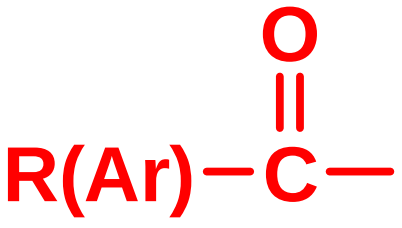
Chapter 11
Derivatives of carboxylic acid

Sec 1 Nomenclature

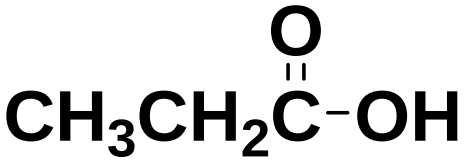
Sec 2 Structure

Sec 3 Chemical Properties

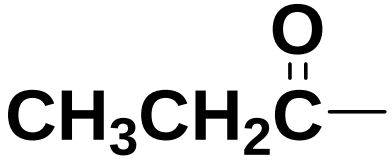
The carbonyl group along with the attached carbon chain (H, R, Ar) is called an *acyl group* (酰基).



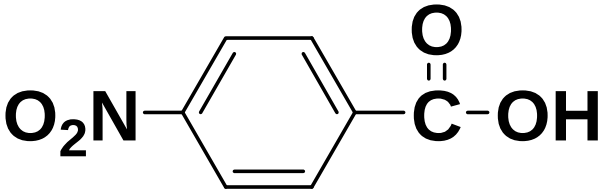
Names of acyl group derive from corresponding carboxylic acid. Drop the "*-oic acid*" ending of the carboxylic acid, and replace it with " *-oyl*".



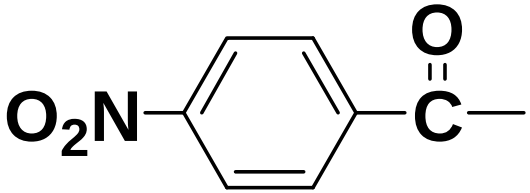
Propanoic acid



Propanoyl (丙酰基)



4-nitrobenzoic acid

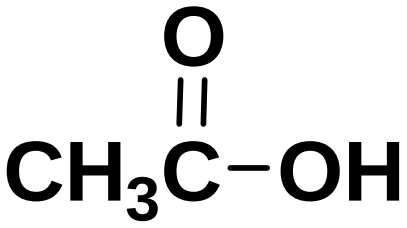


4-nitrobenzoyl (4-硝基苯甲酰)

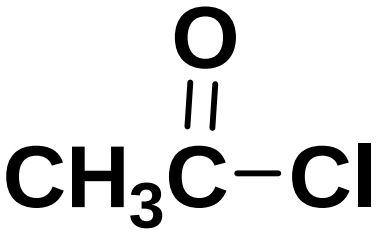
Sec 1 Nomenclature

Ⅰ. Acyl halides　　酰卤：酰基名＋卤素名

Acyl halides are named by replacing the *-ic acid* ending of the carboxylic acid with *-yl* halides.



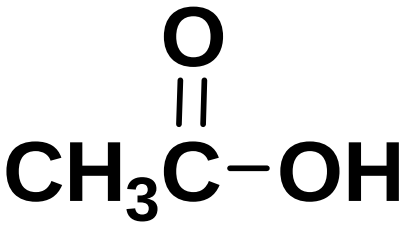
Acetic acid
Ethanoic acid



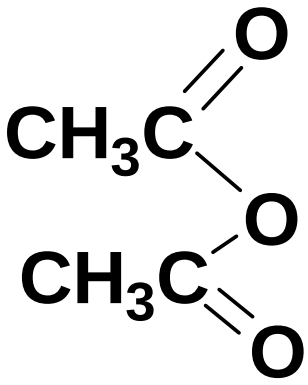
Acetyl chloride　乙酰氯
Ethanoyl chloride

Ⅱ. Acid Anhydrides

- **Symmetrical acid anhydrides are named by replacing the *acid* ending of the carboxylic acid with the word *anhydride*. 单酐：羧酸名＋酐**



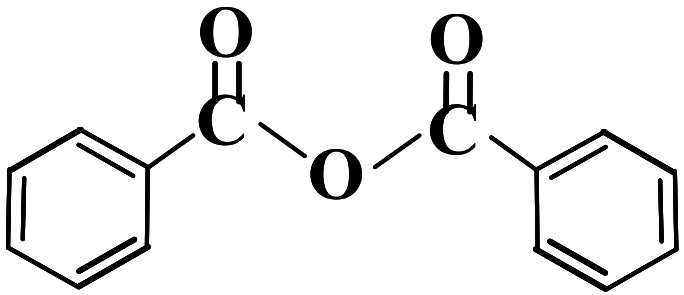
Acetic acid



Ethanoic anhydride

Acetic anhydride

乙酸酐

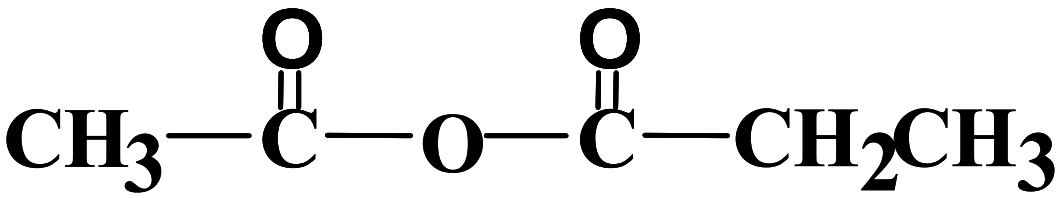


Benzoic anhydride

苯甲酸酐

- **Unsymmetrical anhydrides are named by arranging the names of the two parent carboxylic acids followed by the word anhydride.**

