center.

Step 3

An acid/ base reaction. Deprotonate the oxygen that came from the H20 molecule. The remaining task is a tautomerization are N and O centers.

Step 4

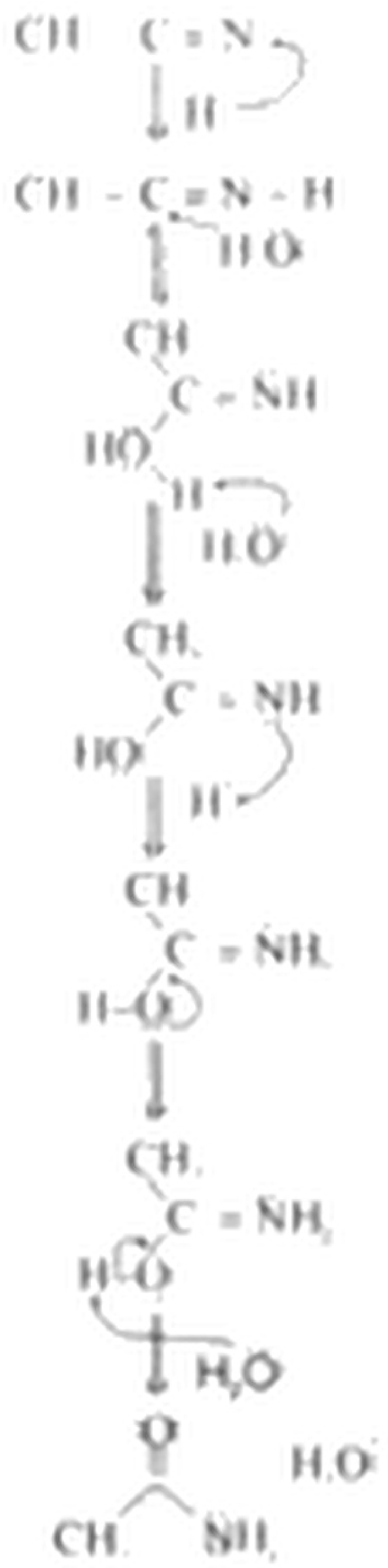
An acid/ base reaction. Protonate the N gives us the — NH_2 we need.

Step 5

Use the electrons of an adjacent O to the neutralise the positive at the N and from the bond in the C = O.

Step 6

An acid/ base reaction/ Deportonation of the oxonium ion reveals the carboxyli in the amide intermediate half way to the acid.



Reduction of Nitricles

$$\underset{\text{Nitrile}}{R-C\equiv N:} \xrightarrow{[R]} \underset{\text{Primay amine}}{R-CH_2\ddot{N}H_2}$$

Reaction types: Nucleophetic Addition.

The nitrile RC N give the 1^{0} amine by conversion of the C N to CH2 — NH2

Nitriles can be reduced by LiAlH4 but Not the less reactive NaBH4. Typical reagents LiAlH4. Typical reagents LiAlH4 ether solvent followed by aqueous work up. Catalytic hydrogenation (H/ catalyst) can also be used giving the same product. R may bc either allcyl or acyl substituents.

Q18: Write down reaction of RMgx with a nitrile?

Answer

Step 1

The nucleophilic C in the organometallic reagents adds to the electrophilic C in the polar nitride group. Electrons from the C N more to the electronegative N creating and intermediate imine salt complex.

Step 2

An acid/ base reaction. On addition of aqueous acid, the intermediate salt protonates giving the imine.

Step 3

An acid/ base reaction. Ammines undergo nucleophilic addition but require activation by protonation.

Step 4

Now the Nucleophilic O of a water molecule H-oö attacks the electrophilic C with the P bond breaking to neutralize the change on then.

