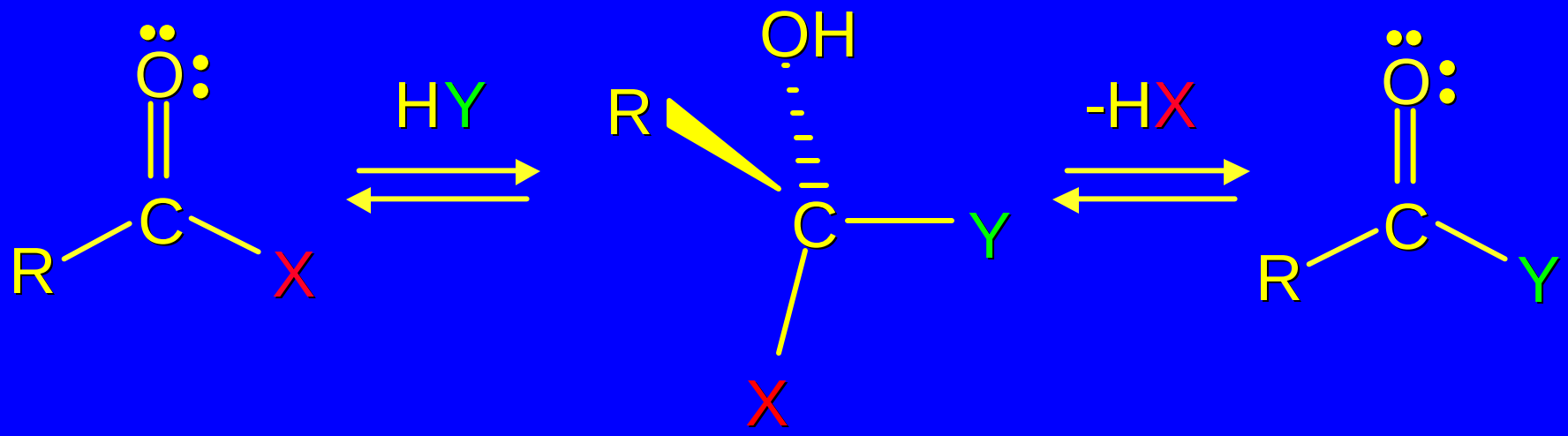
20.3
Nucleophilic Substitution in Acyl Chlorides

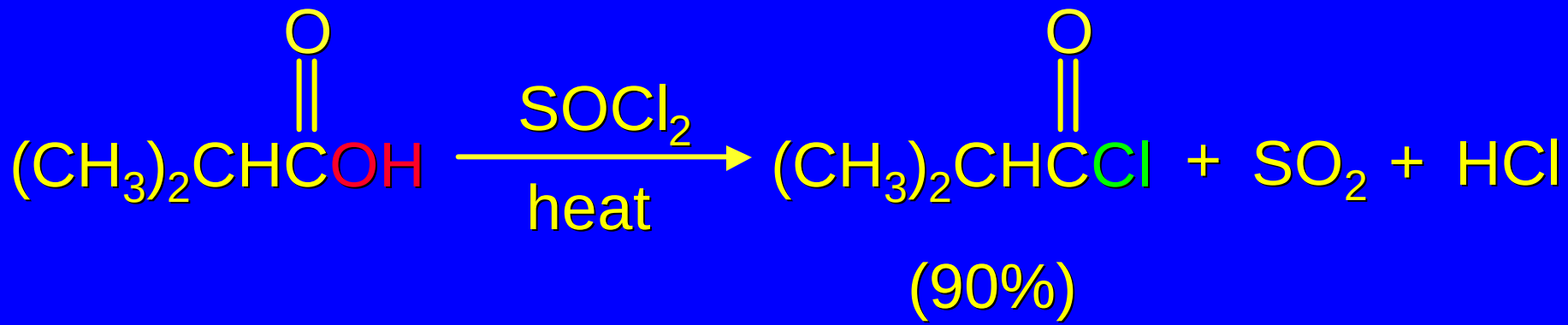
General Mechanism for Nucleophilic Acyl Substitution

involves formation and dissociation
of a tetrahedral intermediate

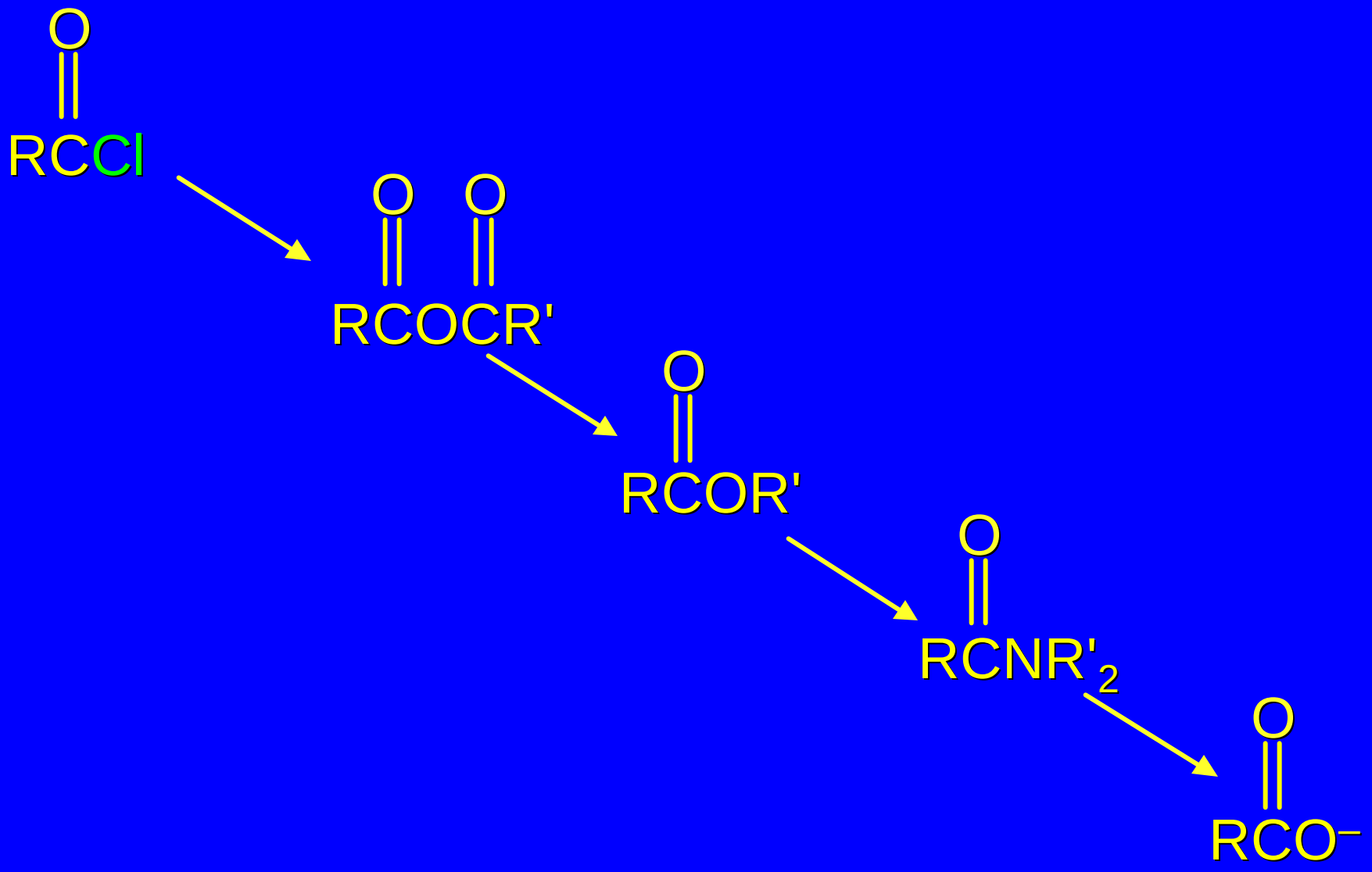


Preparation of Acyl Chlorides

from carboxylic acids and thionyl chloride (Section 12.7)

