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# Novel Synthesis of Carbamate Ester from Carbon Dioxide, Amines, and Alkyl Halides

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A novel synthesis of carbamate ester using carbon dioxide as a direct material is reported in this article. The direct reaction of carbon dioxide, aliphatic amines, and alkyl halides was found to give the corresponding alkyl carbamate esters in good yields. Reactions using secondary alkyl bromides gave carbamate esters in higher yields than those using primary or tertiary alkyl bromides. The carbamate ester yields increased with the addition of *N*,*N*-dimethylformamide to the reaction system of carbon dioxide, amines and, alkyl halides. This reaction is considered to proceed by an $S_N2$ displacement reaction of the alkyl halide by the carbamate anion formed from the reaction of carbon dioxide and the amine.

The chemical utilization of carbon dioxide as a raw material in the synthetic chemical industry has so far been limited, because the reactivity of carbon dioxide is considered to be one of the lowest of all carbon compounds. However, carbon dioxide is well-known, to easily react with nucleophilic reagents, such as Grignard reagent or organometallic compounds.[1] Similarly, amine attacks carbon dioxide to form carbamic acid:

$$R_2NH + CO_2 \rightarrow R_2NCOOH \quad (1)$$

Carbamic acid, itself, however, has not been isolated and has been known only as a reaction intermediate in the hydrolysis reaction of carbamate ester or in the hydration reaction of isocyanate.[2] Thus, carbamic acid is very unstable by easy decomposition to carbon dioxide and amine; its esters, however, are stable compounds.

Carbamate esters[3] have so far been prepared by the reactions of amines with alkyl chloroformate, and alcohols with carbamoyl chloride or isocyanate, which were made from phosgene as a starting material. The starting materials for the preparation of carbamate esters, such as phosgene, isocyanate, carbamoyl chloride, and chloroformate, are highly toxic and inconvenient to use for the syntheses of carbamate esters.

The syntheses of carbamate esters by reactions using carbon dioxide as a direct starting component have been reported in recent years.[4-11] Also, we have previously reported that carbon dioxide and aliphatic amine reacted with epoxide to give 2-hydroxyalkyl carbamate in high yields,[12,13] with vinyl ether to give 1-alkoxyalkyl carbamate selectively,[14] and with ortho ester to give the corresponding alkyl carbamate in high yields.[15] In the course of further studies we found that the reaction of carbon dioxide and amines with alkyl halides formed the corresponding carbamate esters (Eq. 2).[16]

$$R_2NH + CO_2 + R'X \rightarrow R_2NCOOR' + [R_2NH_2]^+X^- + [R_2R'NH]^+X^- \quad (2)$$

The structures and reactivities of alkyl halides and amines are considered to be of importance for reactions with carbon dioxide, since the amine reacts directly with the alkyl halide to form an ammonium halide salt. In this paper, we describe the details of reactions of carbon dioxide with amines and alkyl halides to yield carbamate esters.

## Results and Discussion

Carbon dioxide reacted with secondary aliphatic amines and alkyl halides to give the corresponding alkyl carbamates with two kinds of ammonium halide salts, depending on the reactivities and structures of the amine and alkyl halide and the reaction conditions (Eqs. 2—4):

$$R_2NH + CO_2 + R'\text{-}X \rightarrow R_2NCOOR' + [R_2NH_2]^+X^- \quad (3)$$
$$R_2NH + R'\text{-}X \rightarrow [R_2R'NH]^+X^- \quad (4)$$

One of the ammonium halide salts is a secondary ammonium salt which is formed by a reaction of the amine and hydrogen halide released as by-products of carbamate ester formation. The other is a tertiary ammonium salt which is obtained by a direct reaction of the amine and alkyl halide.