Step 5

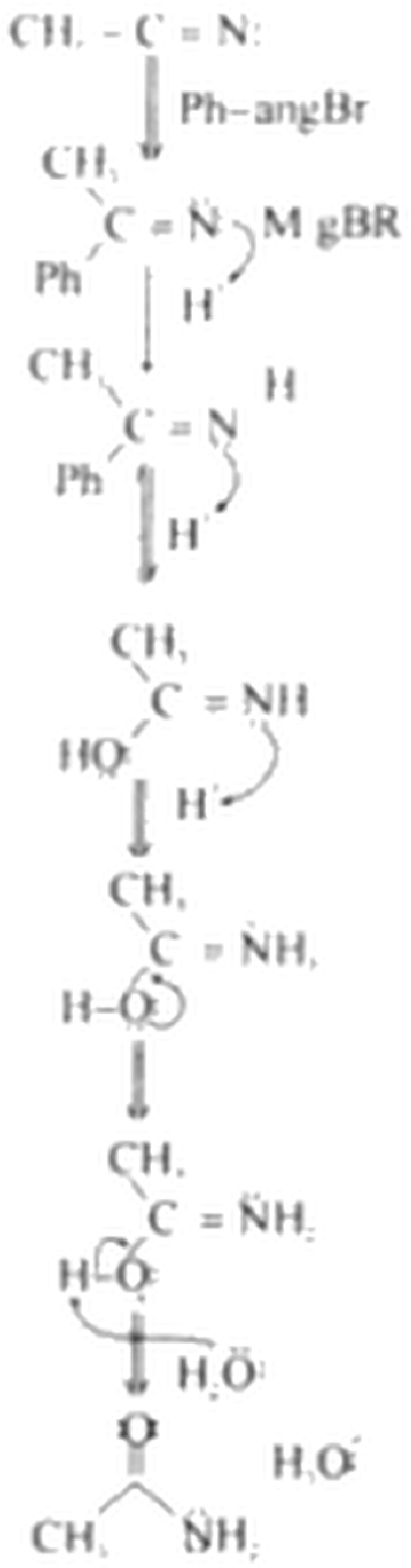
An acid/ base reaction Deprotonate the O from the H20 molecule to neutralize the positive charge.

Step 6

An acid/ -base reaction. Before the N system leaves, it needs to be made into a better leaving group by protonation.

Step 7

Use the electron on the O in order to push out the N leaving group, a neutral molecule of ammonia.

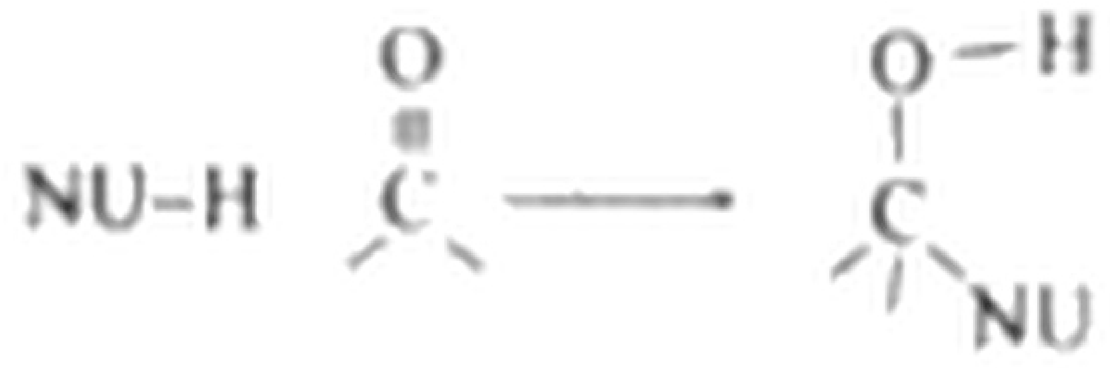


Q19: Write down the reaction of Nitriles, Hydrolysis Reduction and reaction with Grignard's regard.