混酐：简单羧酸名＋复杂羧酸名＋酐

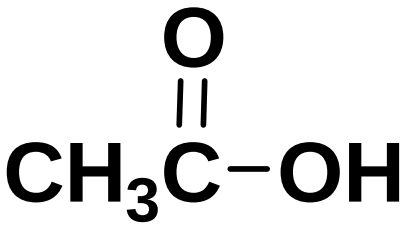


Ethanoic propanoic anhydride

Acetic propanoic anhydride

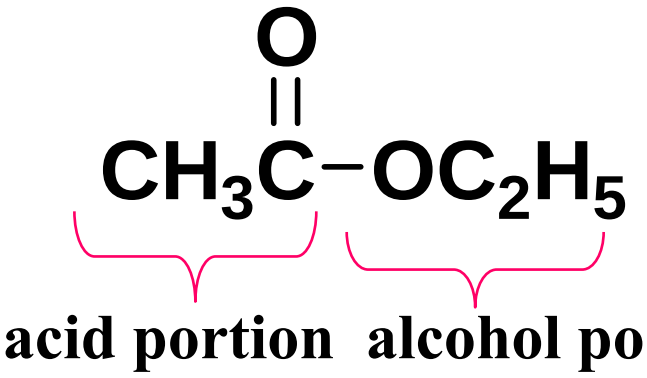
乙丙酐，乙酸丙酸酐

III. Esters



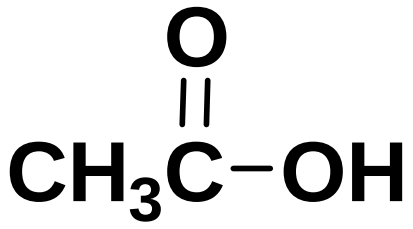
Ethanoic acid
Acetic acid

一元醇的酯：某酸某(醇)酯

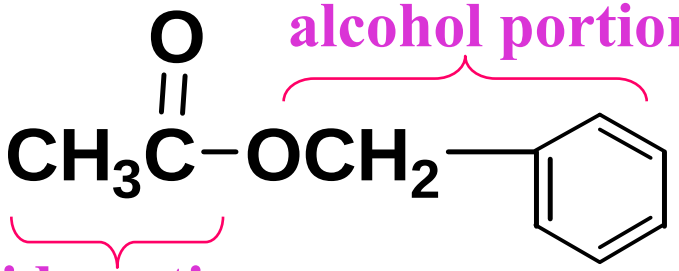


Ethyl ethanoate
Ethyl acetate

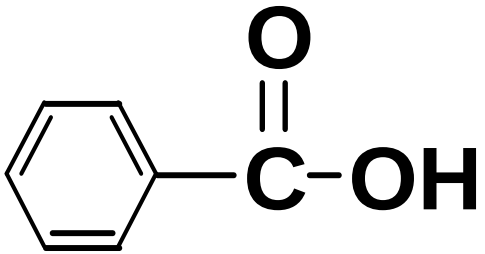
乙酸乙酯



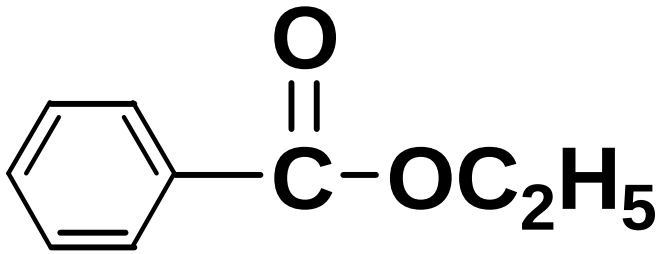
Acetic acid



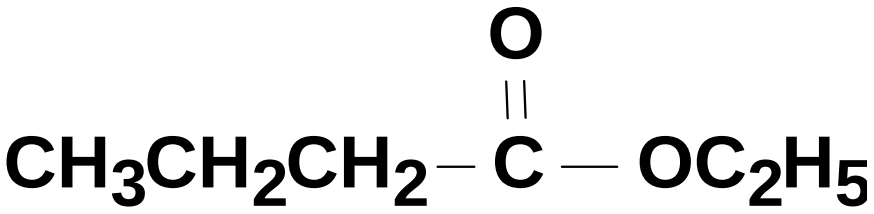
Benzyl ethanoate (Benzyl acetate)



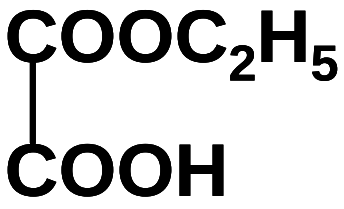
Benzoic acid



Ethyl benzoate

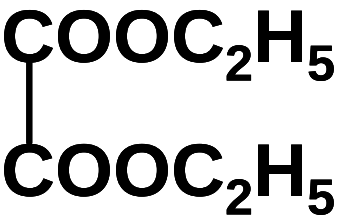


Ethyl butanoate
Ethyl butyrate



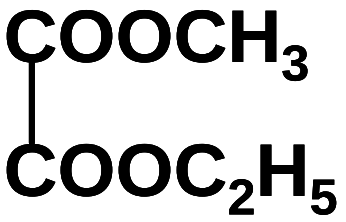
Ethyl hydrogen ethanedioate

(乙二酸氢乙酯)



Diethyl ethanedioate

(乙二酸二乙酯)



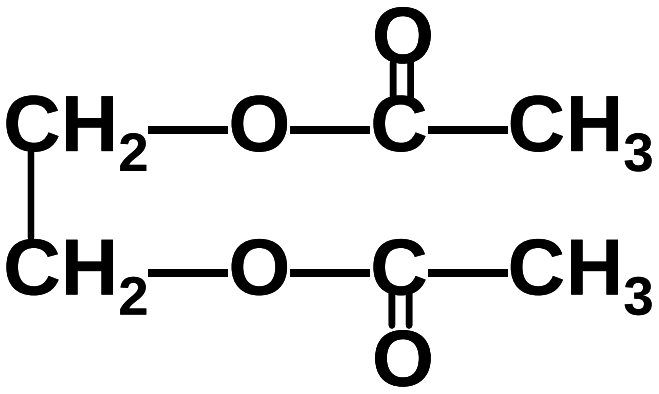
Ethyl methyl ethanedioate

(乙二酸甲乙酯)

Ethyl methyl phthalate

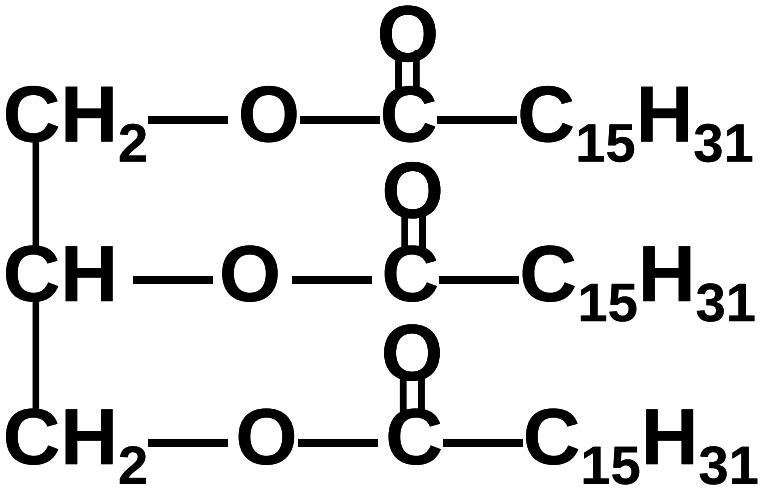
邻-苯二甲酸甲乙酯

- 一元醇的酯：某酸某(醇)酯
- 多元醇的酯：某醇某酸酯



Ethylene diacetate

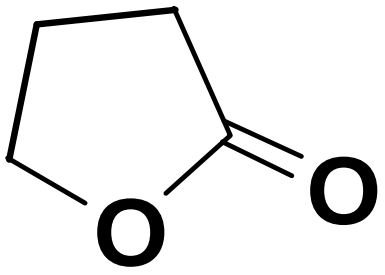
乙二醇二乙酸酯



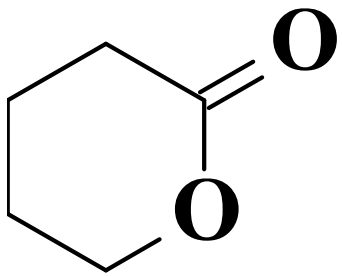
Glyceryl tripalmitate

丙三醇三软脂酸酯

- **Cyclic esters are called lactones. A Greek letter identifies the location of the alkyl oxygen relative to the carbonyl group.**



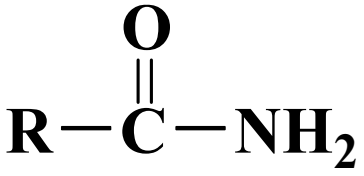
γ -Butanoic lactone
(γ -Butanolactone)
γ –丁内酯



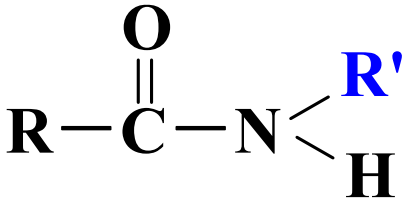
δ -Pentanoic lactone
(δ -Pentanolactone)
δ –戊内酯

Ⅳ. Amides

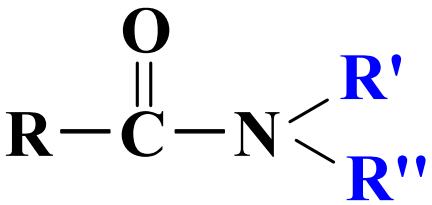
Amides contain three kinds of structures.