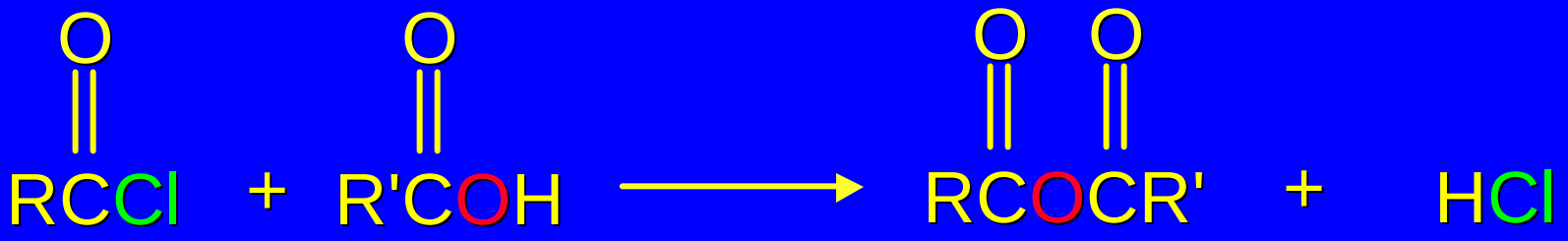


Reactions of Acyl Chlorides



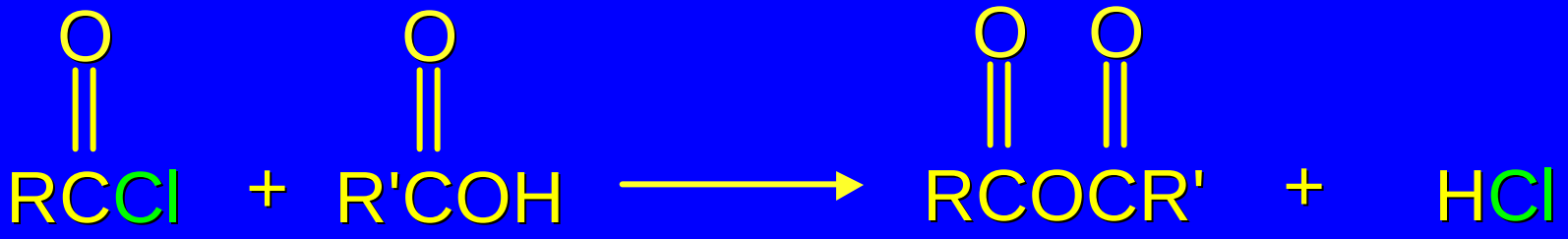
Reactions of Acyl Chlorides

Acyl chlorides react with carboxylic acids to give acid anhydrides:

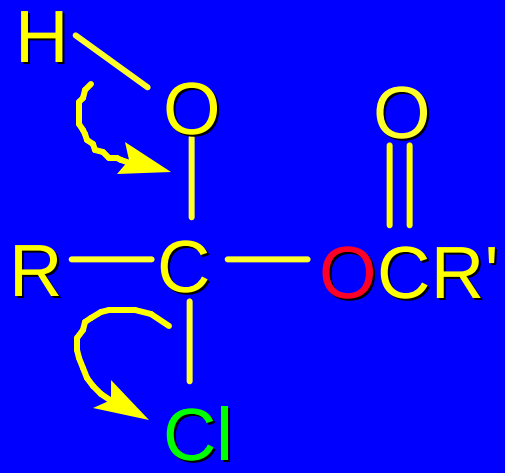


Reactions of Acyl Chlorides

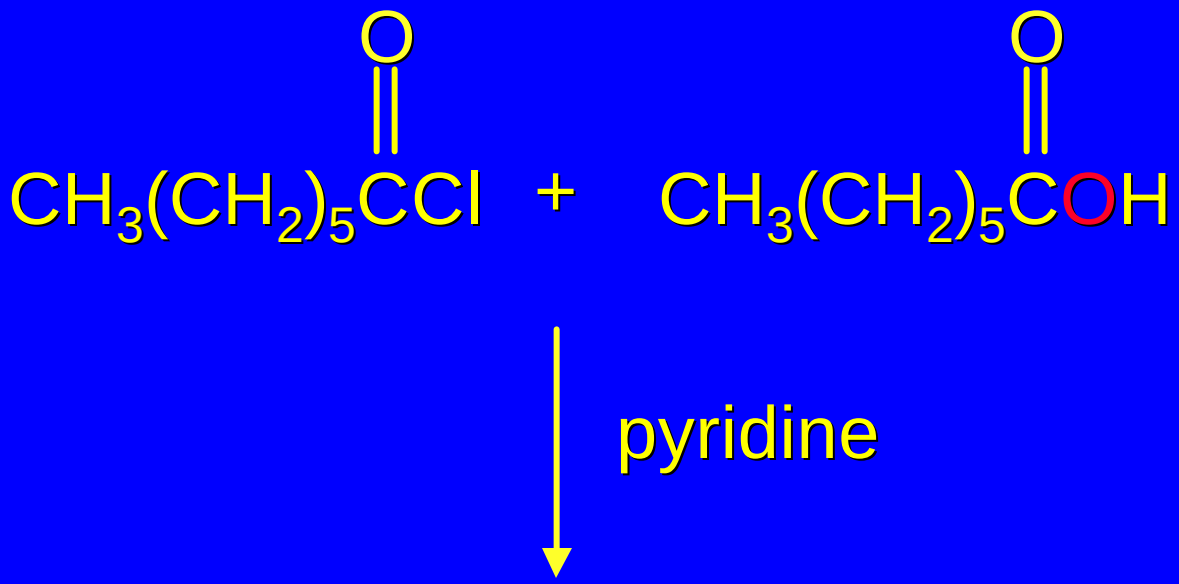
Acyl chlorides react with carboxylic acids to give acid anhydrides:



via:



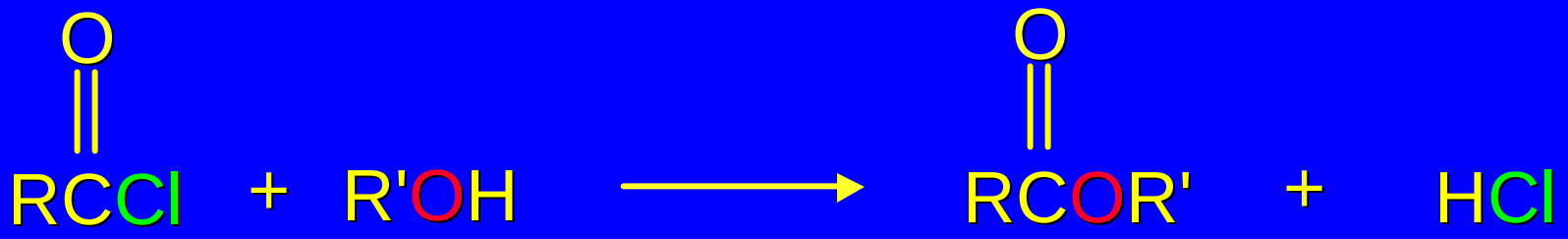
Example



(78-83%)