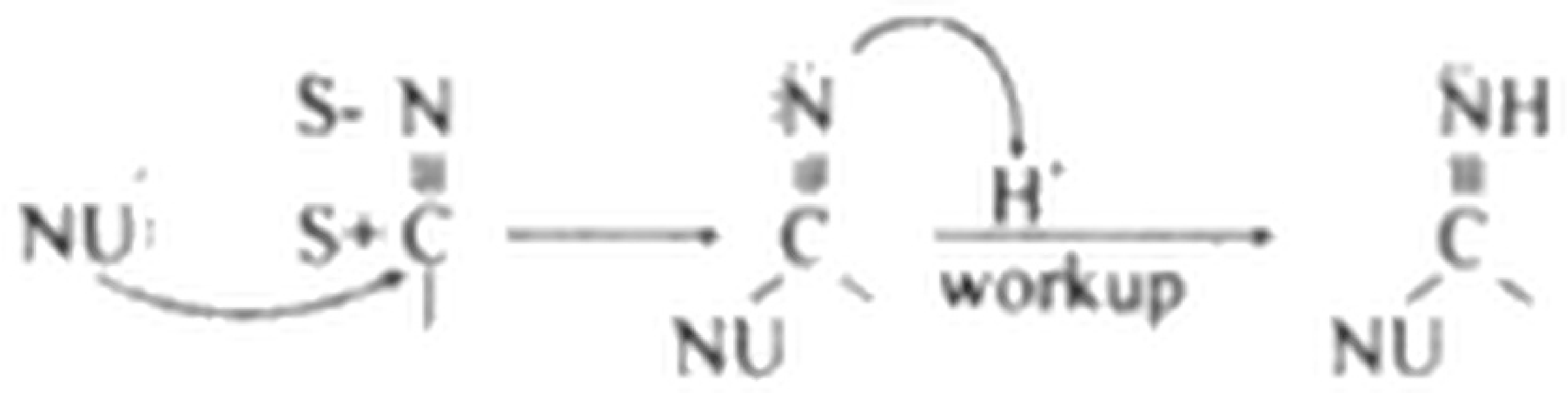
Answer

Nitriles typically undergo nucleophilic addition to give product that often undergo a further reaction.

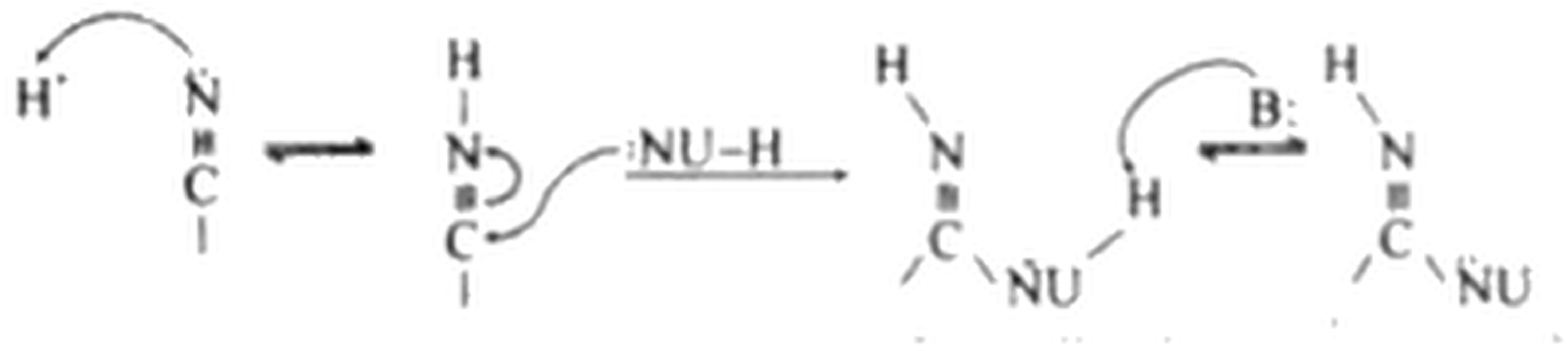
The chemistry of the nitrile functioned group C = O of aldehydes and ketones.



Strong Nucleophilic aniomic add directly to the C N to forman intermediate imine salt that protonates. .



Example are RMgx, RLi, RC CM, LiAlH4. Weaker nucleophiles neutral requires that the C N be activated prior to attack of the No. This can be done increasing an acid catalyst which protonates on the Lewis basic N and make the system more electrophilic.



Example are H_2O, ROH. The protonation of a nitile gives a structure that can be reaction in another resonance from that results the electrophilic character of the C since it is a carbocation.