Primary amide

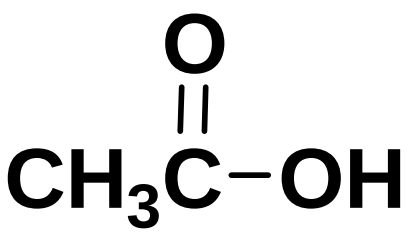


Secondary amide

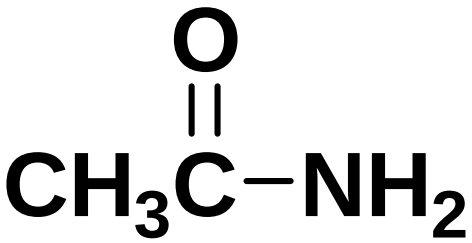


Tertiary amide

- **For 1° amides, the name of the related acid is used first and the -o*ic acid (or ic acid)* ending is replaced by -amide.** 伯酰胺：—— 某酰胺

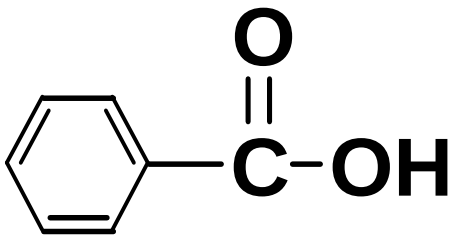


Ethanoic acid (Acetic acid)

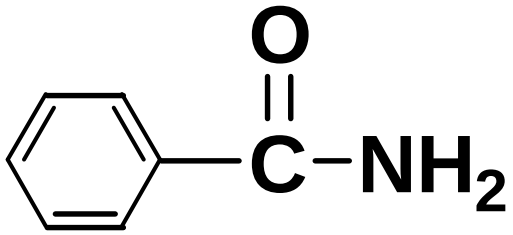


Ethanamide (Acetamide)

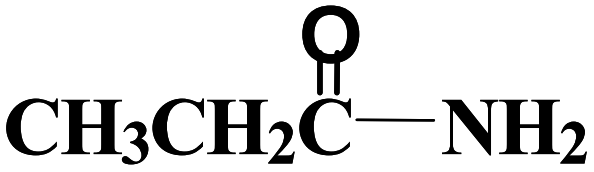
乙酰胺



Benzoic acid

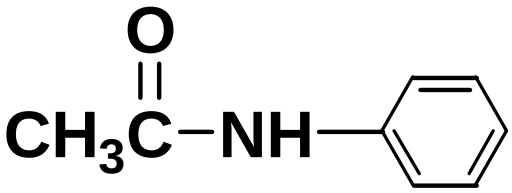


Benzamide

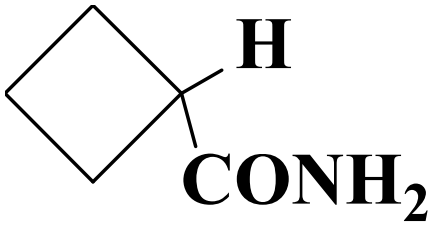


Propanamide

- **Amide of $PhNH_2$ are named as anilides.**



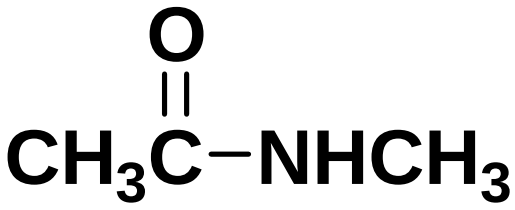
Acetanilide 乙酰苯胺
(Acetyl aniline)



Cyclobutanecarboxamide

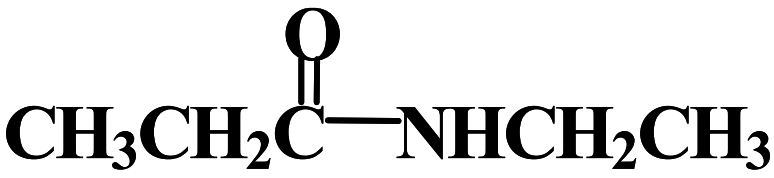
- **For 2° and 3° amides, having alkyl substituents on the nitrogen atom, the substituent(s) are identified by adding the prefix *N*- and the name of the substituent.**

仲酰胺：N-某基某酰胺



***N*-Methylacetamide**

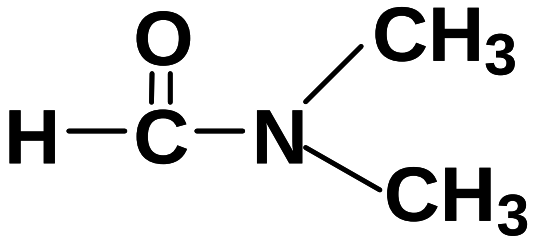
N-甲基乙酰胺



***N*-Ethylpropanamide**

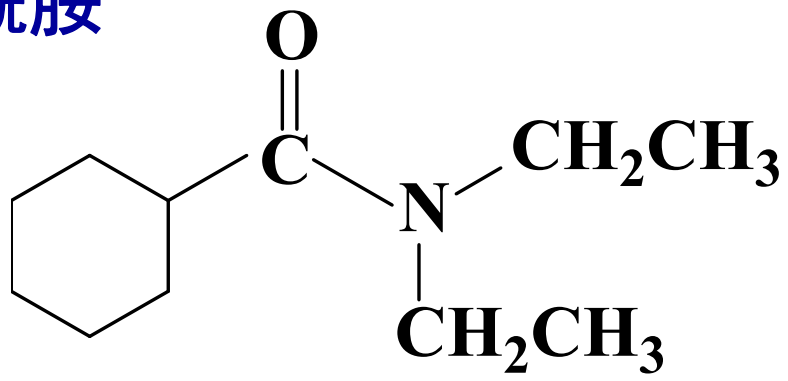
N-乙基丙酰胺

叔酰胺： ***N*,*N*-二某基某酰胺;**
***N*-某基-*N*-某基某酰胺**



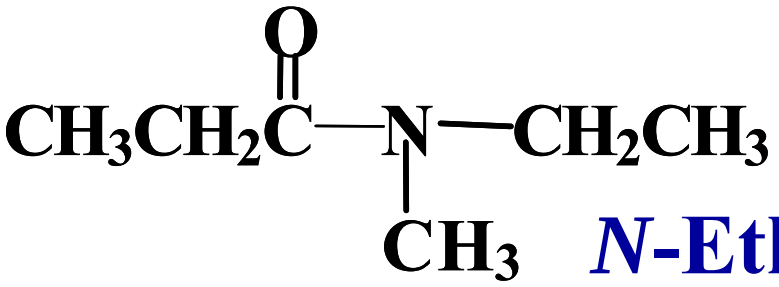
***N*,*N*-Dimethylformamide**

(DMF, N,N-二甲基甲酰胺)



***N*,*N*-Diethylcyclo-hexanecarboxamide**

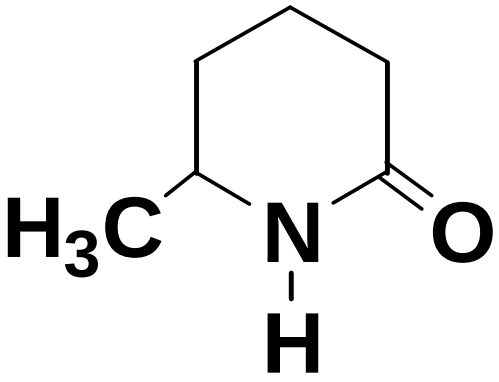
(*N*,*N*-二乙基环己烷甲酰胺)



***N*-Ethyl-*N*-methylpropanamide**

(N-甲基-N-乙基丙酰胺)

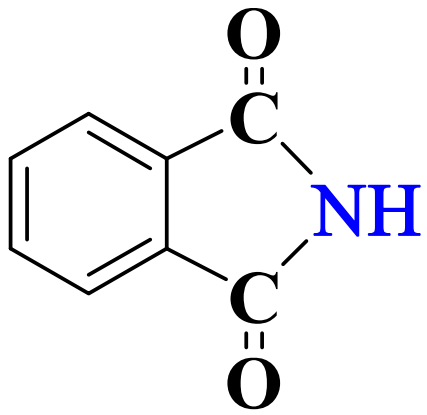
- Cyclic amides are called **lactams** (内酰胺).



δ -Hexanolactam

δ－己内酰胺

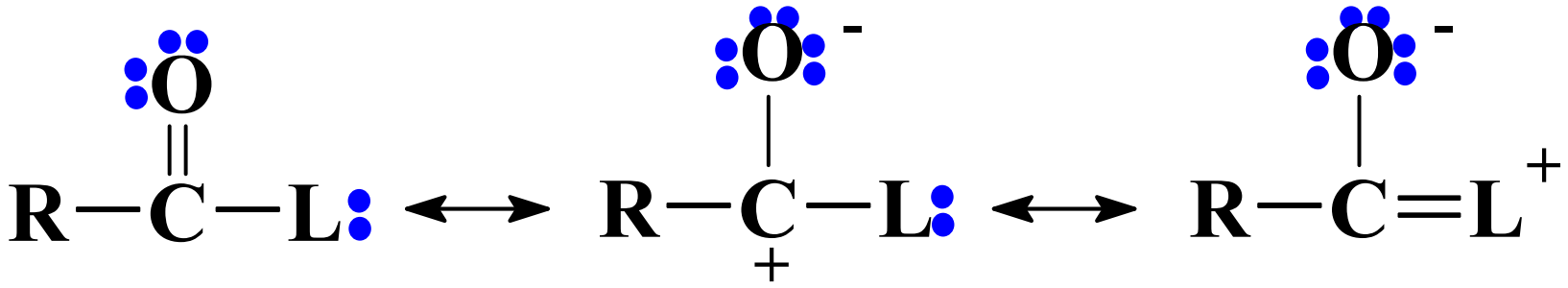
- **Imides** (亚酰胺) are nitrogen analogs of anhydrides.

