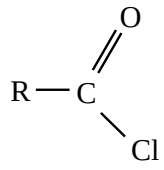
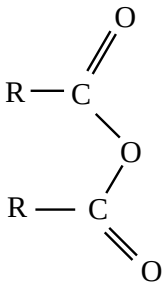
Functional derivatives of carboxylic acids

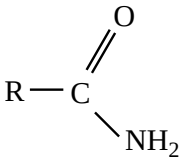
Closely related to carboxylic acids and to each other are a number of chemical families known as fucntional derivatives of carboxylic acids : Acid halide, anhydride, amide and esters. These derivatives are compounds in which the OH of the carboxylic acid has been replaced by X(Cl, Br, I), OOCR, NH_2 or OR.



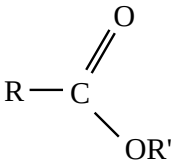
Acid chloride



Acid hydride

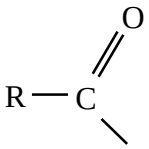


Acid amide



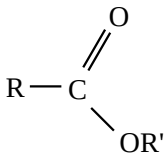
Ester

The all contain the group



1. Esters

They have a general formula



Examples

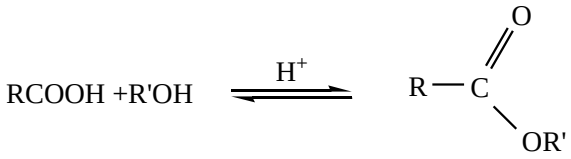
HCO_2CH_3	Methylmethanoate
$CH_3COOCH_2CH_3$	Ethylethanoate
$CH_3CH_2COOCH_2CH_3$	Ethylpropanoate

Physical properties

(i) Insoluble in water but soluble in organic solvent
(ii) They are neutral liquids with pleasant smell
(iii) They have low boiling points compared to carboxylic acids of comparable molecular mass.