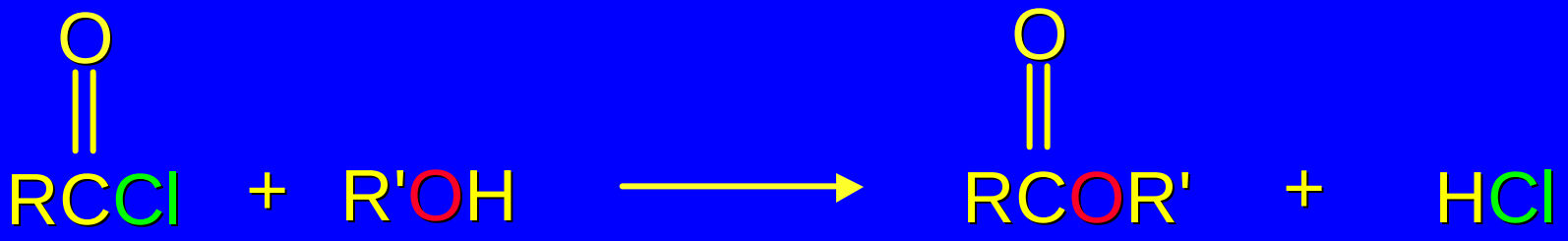
Reactions of Acyl Chlorides

Acyl chlorides react with alcohols to give esters:

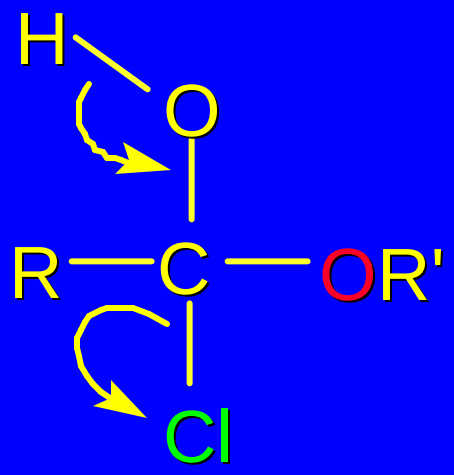


Reactions of Acyl Chlorides

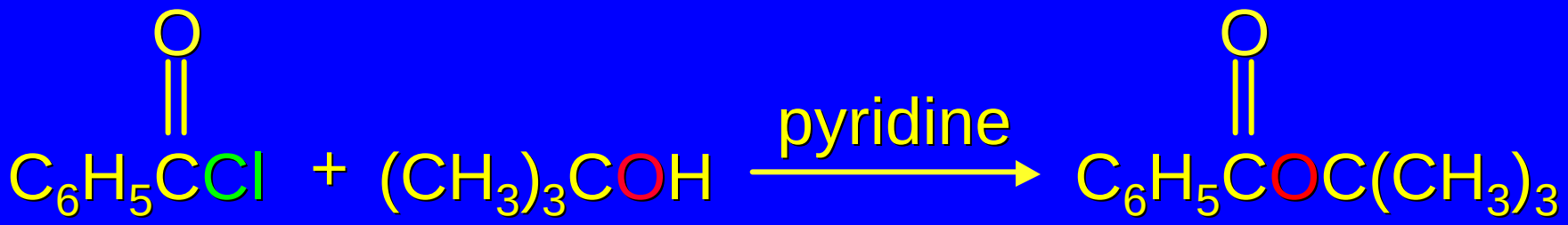
Acyl chlorides react with alcohols to give esters:



via:



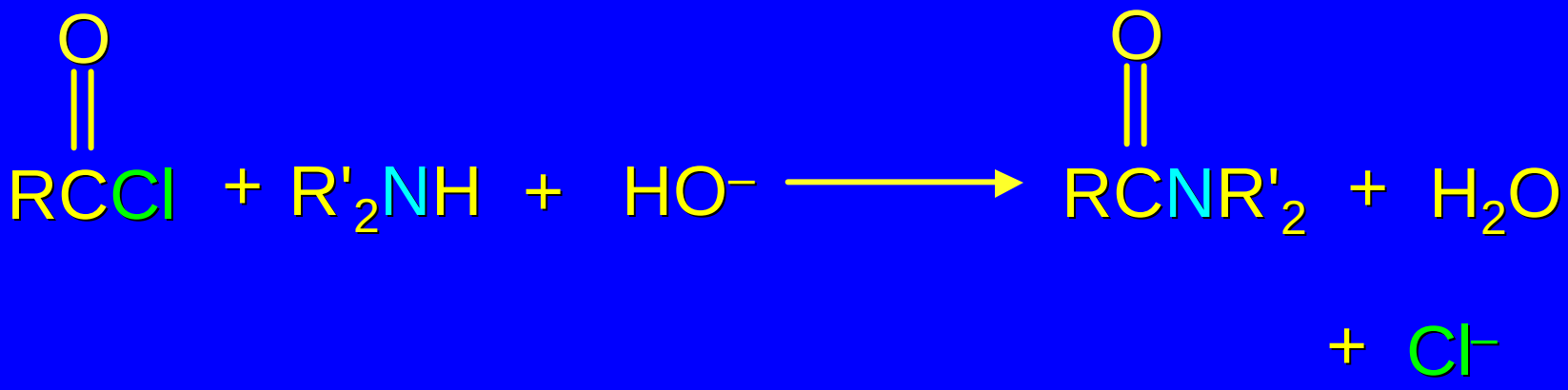
Example



(80%)

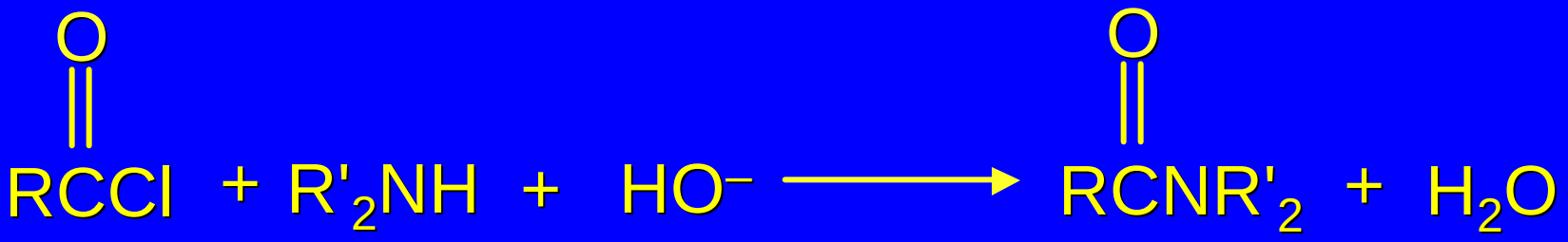
Reactions of Acyl Chlorides

Acyl chlorides react with ammonia and amines to give amides:

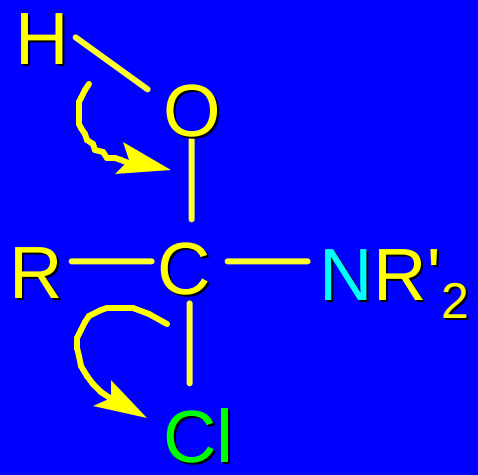


Reactions of Acyl Chlorides

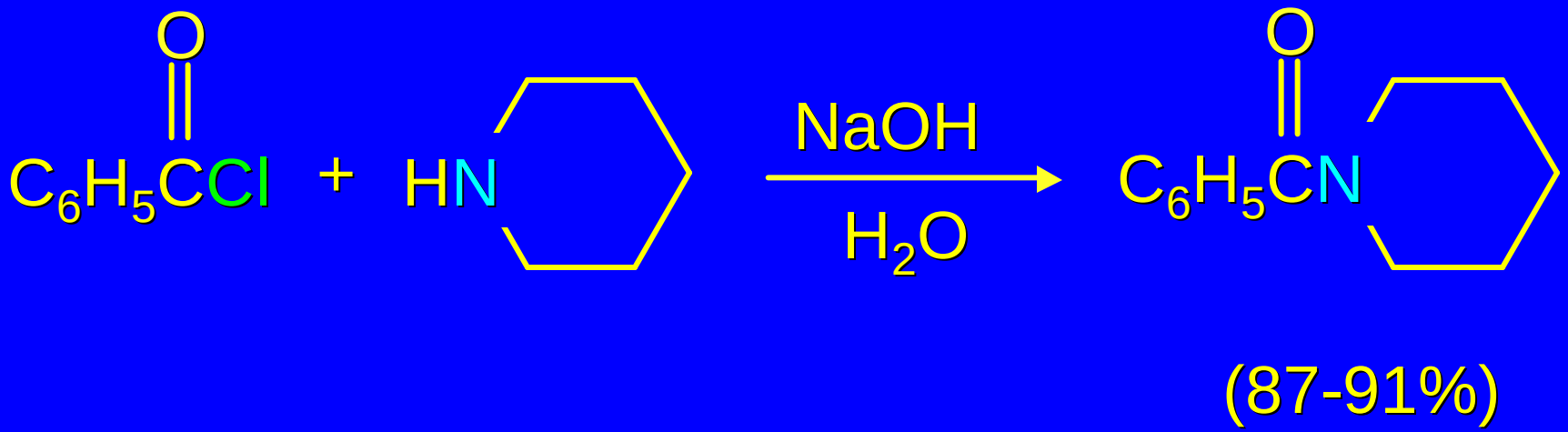
Acyl chlorides react with ammonia and amines to give amides:



via:



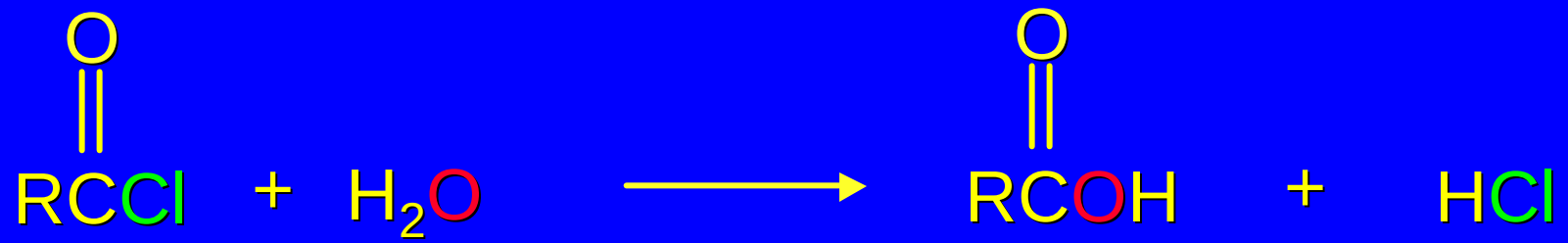
Example

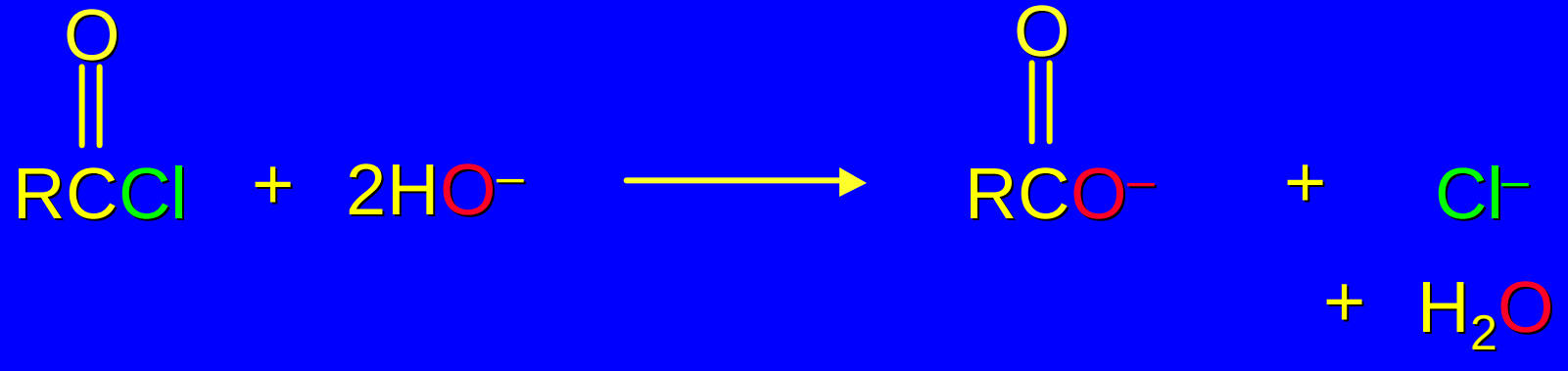


(87-91%)

Reactions of Acyl Chlorides

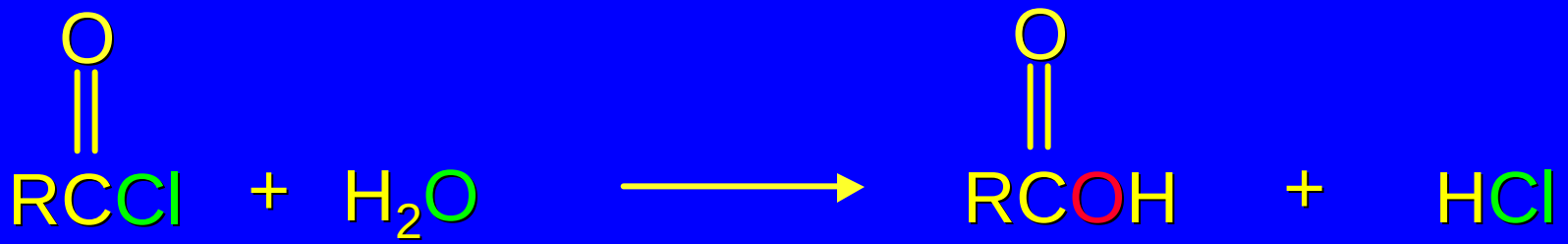
Acyl chlorides react with water to give carboxylic acids (carboxylate ion in base):



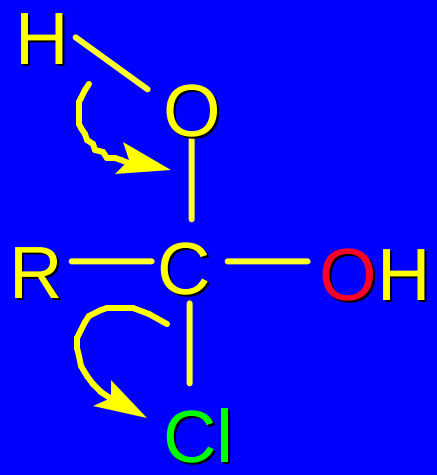


Reactions of Acyl Chlorides

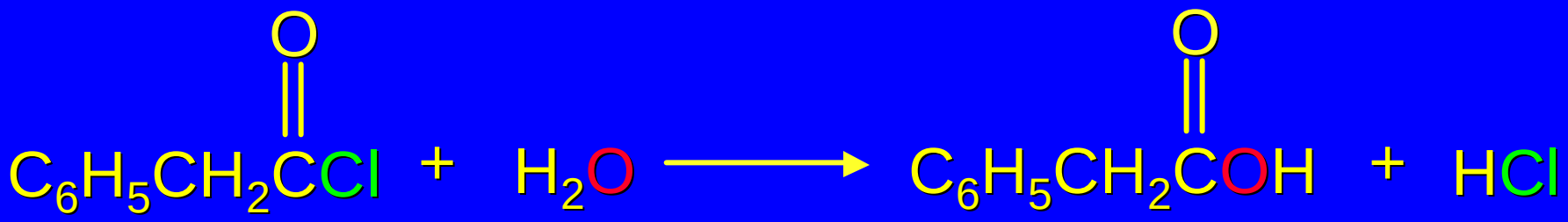
Acyl chlorides react with water to give carboxylic acids (carboxylate ion in base):



via:

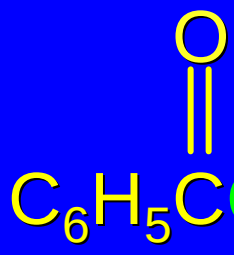


Example

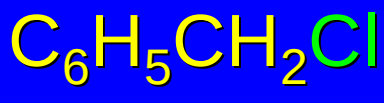


Reactivity

Acyl chlorides undergo nucleophilic substitution much faster than alkyl chlorides.