Reactions of carbon dioxide, diethylamine ($Et_2NH$) and various isomeric butyl halides were investigated in detail concerning the reaction conditions for the synthesis of the carbamate ester. Table 1 shows the carbamate ester yield and the total recovered amount of ammonium salt under various reaction conditions. Butyl chloride hardly gave the carbamate ester at 60 °C, but carbamate ester was obtained in 18% yield at 100 °C and increased slightly at higher temperature (Runs 1—3).

The yield of carbamate ester was nearly constant for longer reaction times, but the formation of tertiary ammonium salt, which was obtained by the direct reaction of diethylamine and butyl chloride, increased (Runs 2 and 4). In the case of butyl bromide, the carbamate ester was obtained in 8% yield at 40 °C, though the amount of secondary ammonium salt,

Table 1. The Reaction of Diethylamine, $CO_2$, and Various Butyl Halides[a]

| Run | *n*-Bu-X | Temp | Time | Yield of products | |
|---|---|---|---|---|---|
| | | | | Carbamate | Ammonium salt |
| | | °C | day | %[b] | g[c] |
| 1 | *n*-Bu-Cl | 60 | 1 | 0.9 | 0 |
| 2 | *n*-Bu-Cl | 100 | 1 | 18 | 4.7 |
| 3 | *n*-Bu-Cl | 120 | 1 | 22 | 7.4 |
| 4 | *n*-Bu-Cl | 100 | 2 | 25 | 6.3 |
| 5 | *n*-Bu-Cl | 120 | 2 | 22 | 6.2 |
| 6 | *n*-Bu-Br | 40 | 1 | 8 | 1.5 |
| 7 | *n*-Bu-Br | 60 | 1 | 21 | 9.8 |
| 8 | *n*-Bu-Br | 70 | 1 | 21 | 12.6 |
| 9 | *n*-Bu-Br | 80 | 1 | 22 | 14.4 |
| 10 | *n*-Bu-Br | 100 | 1 | 20 | 14.1 |
| 11 | *n*-Bu-Br | 120 | 1 | 17 | 14.4 |
| 12 | *n*-Bu-Br | 70 | 2 | 31 | 14.4 |
| 13 | *n*-Bu-Br | 70 | 4 | 31 | 14.5 |
| 14 | *n*-Bu-I | 20 | 1 | 12 | 0 |
| 15 | *n*-Bu-I | 40 | 1 | 20 | 9.0 |
| 16 | *n*-Bu-I | 60 | 1 | 14 | 17.3 |
| 17 | *n*-Bu-I | 70 | 1 | 13 | 15.8 |
| 18 | *n*-Bu-I | 100 | 1 | 10 | 15.4 |
| 19 | *n*-Bu-I | 120 | 1 | 8 | 18.1 |
| 20 | *n*-Bu-I | 40 | 2 | 20 | 10.3 |

a) $Et_2NH$: 0.2 mol, R-X: 0.1 mol, $CO_2$: 40 atm. b) The corresponding alkyl diethylcarbamate. Yield based on R-X by GLC analysis. c) Recovered amount of ammonium salt.

Table 2. The Reaction of Diethylamine, $CO_2$, and Various Alkyl Bromides[a]

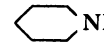
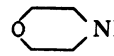
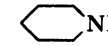
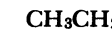
| Run | Bu-X | Temp | Time | Yield of products | |
|---|---|---|---|---|---|
| | | | | Carbamate | Ammonium salt |
| | | °C | day | %[b] | g[c] |
| 1 | *s*-Bu-Br | 60 | 1 | 17 | 1.6 |
| 2 | *s*-Bu-Br | 70 | 1 | 30 | 4.0 |
| 3 | *s*-Bu-Br | 100 | 1 | 56 | 10.7 |
| 4 | *s*-Bu-Br | 120 | 1 | 54 | 12.0 |
| 5 | *s*-Bu-Br | 70 | 2 | 48 | 7.3 |
| 6 | *s*-Bu-Br | 100 | 2 | 62 | 12.7 |
| 7 | *t*-Bu-Br | 60 | 1 | 14 | 6.7 |
| 8 | *t*-Bu-Br | 70 | 1 | 19 | 11.6 |
| 9 | *t*-Bu-Br | 100 | 1 | 18 | 17.6 |
| 10 | *t*-Bu-Br | 120 | 1 | 12 | 13.1 |
| 11 | *t*-Bu-Br | 70 | 2 | 24 | 13.0 |
| 12 | *n*-Bu-Br | 70 | 2 | 31 | 14.4 |