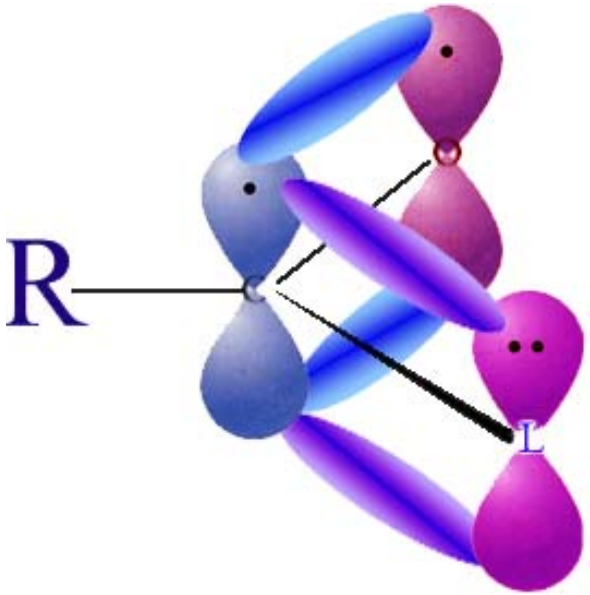


Phthalimide

邻苯二甲酰亚胺

Sec 2 Structure

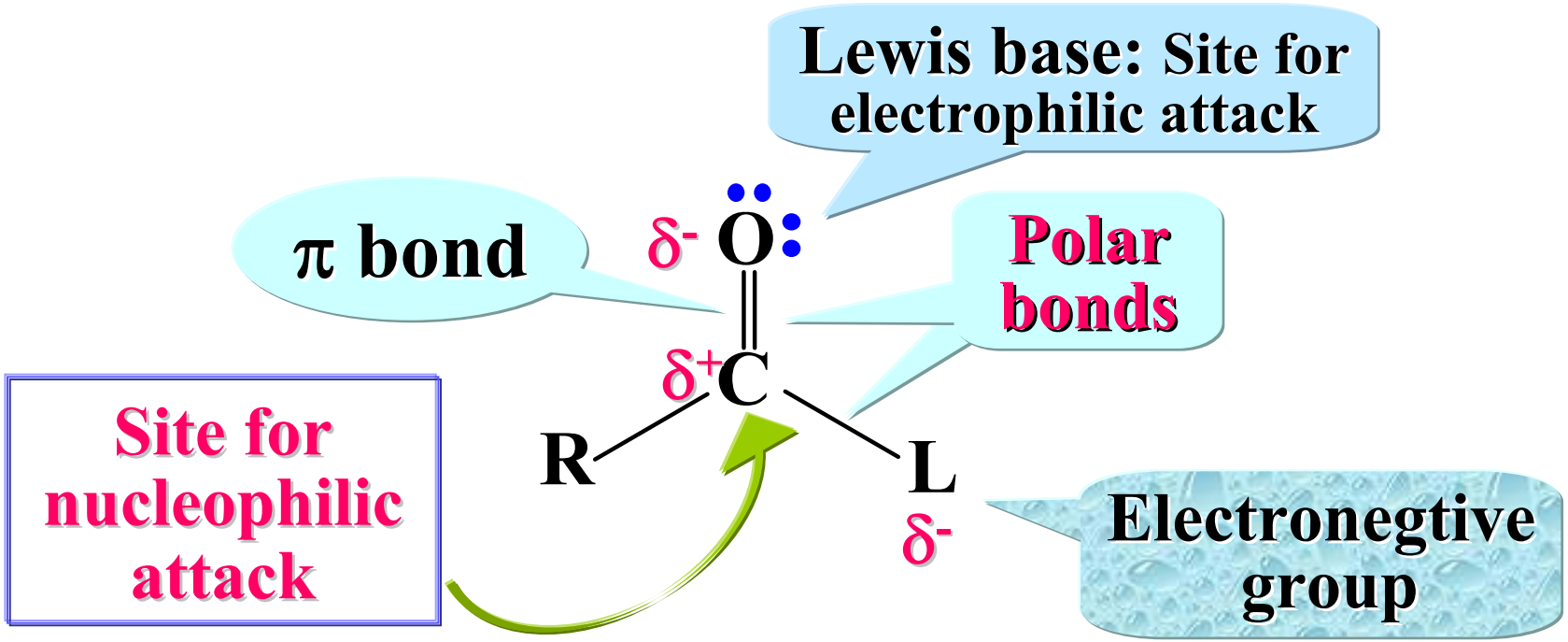




L =

- -Cl, Br — Acyl halide
- -OCOR — Anhydride
- -OR — Ester
- $-NH_2$,$-NHR$,$-NR_2$ — Amide

Sec 3 Chemical Properties

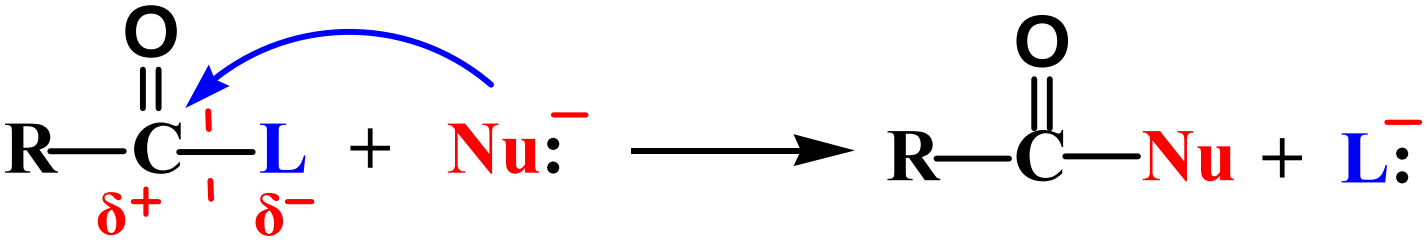


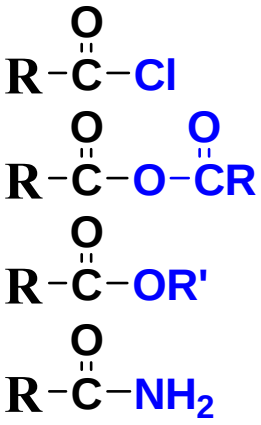
1. Nucleophilic acyl substitution

2. Reactions about α -hydrogen & α -C:

"*Claisen Condensation*"

Ⅰ. Nucleophilic Acyl Substitution Reaction





H:OH

H:OR

$H:NH_2$

H:NHR'

$H:NR_2$

Result:

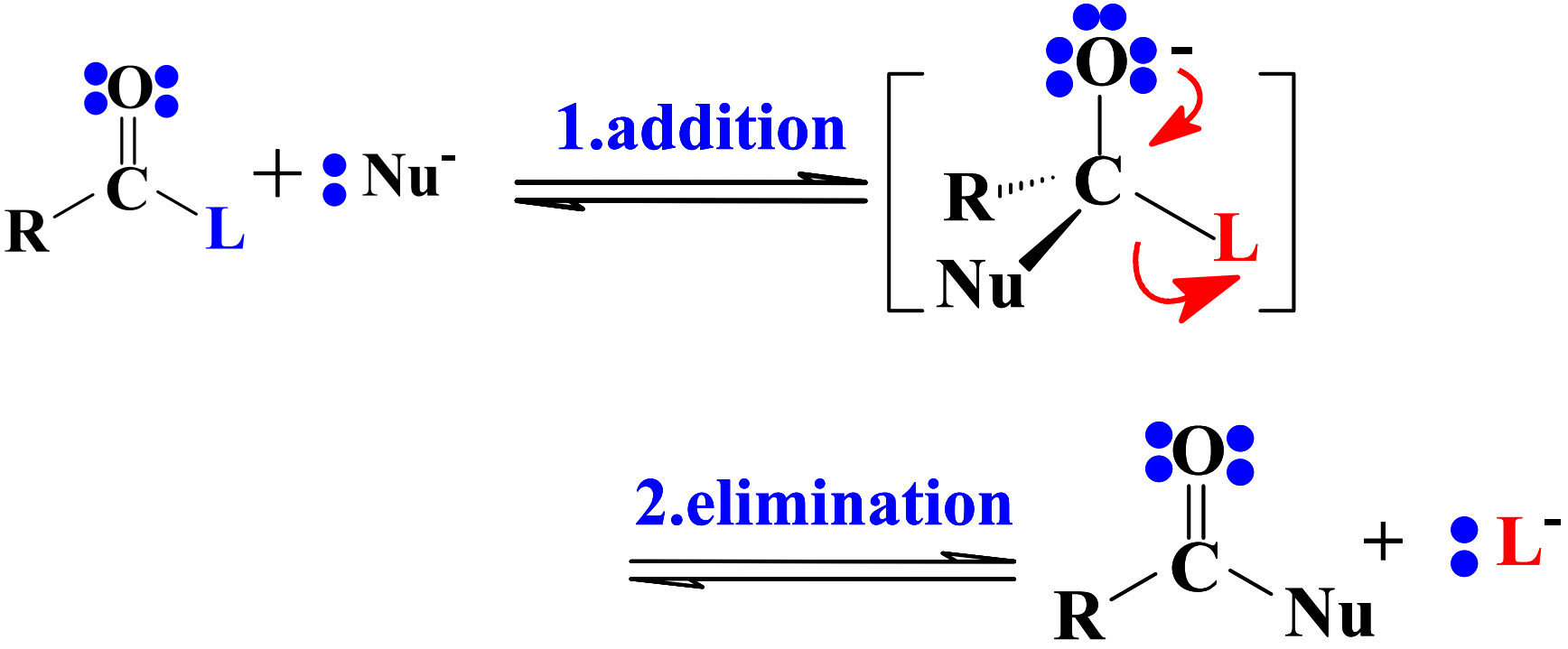
一种羧酸衍生物

↓

另一种羧酸衍生物(或羧酸)

The Reaction Mechanism : Two steps

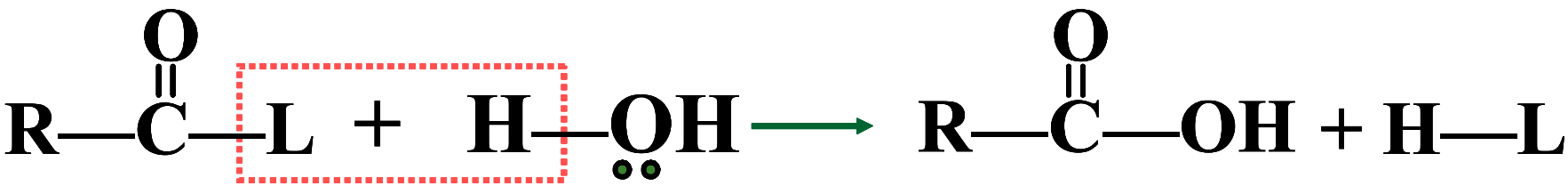
Simulating: mechanism of nucleophilic acyl substitution

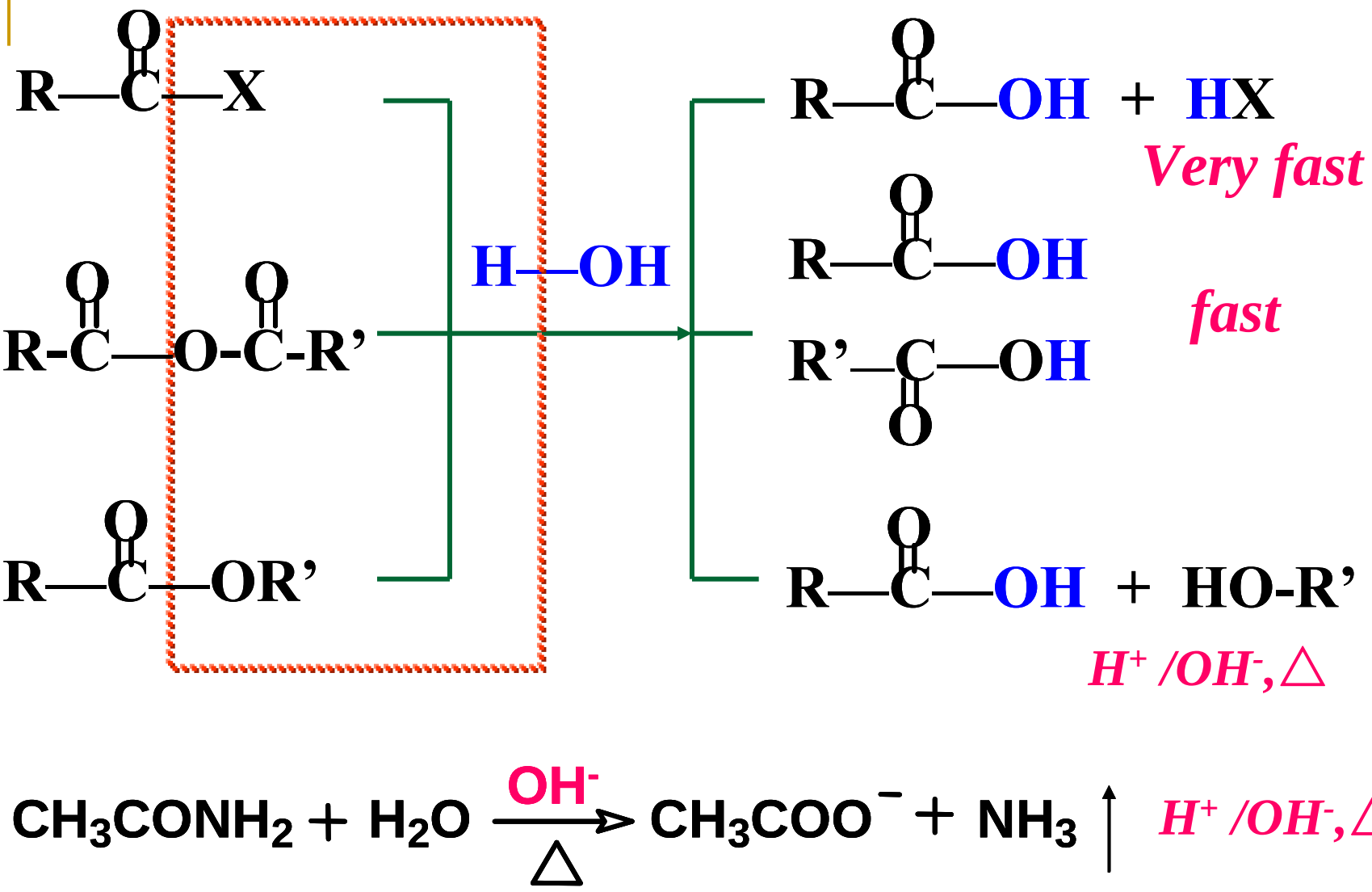


1. Hydrolysis (a carboxylic acid is formed)

All acyl derivatives can be hydrolyzed back to the original carboxylic acid.