C_6H_5CCl



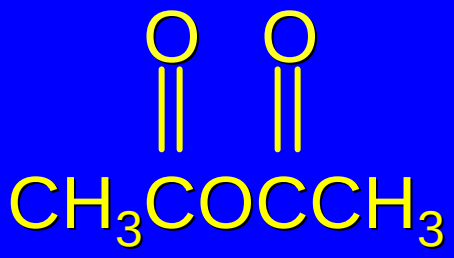
$C_6H_5CH_2Cl$

Relative rates of hydrolysis (25°C)	1,000	1

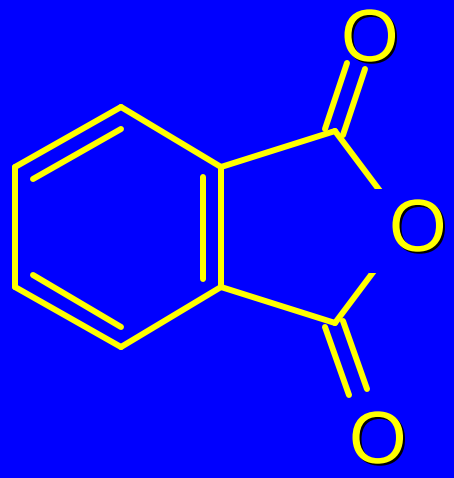
20.4
Preparation of
Carboxylic Acid Anhydrides

Anhydrides can be prepared from acyl chlorides as described in Table 20.2

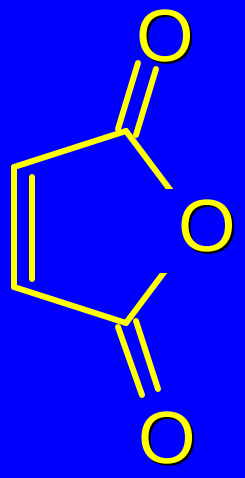
Some anhydrides are industrial chemicals



Acetic anhydride



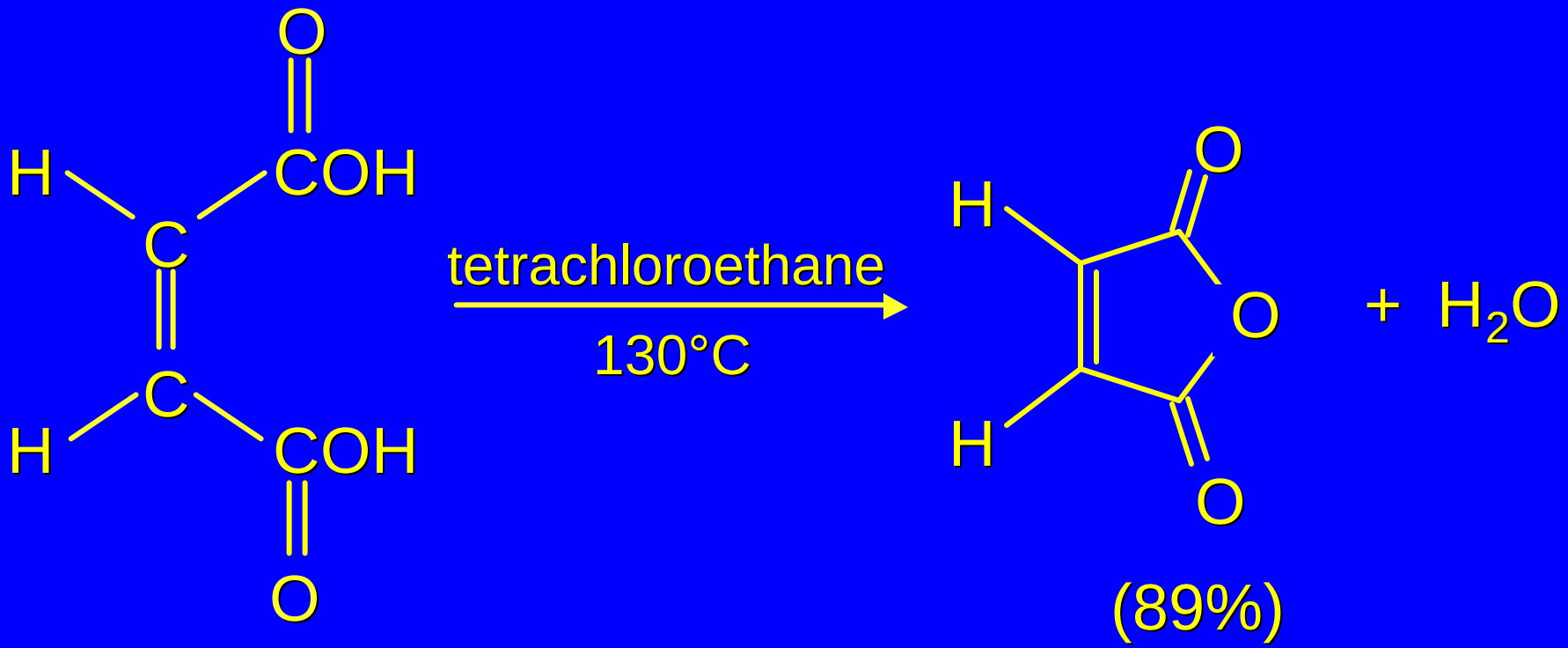
Phthalic anhydride



Maleic anhydride

From dicarboxylic acids

Cyclic anhydrides with 5- and 6-membered rings can be prepared by dehydration of dicarboxylic acids