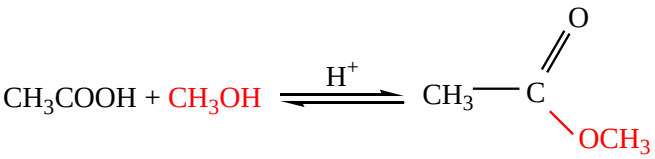
Preparation

(a) By reacting carboxylic acids with alcohol in the presence of mineral acids



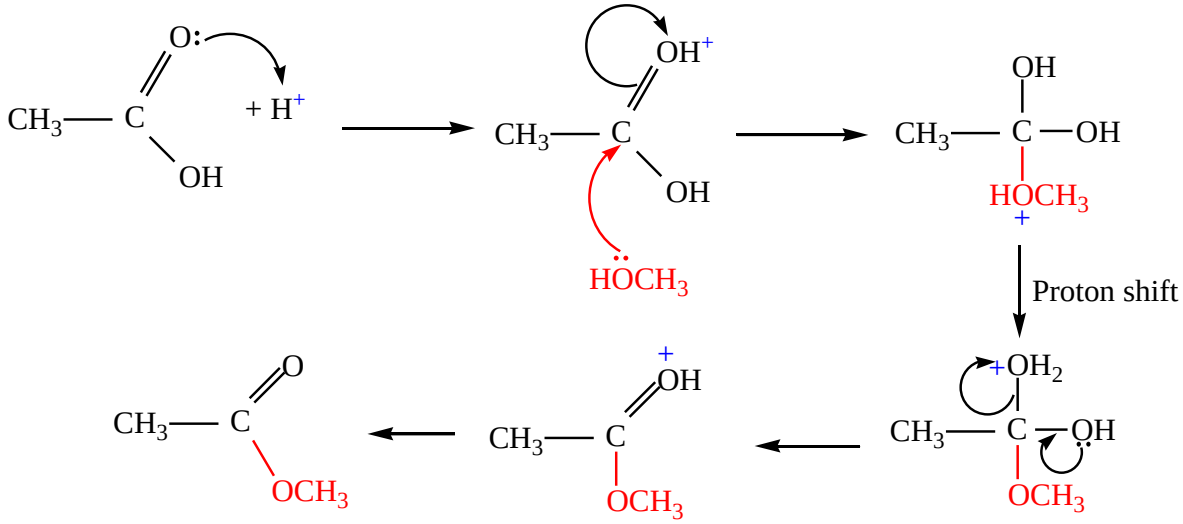
Ester

Example

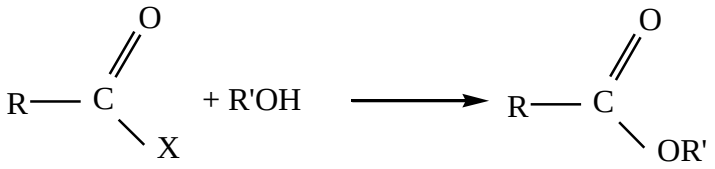


Methylethanoate

Mechanism

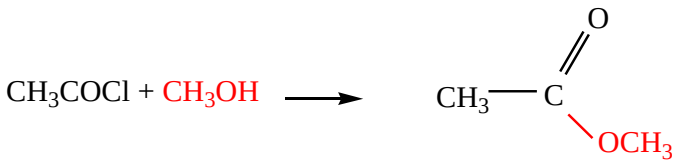


(b) reaction of alcohols with acid halides



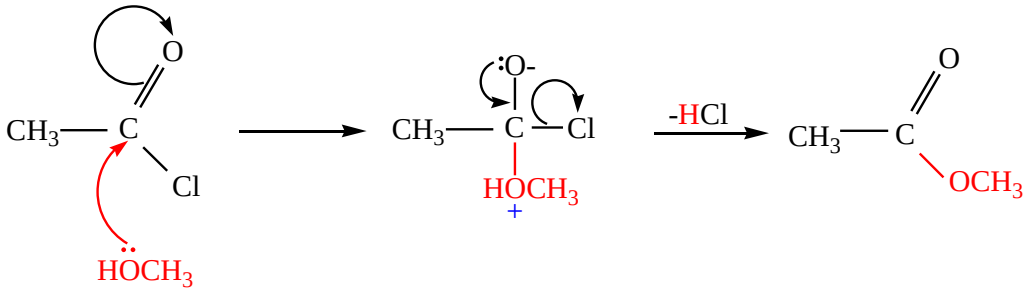
where X = Cl, Br, or I

Example

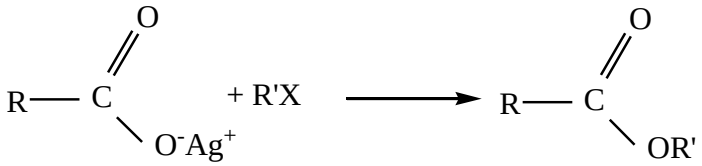


Methylethanoate

Mechanism



(c) By reacting silver salts of carboxylic acid with alkyl halide

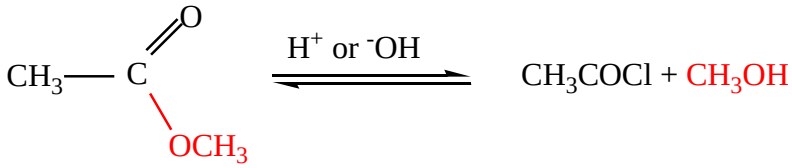


Chemical properties

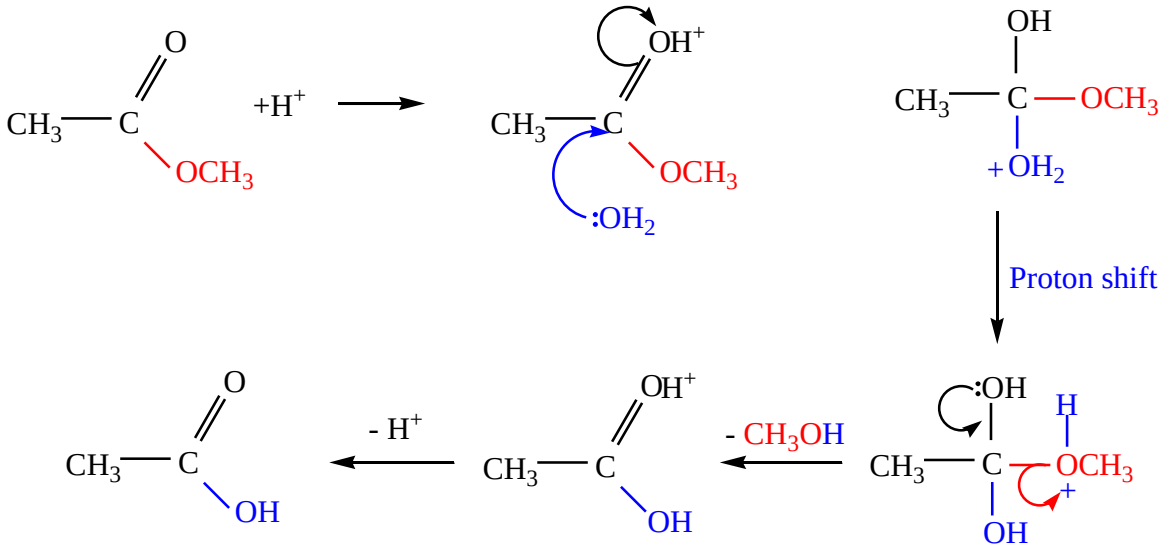
1. Hydrolysis

   Esters are hydrolyzed by mineral acids or alkalis

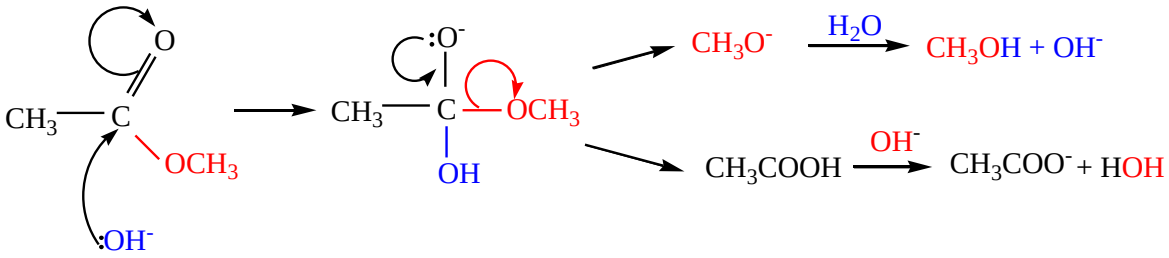
