SHORT COMMUNICATIONS

Transacylation from Acid Amides to Amines Catalyzed by Carbon Dioxide

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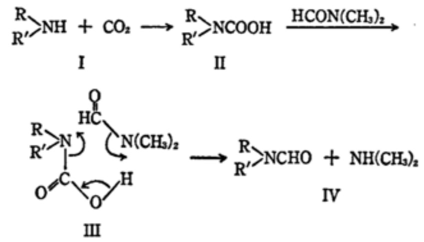
We wish to report our recent finding that certain acid amides undergo transacylation to amines when a mixture of the two compounds is simply heated in the presence of carbon dioxide.

A typical experiment for the transformylation from dimethylformamide (DMF) to amines was carried out as follows: a mixture of 10 g of *n*-butylamine in 50 m*l* of DMF was warmed at 60°C for 5 hr under a stream of dry carbon dioxide, and then the solvent, DMF, was evaporated under reduced pressure. The distillation of the residue gave 6.4 g (46%) of *N*-butylformamide, bp 107—109°C/3 mmHg. A similar transformylation from DMF was observed in *n*-tetradecylamine (66%), piperidine (48%), and morpholine (67%), giving the corresponding *N*-formyl derivatives in the yields indicated in the parentheses. These reactions did not occur in the absence of carbon dioxide. Aromatic amines such as aniline and tertiary amines such as pyridine were not formylated by this method.

Transacylation from acetamide or cyanoacetamide to amines was also attempted by heating a mixture of the amide and amine in dioxane under a stream of carbon dioxide. The transcyanoacetylation from cyanoacetamide took place in both *n*-hexadecylamine and *n*-hexylamine, giving *N*-*n*-hexadecylcyanoacetamide (63%) and *N*-*n*-hexylcyanoacetamide (37%) respectively. On the other hand, the transacetylation from acetamide took place only in *n*-hexadecylamine, giving *N*-*n*-hexadecylacetamide (6%).*[1] The attempt at transacetylation from *N*,*N*-dimethylacetamide to amines was unsuccessful.

These results indicate that the reactivity of the amides for transacylation to amines decreases in the order: DMF > cyanoacetamide > acetamide > *N*,*N*-dimethylacetamide. This order of reactivity would seem to show that the ability of the amides to transacylate decreases with a decrease in the positive charge on the carbonyl carbon atom of the amides.

All of the results presented here might be explained in terms of the following mechanism:



R: alkyl, R: alkyl or H

The amine (I) reacts with carbon dioxide to produce the corresponding carbamic acid (II), which itself subsequently reacts with DMF to form an intermediate (III). This intermediate III spontaneously collapses to the product (IV), ejecting carbon dioxide and dimethylamine. At this stage of the reaction the nucleophilic reactivity of the amine may be enhanced to some extent, because the temporary formation of an amide ion would be expected at the moment of the elimination of carbon dioxide and a proton which is taken up by the amino nitrogen of formamide.

A similar mechanism would operate in the other transacylation reactions. It is interesting to point out that carbon dioxide, which is an inert gas, might be able to play an important role in some chemical reactions such as those reported in this communication. In this connection, it is also noteworthy that carbon disulfide acts as an effective dehydrating reagent in the formation of pyrophosphates from phosphates.[2]

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*[1] The long-chain aliphatic amines such as *n*-hexadecylamine are known to react readily with carbon dioxide to form the stable carbamic acid.[1] This seems to be a reason for the relatively high reactivity for the transacylation from acid amides to *n*-hexadecylamine.

1) R. Goto, A. Watanabe, K. Hojo and M. Kosaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 1220 (1966).

2) R. E. Atkinson and F. I. G. Cadogan, *J. Chem. Soc. (C)*, **1967**, 1356.