General equation:



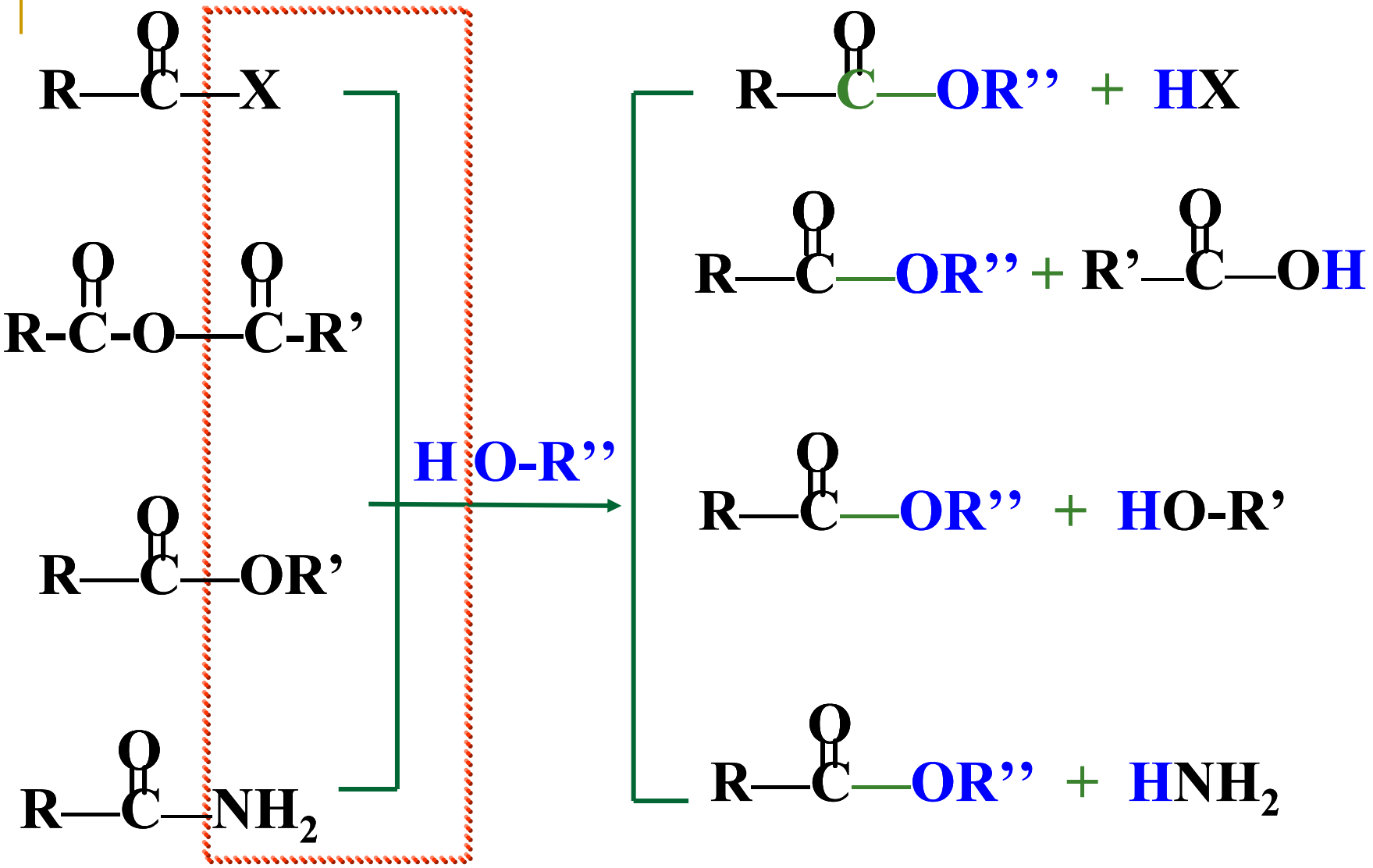


$$CH_3CONH_2 + H_2O \xrightarrow[\triangle]{OH^-} CH_3COO^- + NH_3\uparrow \quad H^+/OH^-,\triangle$$

2. Alcoholysis (an ester is formed)

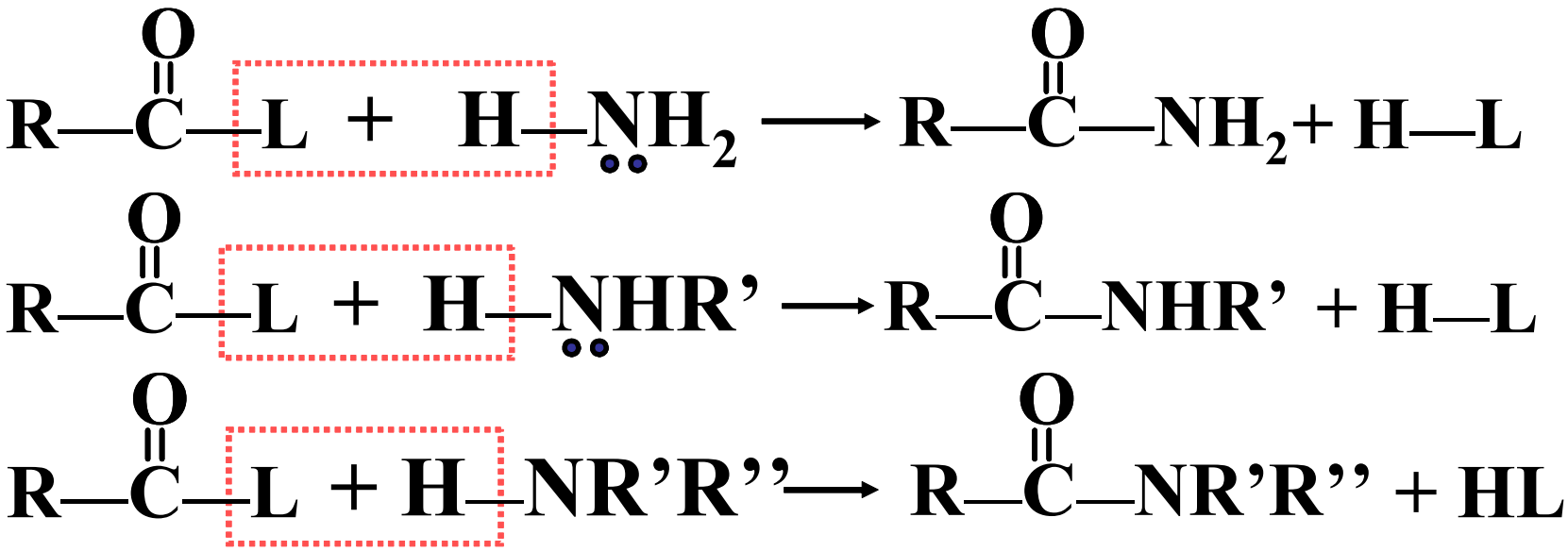
Acyl halides, acid anhydrides, esters and amides can react with alcohol to form esters. (alcoholyze)

General equation:

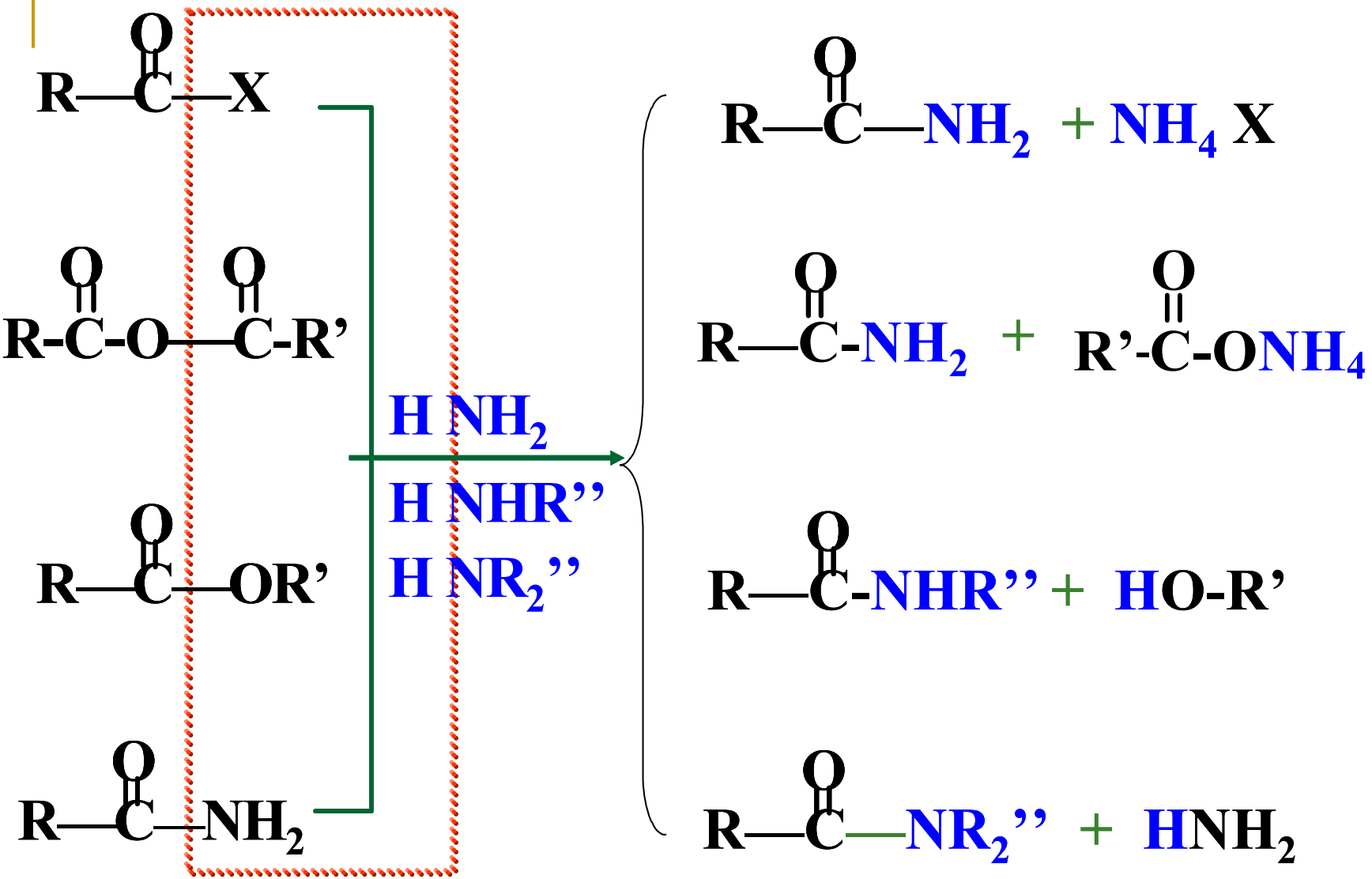

R—C—X
R-C-O—C-R’
R—C—OR’
R—C—NH2
HO-R’’
R—C—OR’’ + HX
R—C—OR’’ + R’—C—OH
R—C—OR’’ + HO-R’
R—C—OR’’ + HNH2

3. Ammonolysis (*aminolysis*, an amide is formed)

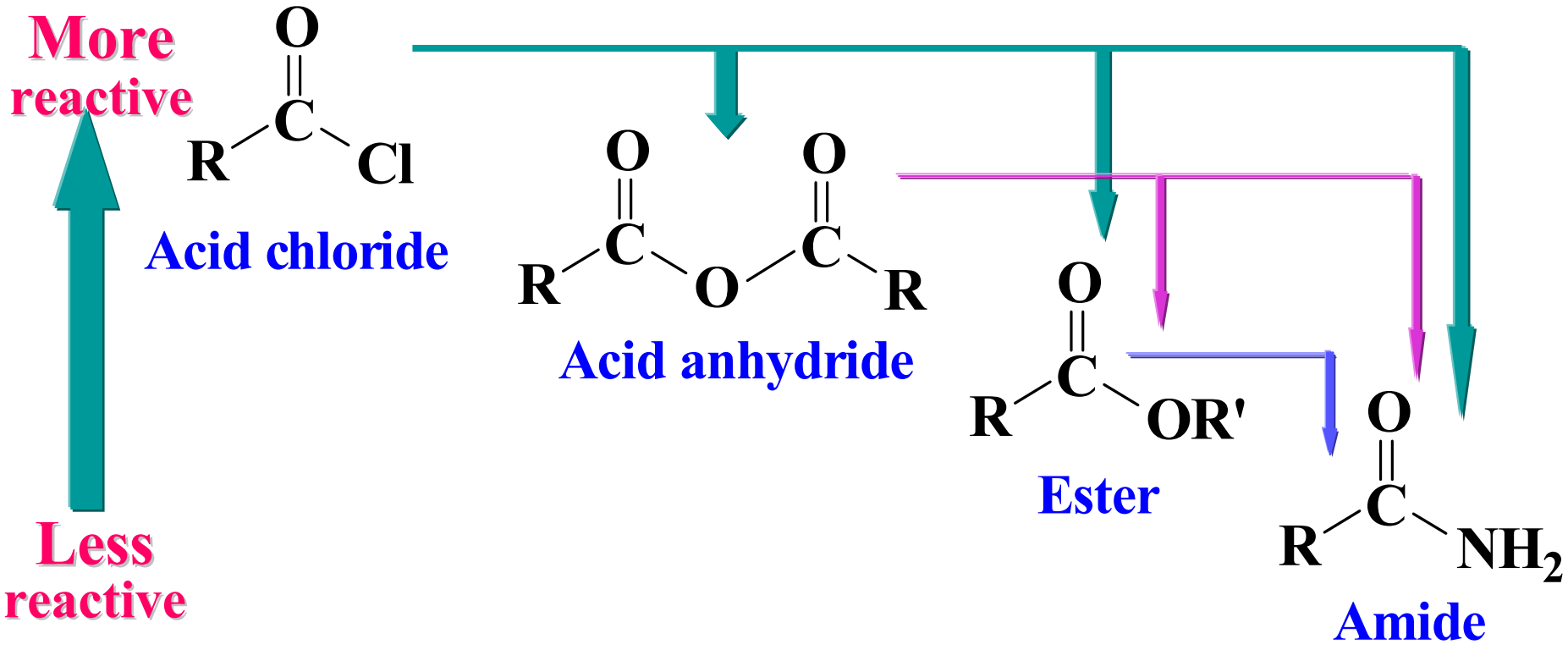
- **Acyl halides, acid anhydrides, esters and amides can react with ammonia or 1° or 2° amines to obtain amides (ammonolyzed or aminolysis).**



Nucleophilicity of ammonia or amines is stronger than water, so reaction of aminolysis is faster than hydrolysis.


R—C—X
R-C-O—C-R’
R—C—OR’
R—C—NH2
H NH2
H NHR’’
H NR2’’
R—C—NH2 + NH4 X
R—C-NH2 + R’-C-ONH4
R—C-NHR’’ + HO-R’
R—C—NR2’’ + HNH2

The order of reactivity of acid derivatives

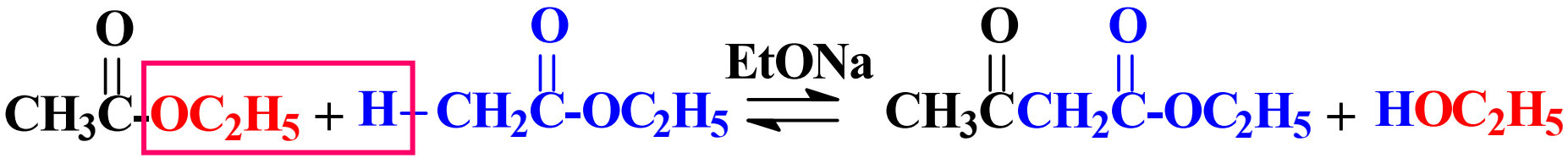


Acylating agent（酰化剂）:

The agent that can provide acyl group to other compound.

are the best acylating agents.

Ⅱ. Claisen Condensation Reaction



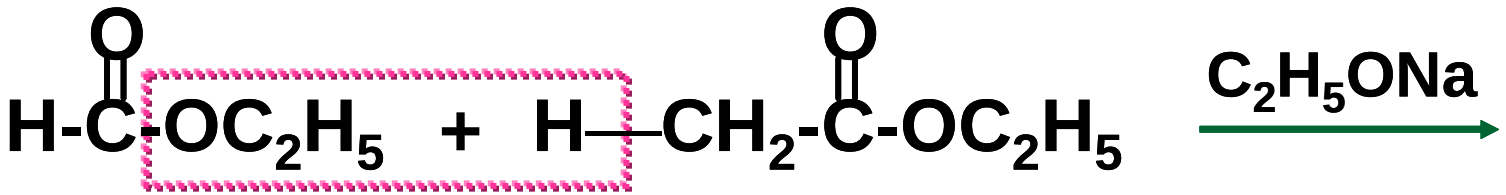
Ethyl acetate

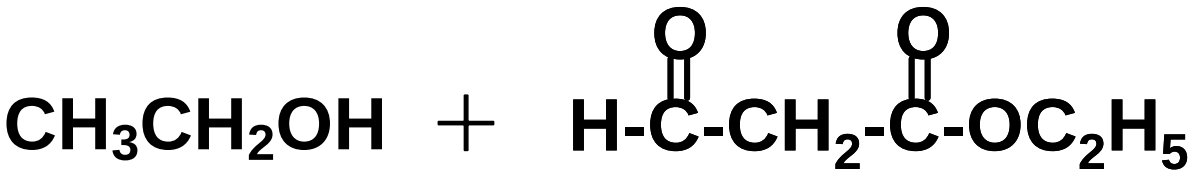
Ethyl acetoacetate(乙酰乙酸乙酯)

a β-keto ester (75%)

This reaction between two ester components is known as the *Claisen Condensation reaction*.