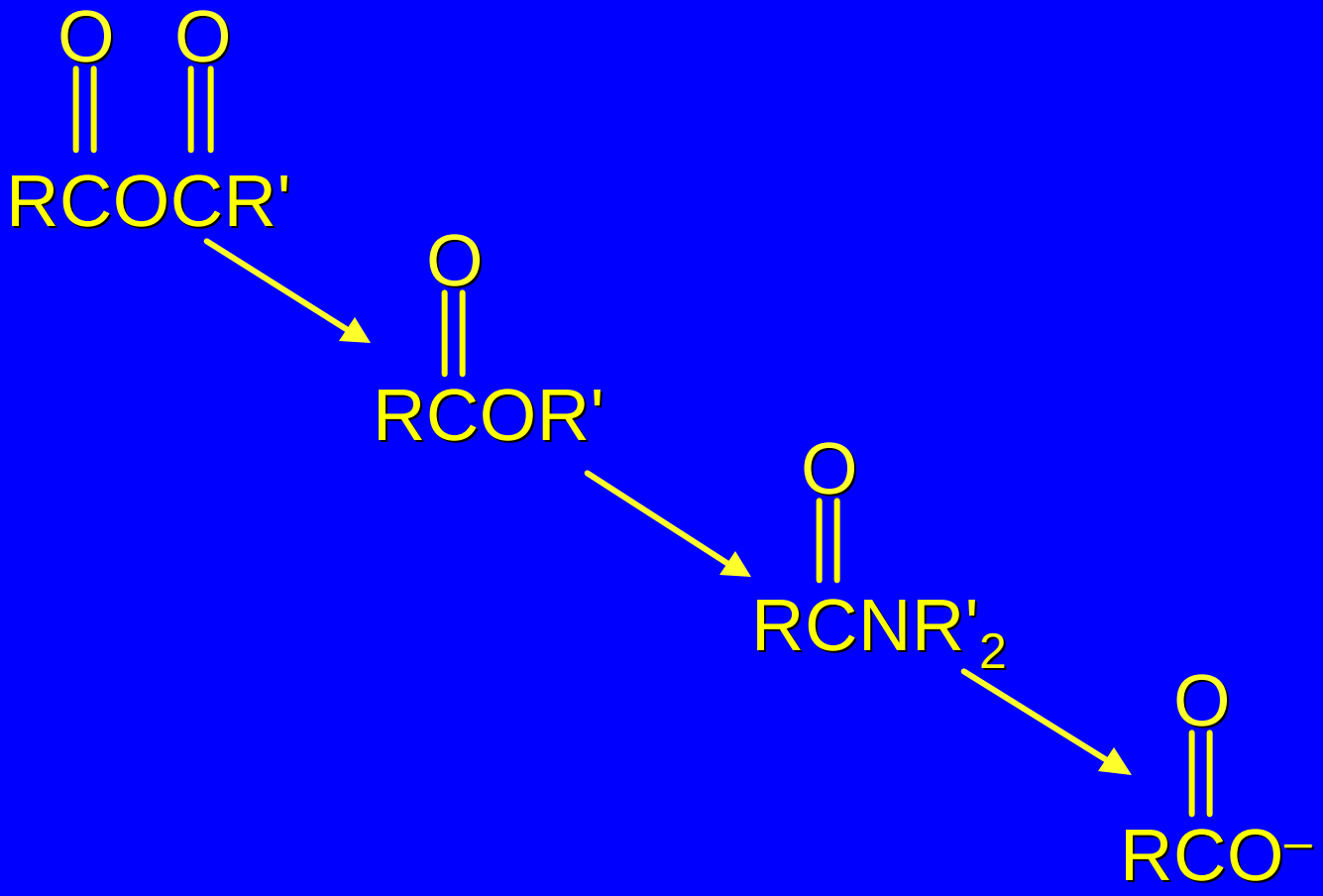


(89%)

20.5
Reactions of
Carboxylic Acid Anhydrides

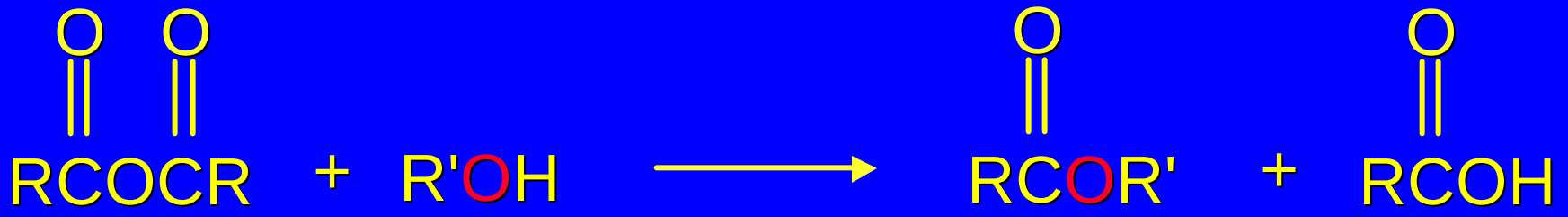
Table 20.3

Reactions of Anhydrides



Reactions of Acid Anhydrides

Carboxylic acid anhydrides react with alcohols to give esters:

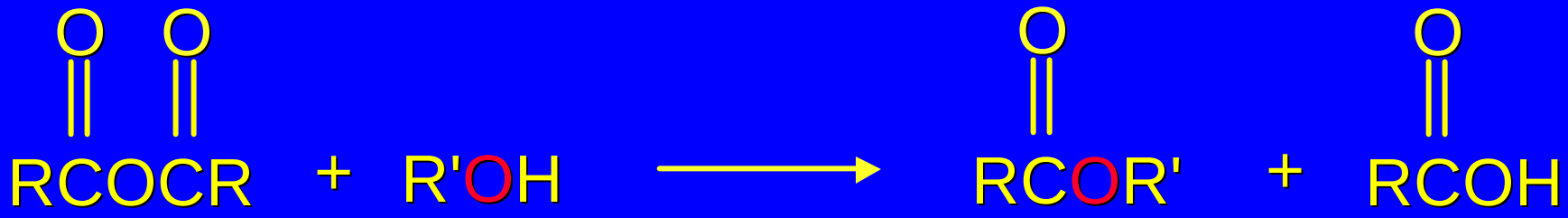


normally, symmetrical anhydrides are used (both R groups the same)

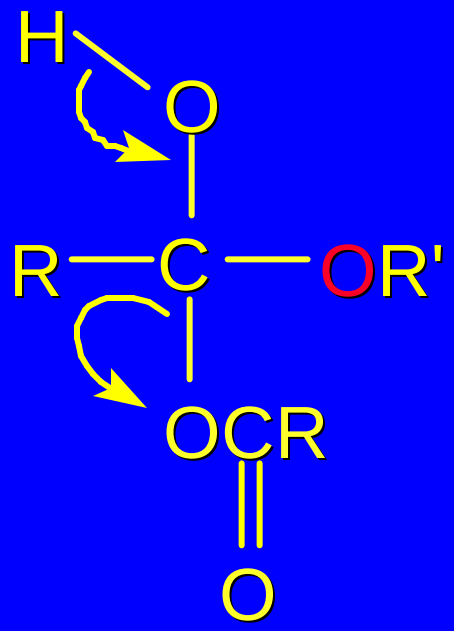
reaction can be carried out in presence of pyridine (a base) or it can be catalyzed by acids

Reactions of Acid Anhydrides

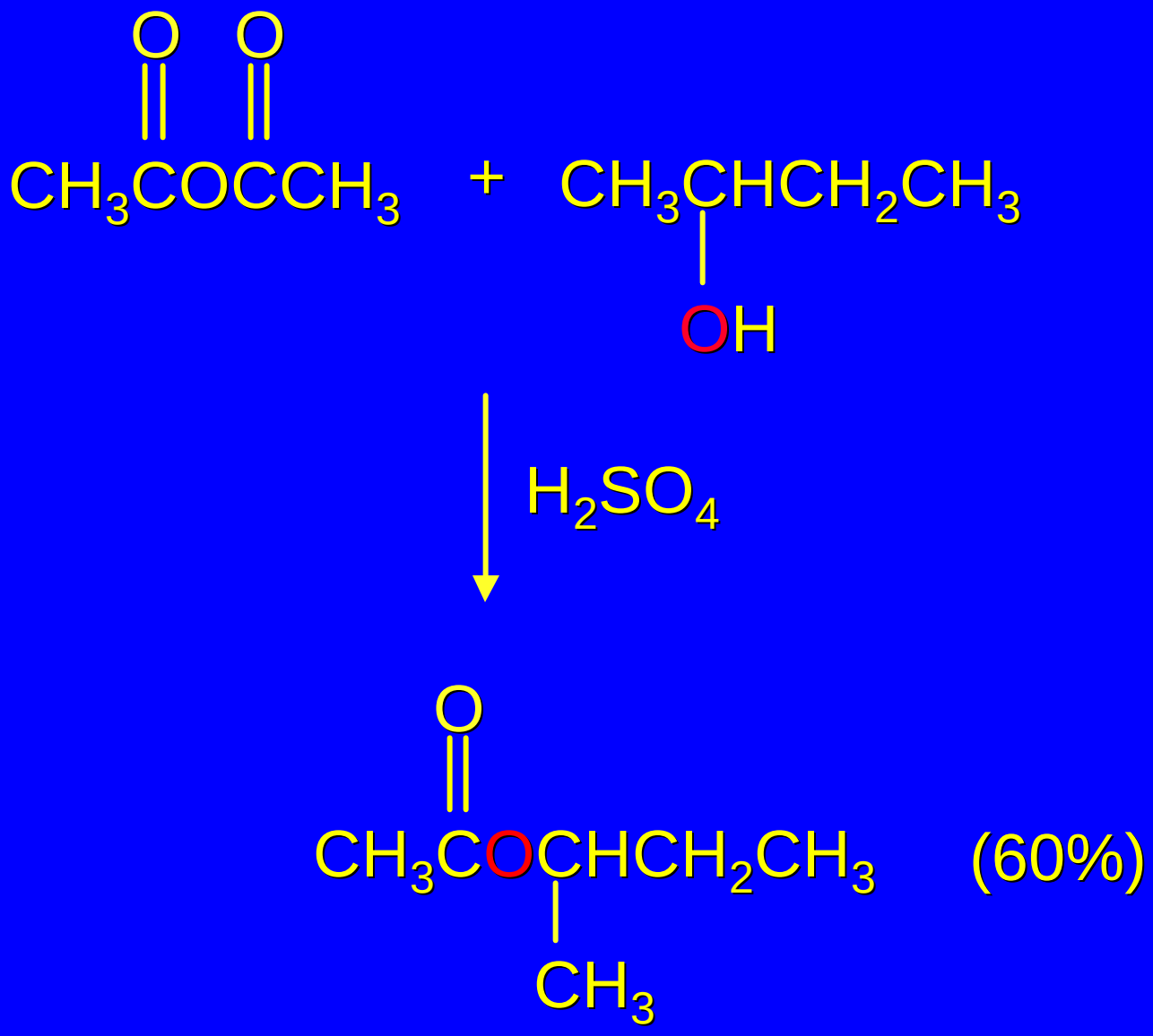
Carboxylic acid anhydrides react with alcohols to give esters:



via:

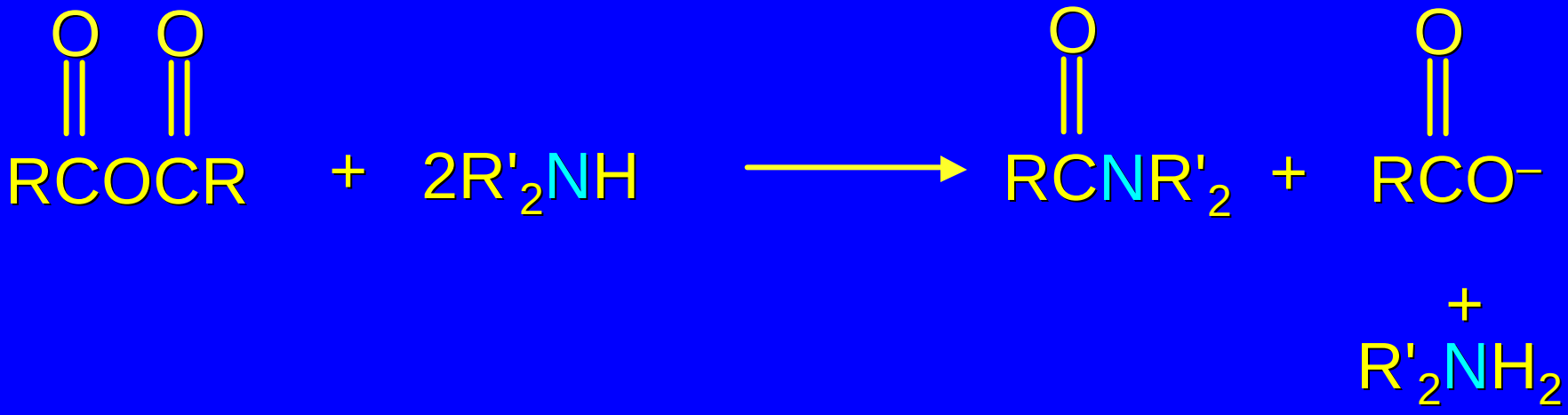


Example



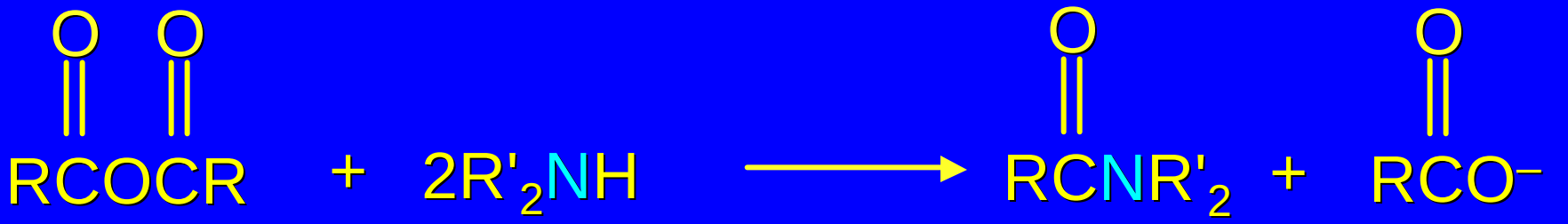
Reactions of Acid Anhydrides

Acid anhydrides react with ammonia and amines to give amides:

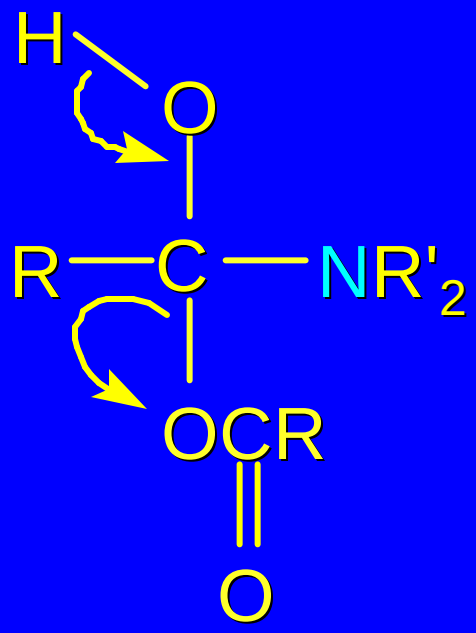


Reactions of Acid Anhydrides

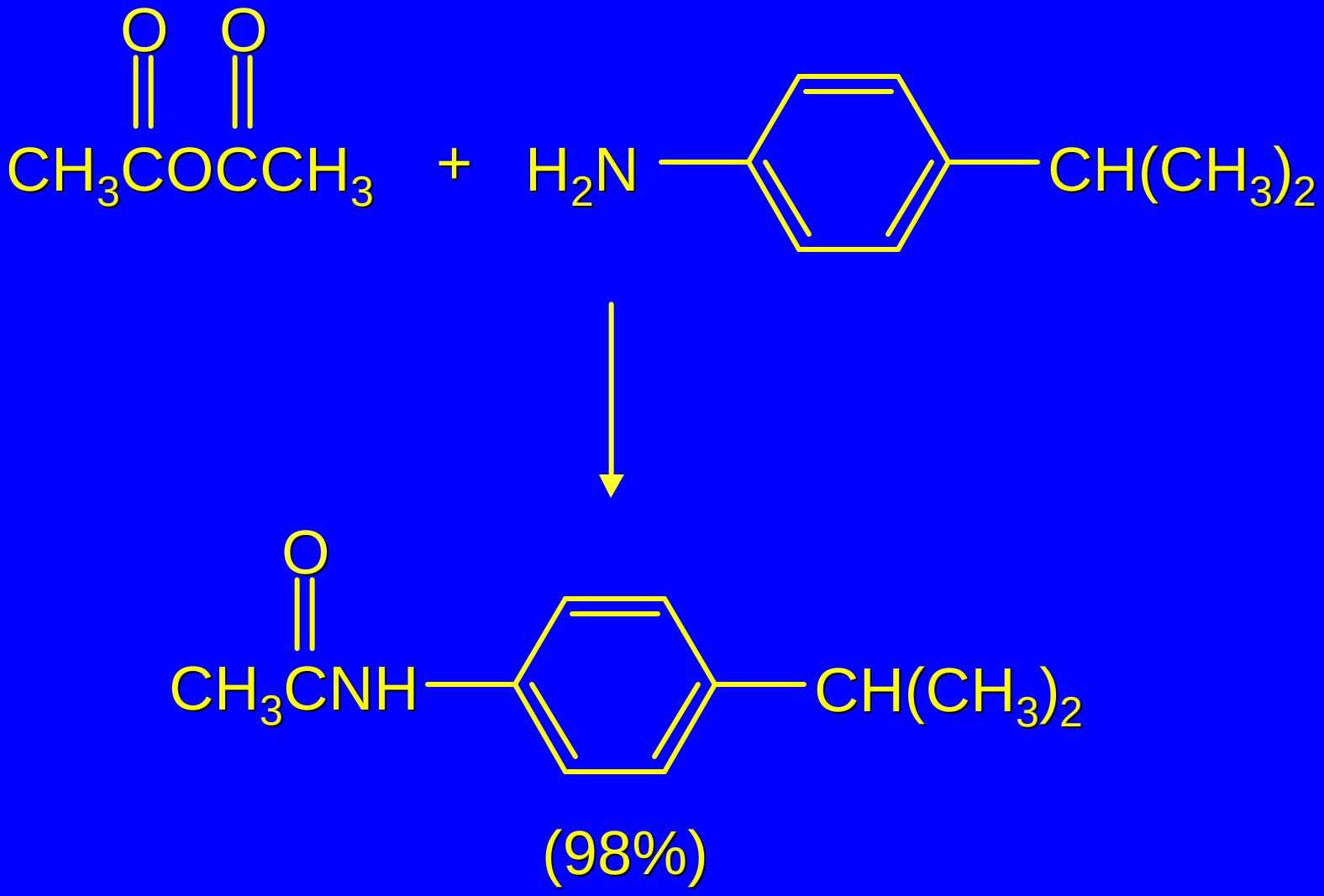
Acid anhydrides react with ammonia and amines to give amides:



via:



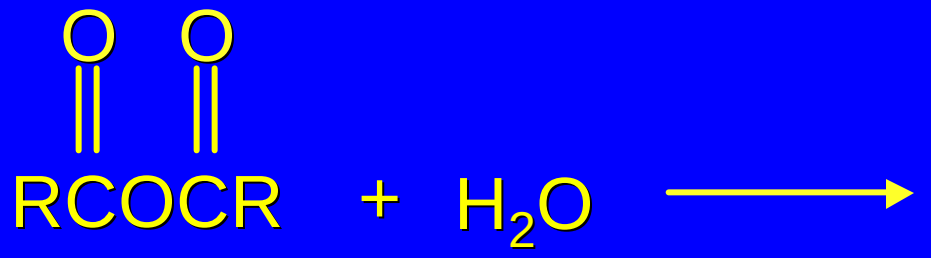
Example

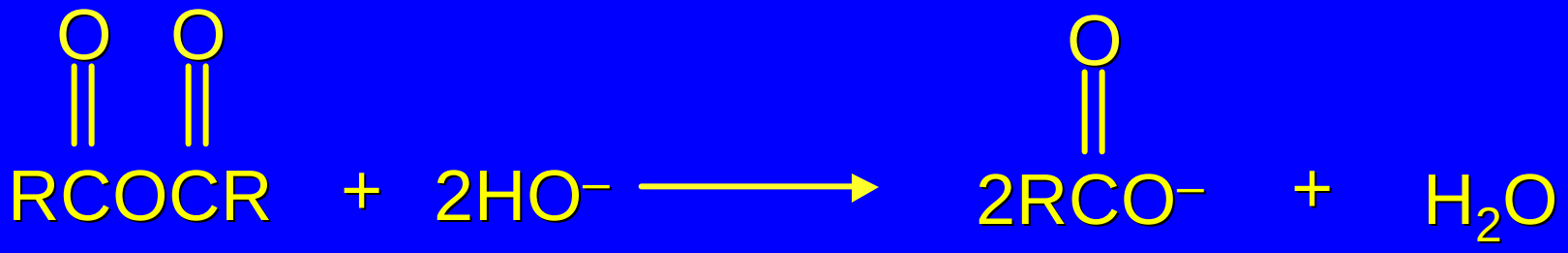


(98%)

Reactions of Acid Anhydrides

Acid anhydrides react with water to give carboxylic acids (carboxylate ion in base):





Reactions of Acid Anhydrides

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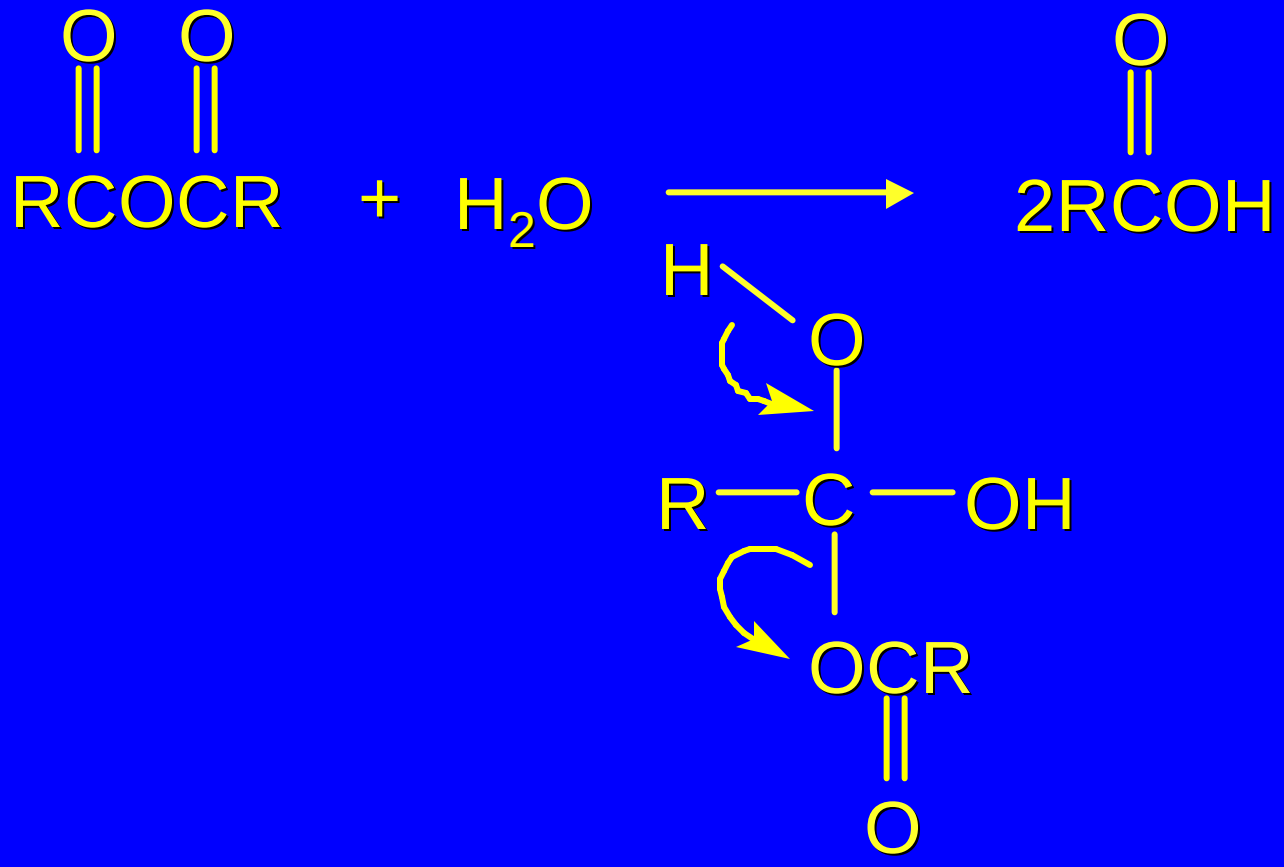

Example