a) $Et_2NH$: 0.2 mol, R-X: 0.1 mol, $CO_2$: 40 atm. b) The corresponding alkyl diethylcarbamate. Yield based on R-X by GLC analysis. c) Recovered amount of ammonium salt.

which corresponded to the amount of ammonium salt obtained as the by-product of the carbamate ester synthesis, was also obtained (Run 6). The carbamate ester yield was 20—22% from 60 to 100 °C (Runs 7—10). Also, the amount of tertiary ammonium salt, obtained by a direct reaction of the amine and alkyl halide, increased with increasing the reaction temperature (Runs 6—11). Under reaction conditions greater than 80 °C, about 50% of the butyl bromide directly reacted with the amine to give the tertiary ammonium salt (Eq. 4). At 70 °C for 2 days, carbamate ester was obtained in 31% yield; then, the ester yield was almost constant (Runs 12 and 13). Butyl iodide gave the carbamate ester in 20% yield at 40 °C; however, a direct reaction of amine and alkyl halide was preferred to a carbamate ester synthesis at higher temperatures (Runs 14—20).

In conclusion, various butyl halides such as the chloride, bromide, and iodide reacted with carbon dioxide and diethylamine to yield butyl diethylcarbamate in 25, 31, and 20%, respectively, under each best reaction condition (Runs 4, 12, and 15). Since the reactivity of butyl chloride to nucleophilic reagents is low, a higher reaction temperature was required for the carbamate ester synthesis. In the case of butyl iodide, the reaction was accompanied by the formation of a considerable amount of tertiary ammonium iodide salt, which was obtained from a direct reaction of

Table 3. Reaction of $CO_2$, Various Amines, and Alkyl Halides[a]

| Run | Amine | Alkyl halide | Product | |
|---|---|---|---|---|
| | | | Carbamate | Yield/%[b] |
| 1 | $Et_2NH$ | $CH_3CH_2$-Br | $Et_2NCOO$-$CH_2CH_3$ | 22 |
| 2 |  | $CH_3CH_2$-Br |  | 3.5 |
| 3 |  | $CH_3CH_2$-Br |  | 0 |
| 4 | $Et_2NH$ | $CH_3CH_2CH_2$-Br | $Et_2NCOO$-$CH_2CH_2CH_3$ | 32 |
| 5 |  | $CH_3CH_2CH_2$-Br |  | 0.5 |
| 6 | $((CH_3)_2CH)_2NH$ | $CH_3(CH_2)_3$-Br | $((CH_3)_2CH)_2NCOO$-$(CH_2)_3CH_3$ | 11 |
| 7 | $Et_2NH$ | $PhCH_2$-Cl | $Et_2NCOO$-$CH_2Ph$ | 7 |
| 8 | $Et_2NH$ | $(CH_3)_2CH$-Br | $Et_2NCOO$-$CH(CH_3)_2$ | 53 |
| 9 |  | $(CH_3)_2CH$-Br |  | 37 |
| 10 | $Et_2NH$ | $(CH_3)_2CHCH_2$-Br | $Et_2NCOO$-$CH_2CH(CH_3)_2$ | 29 |
| 11 | $Et_2NH$ |  | $Et_2NCOO$- | 3 |
| 12[c] | $CH_3CH_2CH_2NH_2$ | $CH_2Br_2$ | $(CH_3CH_2CH_2NHCOO)_2CH_2$ | 1[d] |
| 13 | $Ph_2NH$ | $CH_3CH_2CH_2$-Br | — | 0 |
| 14 | $Ph(CH_3)NH$ | $CH_3CH_2CH_2$-Br | — | 0 |
| 15 | $PhNH_2$ | $CH_3(CH_2)_3$-Br | — | 0 |