Esters without α -hydrogen don't occur Claisen Condensation reaction, but they can condense with other esters with α -hydrogen , called as Cross Claisen Condensation.

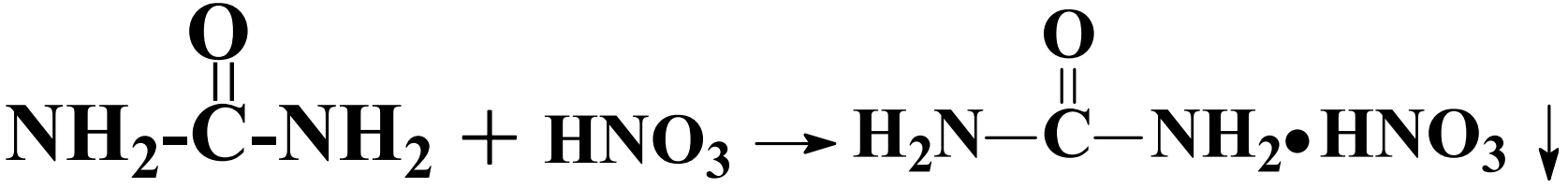




Ⅳ. Carbamide (urea)

1. Weak basicity:

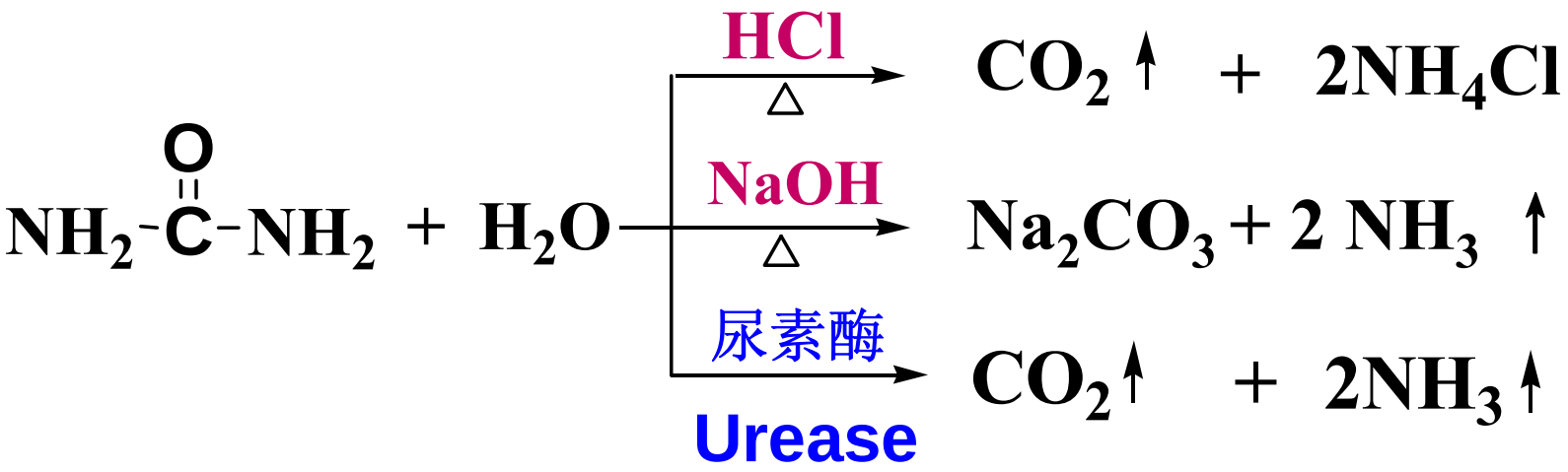
Urea is a weak base, it can form salts with strong acids, sparingly soluble salts of nitric and oxalic acid are known.



Urea nitrate (white colour)

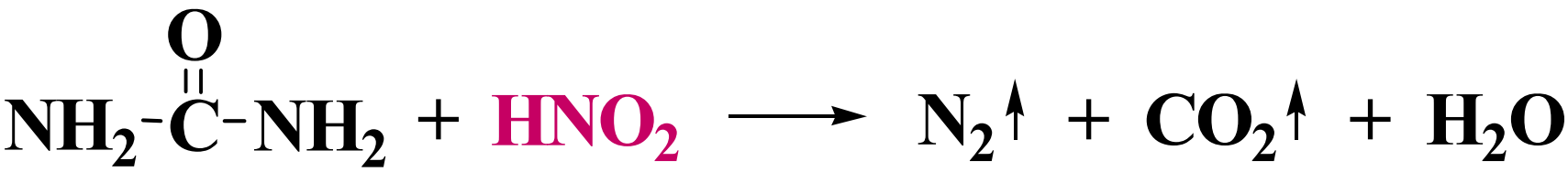
2. Hydrolysis

Urea, like other amides, is hydrolysed under both acidic or alkaline conditions to form ammonium, carbon dioxide or ammonia, carbonate.



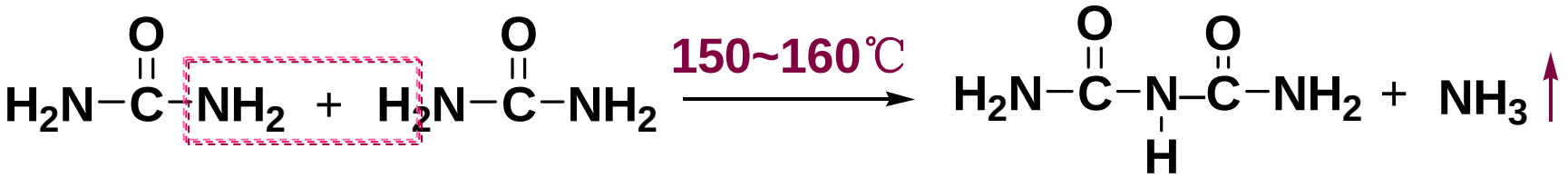
3. React with Nitrous Acid

Like other primary amide, urea reacts with nitrous acid to give nitrogen.

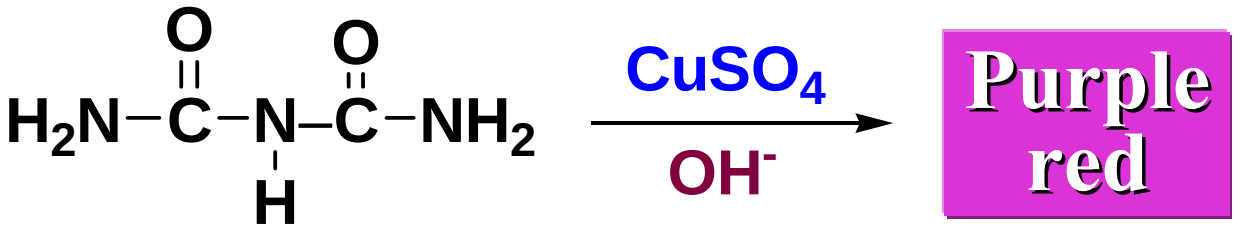


4. Formation of Biuret and Biuret Reaction

When urea is heated to 150~160℃, two urea molecules condense to form biuret (缩二脲).



The basic solution of the biuret can show purple red with cupper sulfate, the reaction is called Biuret Reaction (缩二脲反应), It can be used to identify the peptides or proteins.



It is a test for all compounds containing two or more than two *peptide bond* (−CO−NH−).

Additional Questions

10-1 Write the structures of the following compounds…

10-2 Name the following compounds by IUPAC system:

10-3 Write the products of reaction of benzoyl chloride with …

10-4 Write the products of reaction of propanoic anhydride

10-5 Write reaction equations for the following amides with…

10-6 Write equations for the following Claisen condensations…

10-7 Write the products of the following:

***10-8 Complete the following transformation:**

10-9 Distinguish the compounds within each set by simple …

10-10 Arrange the following series compounds in order of …

10-11 Compound A ($C_6H_{12}O_2$) reacts with acidic water solution …

10-12 Compound A ($C_5H_6O_3$) reacts with 1 mol ethanol to …