   Example



   Mechanism (acid catalyzed)

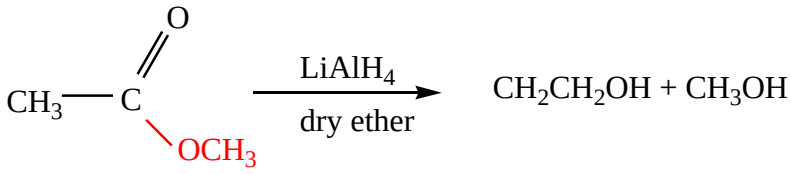


(ii) base catalyzed

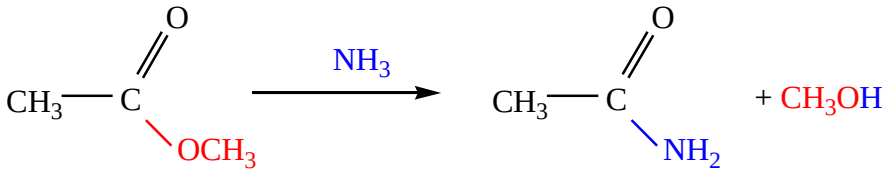


2. Esters are reduced by $LiAlH_4$ to alcohols

   Examples



3. Esters react with amides to form acid amide

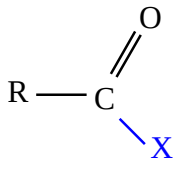


Uses of esters

In formation of perfumes

Acid halides

These have a general formula



where x = Cl, Br or I

Examples

C_6H_5COCl Benzoylchloride

CH_3COBr Ethanoylbromide

CH_3CH_2COI Propanoyliodide

Preparation

By reacting carboxylic acid with phosphorus halide or thionylchloride

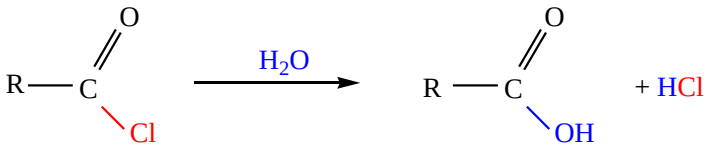
Examples

$CH_3COOH + PBr_3 \longrightarrow CH_3COBr$

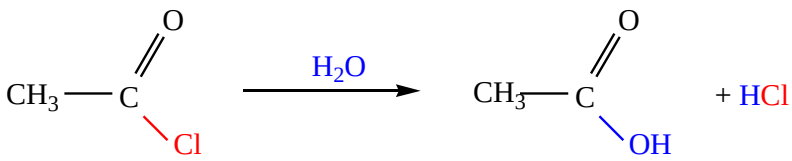
$CH_3CH_2CO_2H + SOCl_2 \longrightarrow CH_3CH_2COCl$