a) Amine; 0.25 mol, alkyl halide; 0.1 mol, $CO_2$; 40 atm, time; 48 h, temp; 70°C. b) The carbamate ester yields based on alkyl halide were determined by GLC. c) $CH_3CH_2CH_2NH_2$: 0.4 mol, $CH_2Br_2$: 0.1 mol. d) The isolated yield.

diethylamine and butyl iodide. The reaction of butyl bromide, carbon dioxide and diethylamine gave the carbamate ester in the highest yield of all butyl halides.

The steric effect of the alkyl group in the reaction of carbon dioxide, diethylamine, and various isomeric butyl bromides was studied (Table 2). The carbamate ester yields obtained using a secondary alkyl bromide were compared with those using primary and tertiary alkyl bromides. In the case of using *s*-butyl bromide, the formation of the carbamate ester was preferred to the formation of ammonium salt (the direct reaction of amine and alkyl bromide), and occurred in higher yields (Run 6). Since the reactivities of primary alkyl bromides, such as butyl and isobutyl bromides, with an amine are higher than that of *s*-butyl bromide, the direct reaction with the amine was preferred to the carbamate ester synthesis (Table 2: Runs 5 and 12, and Table 3: Run 10). Owing to the steric hindrance of the tertiary alkyl group, the reactivity of the *t*-butyl bromide to the nucleophilic reagents was low (Runs 7—11).

The effect of the molar ratio of diethylamine to butyl bromide, [$Et_2NH$]/[*n*-BuBr], on carbamate ester yield, was examined in detail, as shown in Fig. 1. The carbamate ester yield increased with an increase in the molar ratio, [$Et_2NH$]/[*n*-BuBr]. The ester yield was approximately constant when the value of [$Et_2NH$]/[*n*-BuBr] was over 2.

The results of the reaction of carbon dioxide, various amines, and various alkyl halides are summarized in Table 3. While aliphatic amines gave the corresponding carbamate esters (Runs 1, 2, and 4—12), no aromatic amines gave the carbamate esters at all (Runs 13—15). Also, the aliphatic substituent groups of the amine exerted an influence on the synthesis of the carbamate ester by the reaction of carbon dioxide, amine, and alkyl halide (Runs 1, 2 and 3: 4 and 5: 8 and 9).

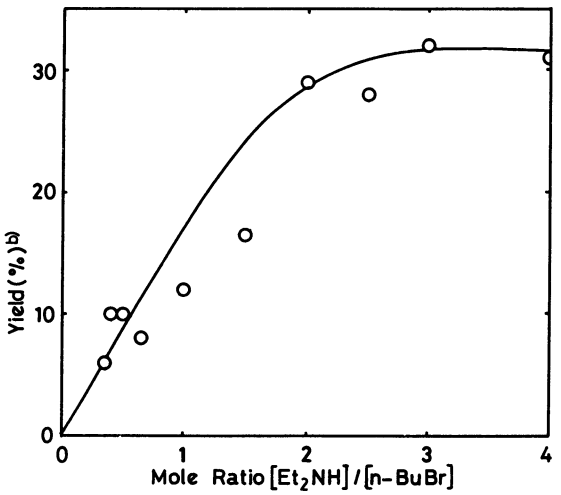



Fig. 1. Effect of [$Et_2NH$]/[*n*-BuBr] mole ratio on the reaction of $Et_2NH$, *n*-BuBr, and $CO_2$.[a]
a) Time: 24 h, temp: 70°C. b) Yield of $Et_2NCOO$-*n*-Bu based on *n*-BuBr.

