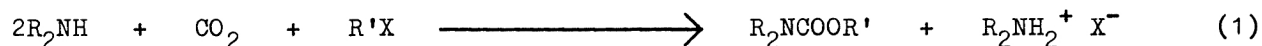


A DIRECT SYNTHESIS OF CARBAMATE ESTER FROM CARBON DIOXIDE,
AMINE AND ALKYL HALIDE

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Carbon dioxide reacted with diethylamine and alkyl halide derivatives to give the corresponding alkyl N,N-diethylcarbamate esters in fair yields.

Carbamate esters¹⁾ have been prepared by the reactions of amine with alkyl chloroformate, and alcohol with carbamoyl chloride or isocyanate, which were made from phosgene as starting materials, because carbamic acid is unstable and decomposes to carbon dioxide and amine. A few direct syntheses of carbamate ester from carbon dioxide were reported so far,²⁻⁷⁾ and we have previously reported that carbon dioxide and aliphatic amine reacted with epoxide to give 2-hydroxyalkyl carbamate ester in high yields,^{8,9)} and with vinyl ether to give 1-alkoxyalkyl carbamate ester selectively.¹⁰⁾ In the course of further studies, we found the reaction of carbon dioxide and amine with alkyl halide to form the corresponding carbamate ester.



A typical example of the reaction is as follows. A mixture of diethylamine (0.25 mol) and alkyl halide (0.1 mol) was placed in a 100 cm³-autoclave under pressure of carbon dioxide (40 atm; 4.1 x 10⁶ Pa) at 70 °C for 48 h. The reaction mixture was filtered to remove ammonium halide salts and the filtrate was subjected to distillation under reduced pressure. The yields of the products were determined by gas chromatography analysis. The products obtained were identified by IR, ¹H NMR, and GC-MS analyses.

The results of the reactions of carbon dioxide, diethylamine with various alkyl halides were summarized in Table 1. Various n-butyl halides, such as chloride, bromide and iodide, reacted with carbon dioxide and diethylamine at 70 °C for 48 h to yield n-butyl N,N-diethylcarbamate in 6%, 42%, and 12%, respectively (Table 1, Nos. 1-3). As the reactivity of n-butyl chloride with nucleophilic reagents is low, a small amount of carbamate ester was obtained. In the case of n-butyl iodide, the reaction was accompanied by the formation of a considerable amount of ammonium iodide salt, which was obtained from the direct reaction of diethylamine and n-butyl iodide. The reaction of n-butyl bromide with carbon dioxide and diethylamine gave the carbamate ester in the highest yield in the

Table 1. Reaction of Carbon Dioxide, Amine and Alkyl Halide^{a)}

No.	Alkyl halide	Product	
		Carbamate	Yield / % ^{b)}
1	CH ₃ (CH ₂) ₃ -Cl	Et ₂ NCOO-(CH ₂) ₃ CH ₃	6
2	CH ₃ (CH ₂) ₃ -Br	Et ₂ NCOO-(CH ₂) ₃ CH ₃	42
3	CH ₃ (CH ₂) ₃ -I	Et ₂ NCOO-(CH ₂) ₃ CH ₃	12
4	Me ₂ CHCH ₂ -Br	Et ₂ NCOO-CH ₂ CHMe ₂	20 ^{c)}
5	CH ₃ CH ₂ CHMe-Br	Et ₂ NCOO-CHMeCH ₂ CH ₃	43 ^{c)}
6	Me ₃ C-Br	Et ₂ NCOO-CMe ₃	10 ^{c)}
7	CH ₃ CH ₂ CH ₂ -Br	Et ₂ NCOO-CH ₂ CH ₂ CH ₃	32
8	Me ₂ CH-Br	Et ₂ NCOO-CHMe ₂	53

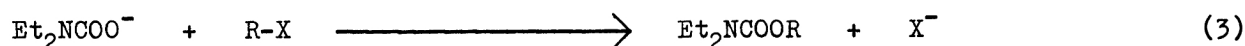
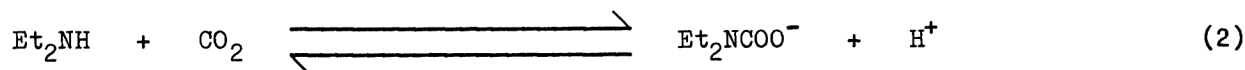
a) CO₂, 40 atm; Et₂NH, 0.25 mol; R-X, 0.1 mol; temp, 70 °C; time, 48 h.

b) Estimated by GLC on the basis of alkyl halide.

c) Isolated.

reactions using various n-butyl halides. Other alkyl bromides, such as isobutyl, sec-butyl, tert-butyl, n-propyl, and isopropyl bromide were tried, and also gave the corresponding carbamate esters without other isomeric carbamates (Table 1, Nos. 4-8). Using secondary alkyl bromides instead of n-butyl bromide, the carbamate esters were obtained in higher yields (Table 1, Nos. 2, 4-8).

The reaction is considered to proceed as follows. Carbon dioxide reversibly reacts with the aliphatic amine to form carbamic acid, as Eq. 2. Carbamate anion formed attacks alkyl halide to give carbamate ester, Eq. 3.



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