Chemical properties

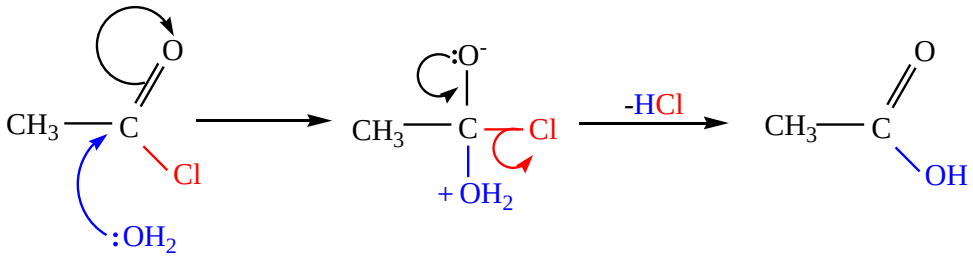
1. Acid halides are hydrolyzed by water to carboxylic acids



Example



Mechanism

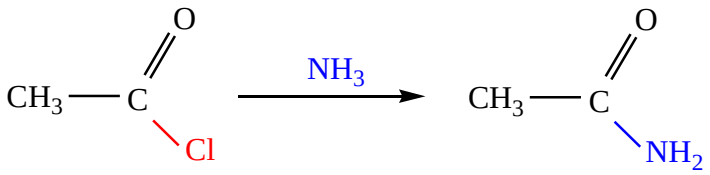


When ethanoyl chloride is exposed to moist air white fumes are seen due to the production of HCl.

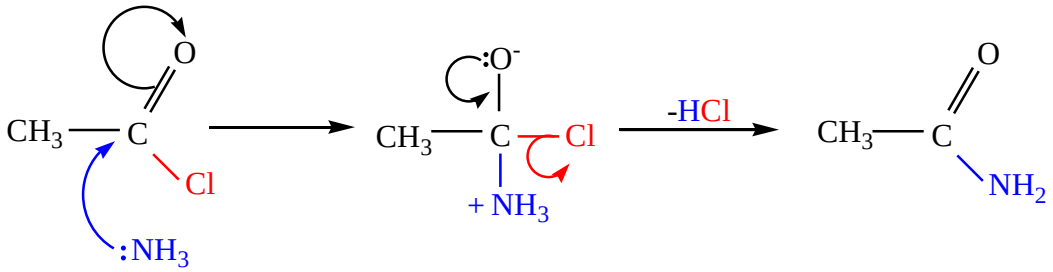
i.e. $CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$