As the carbon number in the alkyl bromides increased, the yield of the carbamate ester increased. The reaction of carbon dioxide and diethylamine with ethyl, propyl, or butyl bromide, gave the corresponding carbamate ester in 22, 32, or 42%,[16] respectively (Runs 1 and 4). The carbamate ester yields by a reaction using secondary alkyl bromides are higher than those

using primary alkyl bromides (Runs 4 and 8: 5 and 9). Cyclohexyl bromide gave the corresponding carbamate ester in 3% yield, because of the steric effect of the cyclohexane ring (Run 11). Methylene dibromide reacted with carbon dioxide and propylamine to give methylene bis(propylcarbamate) (Run 12). This product can not be obtained by other synthetic methods, since it is the ester of methanediol and propylcarbamic acid, which are both unstable and not isolable.

It was considered that the polarity of the reaction system influenced the reaction rate, since the synthetic reaction of carbamate ester from aliphatic amines, alkyl halides, and carbon dioxide is a nucleophilic substitution. The addition of DMF (*N,N*-dimethylformamide) into the reaction mixture resulted in an increase in the carbamate ester yield at the lower temperatures. By the addition of 5 mol% DMF for diethylamine, the carbamate ester yield increased from 8 to 11% at 40 °C, and from 22 to 32% at 80 °C. However, the addition of DMF did not exert any influence on the carbamate ester yield at 120 °C. The carbamate ester yields gradually decreased with an increase in the DMF concentration at any temperature, because the addition of DMF resulted in a dilution of the reaction system. No additive effects of other solvents such as dimethyl sulfoxide, acetonitrile, alcohols, tertiary amine, and ether were observed in the synthetic reaction of carbamate ester at any reaction temperature using any additive amount.

The reaction is considered to proceed as follows. Carbon dioxide reversibly reacts with the aliphatic amine to form carbamic acid (Eq. 1). Carbamic acid dissociates to a carbamate anion and a proton (Eq. 5). Then, the carbamate anion attacks the alkyl halide to produce the carbamate ester (Eq. 6). This reaction is considered to be an $S_N2$ displacement reaction, because the yield of the carbamate ester obtained using cyclohexyl bromide is considerably lower than that using acyclic alkyl bromides.[17] Also, any reactions of carbon dioxide, amines, and alkyl halides give the corresponding carbamate esters without the formation of other isomeric alkyl carbamate esters:

$$R_2NCOOH \rightarrow R_2NCOO^- + H^+ \quad (5)$$

$$R_2NCOO^- + R'\text{-}X \rightarrow R_2NCOOR' + X^- \quad (6)$$

In conclusion, the reaction of amine, carbon dioxide, and alkyl halide to form the carbamate ester accompanied the direct reaction of amine and alkyl halide to yield ammonium salt. In this reaction the secondary alkyl bromides gave the corresponding carbamate ester in high yields. This reaction mechanism is an $S_N2$ displacement reaction in which the carbamate anion, formed from carbon dioxide and amine, attacks alkyl halide.

## Experimental

**Materials.** Various commercially available amines and alkyl halides were purified by refluxing and distilling over calcium hydride and stored under a nitrogen atmosphere. Commercial available high-purity carbon dioxide gas was introduced directly into an autoclave from a gas cylinder without further purification.

**Measurements.** IR spectra were recorded on a Hitachi 260-50 apparatus, and NMR spectra were recorded on a Hitachi R-24 spectrometer operating at 60 MHz and JEOL FX90Q at 90 MHz, using hexamethyldisiloxane (HMDS) as the internal standard. GC-MS spectra were measured by a Shimadzu QP-1000 spectrometer, and gas-liquid chromatogram (GLC) were recorded on a Shimadzu GC-4C apparatus with a thermal conductivity detector.

**Preparations of Carbamate Ester.** A typical example for the synthesis of 1-methylpropyl diethylcarbamate (*s*-butyl diethylcarbamate) is as follows.