2. Acid halides react with ammonia and amines to produce amides

Example

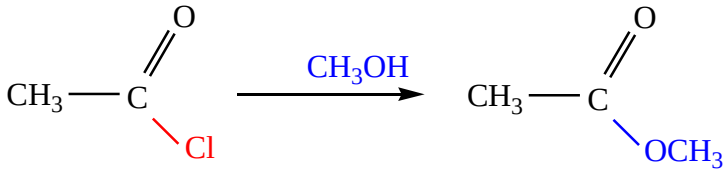


Mechanism

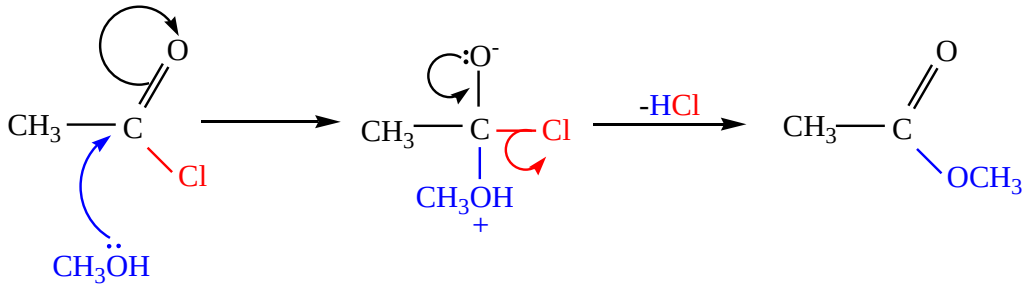


3. Acid halide react with alcohols to form esters

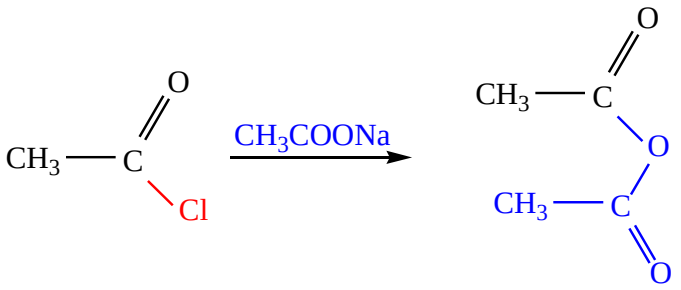
Example



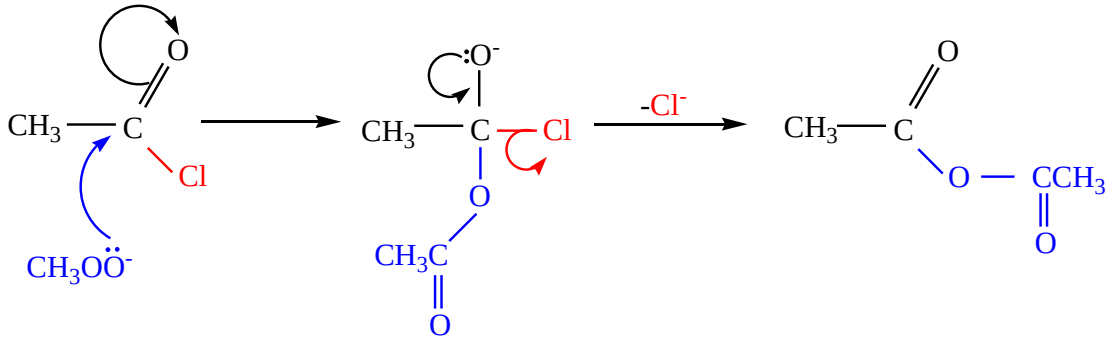
Mechanism



4. Acid halides react with anhydrous sodium salt of carboxylic acid to form acid anhydride
   Example

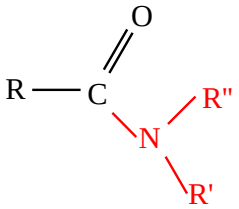


Mechanism



Acid amide

These have a general formula



where R, R' and R" are hydrogen atoms or alkyl groups

Examples

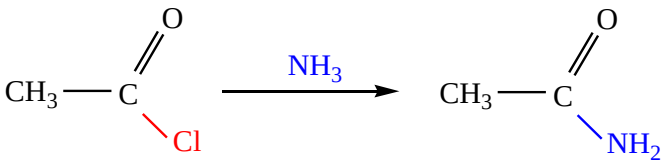
CH_3CONH_2	Ethanamide
$CH_3CH_2CONH_2$	Propanamide

Physical properties

- They are white crystalline salts except methanamide
- Lower members are soluble in water but the solubility decreases with increasing molecular mass.
- They have relatively high boiling points due to formation of intermolecular hydrogen bonds

Preparation

1. By reaction of ammonia with ester, acid anhydride or acid halides
   Examples

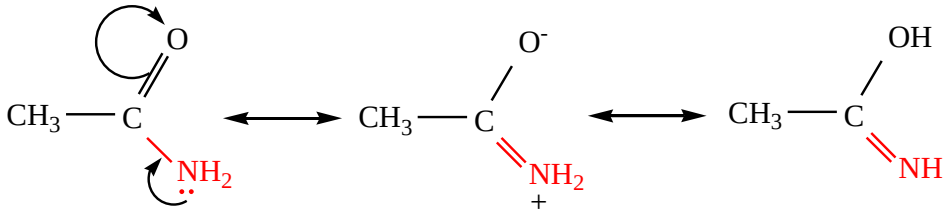


2. Dehydration of carboxylic acids with ammonium carbonate

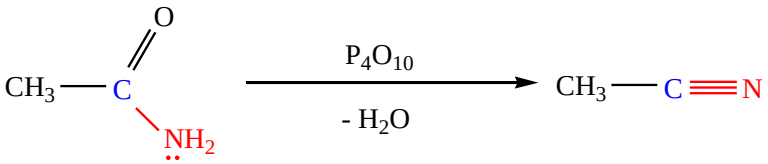
$$CH_3COOH + (NH_4)_2CO_3 \longrightarrow CH_3CONH_2 + H_2O + CO_2$$

Chemical properties

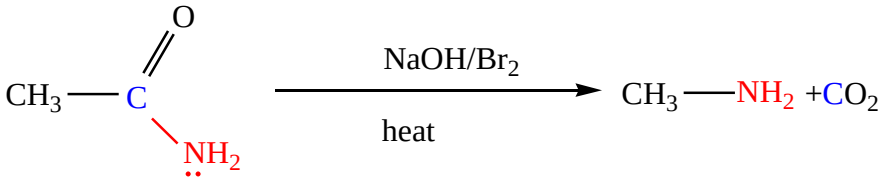
1. They are weaker bases compared to amines and are neutral to litmus. The do not form salts with acids as amines do because their lone pair of electron on the nitrogen atom is delocalized.



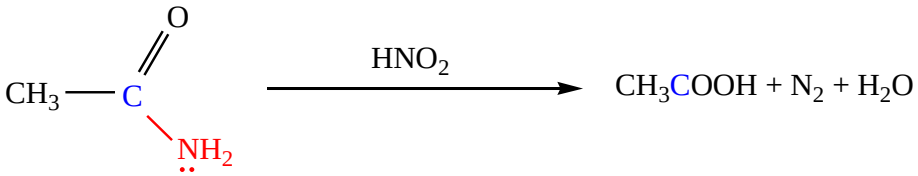
2. Amides form nitriles when distilled over phosphorus pentoxide, P_4O_{10}.



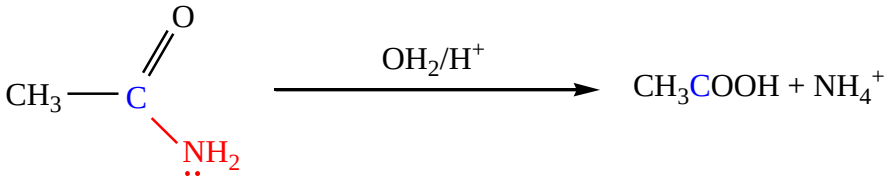
3. Amides react with hot alkaline bromine solution to give amines

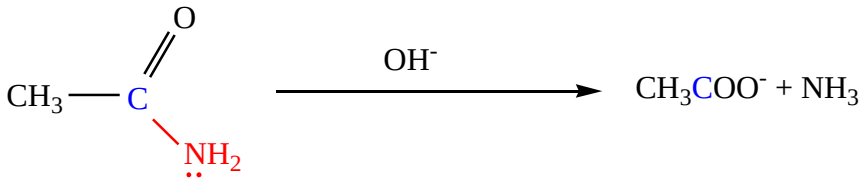


4. Like amines, amides react with nitrous acid liberating nitrogen



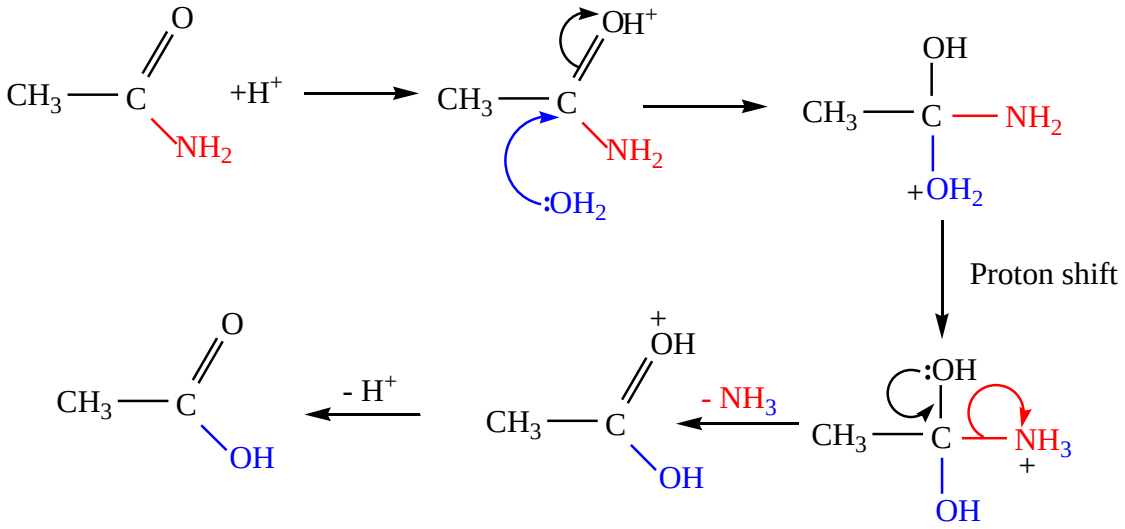
5. Amides are hydrolyzed with mineral acid or alkais
   Example





Mechanism

(a) Acid catalyzed



Thank you