A 100 $cm^3$ stainless-steel autoclave was swept free of air by displacement with nitrogen. Into the autoclave was added a mixture of diethylamine (18.3 g, 0.25 mol) and *s*-butyl bromide (13.7 g, 0.10 mol). Carbon dioxide gas was then introduced directly from the gas cylinder until the pressure reached 40 atm ($4.1\times10^6$ Pa). After the autoclave was allowed to stand in an oil bath controlled at 70 °C for 48 h, the excess carbon dioxide gas was released and the contents of the reaction mixture were filtered to remove any ammonium bromide salts. The filtrate was subjected to fractional distillation under reduced pressure to isolate the product, *s*-butyl diethylcarbamate, bp 67.0—67.3 °C/6 mmHg† (7.5 g, 43%).

Preparations of other carbamate esters were carried out using a similar procedure.

**Identification of the Products. Butyl Diethylcarbamate:** bp 111.2—111.4 °C/30 mmHg (lit,[18] 60 °C/0.05 mmHg); IR (neat) 1705 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.8—1.8 (13H, m, $(CH_3CH_2)_2N$ and $CH_3CH_2CH_2CH_2$-O), 3.30 (4H,q,$(CH_3CH_2)_2N$), and 4.06 (2H, t, $CH_3CH_2CH_2CH_2$-O); MS(70 eV) *m/z* 173($M^+$); Calcd for $C_9H_{19}NO_2$: M, 173.

**2-Methylpropyl Diethylcarbamate (Isobutyl Diethylcarbamate):** bp 73.0—73.8 °C/5.0 mmHg; IR (neat) 1700 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.6—1.3 (12H, m, $(CH_3CH_2)_2N$ and $(CH_3)_2CHCH_2$-O), 1.8 (1H, m, $(CH_3)_2CHCH_2$-O), 3.17 (4H, q, $(CH_3CH_2)_2N$), and 3.70 (2H, d, $(CH_3)_2CHCH_2$-O); Found: C, 62.21; H, 11.00; N, 8.13%; $M^+$, 173. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09%; M, 173.

**1-Methylpropyl Diethylcarbamate (*s*-Butyl Diethylcarbamate):** bp 67.0—67.3 °C/6.0 mmHg; IR (neat) 1695 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.6—1.9 (14H, m, $(CH_3CH_2)_2N$ and $CH_3CH_2CH(CH_3)$-O), 3.17 (4H, q, $(CH_3CH_2)_2N$), and 4.63 (1H, m, $CH_3CH_2CH(CH_3)$-O); Found: C, 62.41; H, 11.07; N, 8.09%; $M^+$, 173. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09%; M, 173.

**1,1-Dimethylethyl Diethylcarbamate (*t*-Butyl Diethylcarbamate):** bp 28.4 °C/3.0 mmHg; IR (neat) 1690 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.74 (6H, t, $(CH_3CH_2)_2N$), 1.07 (9H, s, $(CH_3)_3C$-O), and 2.87 (4H, q, $(CH_3CH_2)_2N$); Found: C, 62.32; H, 11.05; N, 8.08%; $M^+$, 173. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09%; M, 173.

† 1 mmHg≈133.322 Pa.

**Ethyl Diethylcarbamate:** bp 60.8—61.2 °C/13 mmHg (lit,[19] bp 62—63 °C/14 mmHg); IR (neat) 1700 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=1.1 (9H, m, ($CH_3CH_2$)$_2$N and $CH_3CH_2$-O), 3.24 (4H, q, ($CH_3CH_2$)$_2$N), and 4.12 (2H, t, $CH_3CH_2$-O).

***N*-Ethoxycarbonylpiperidine:** bp 57.7—58.0 °C/1.5 mmHg (lit,[20] bp 55—56 °C/0.9 mmHg); IR (neat) 1705 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.97 (3H, t, $CH_3CH_2$-O), 1.3 (6H, m, -($CH_2$)$_3$-), 3.20 (4H, m, -$CH_2NCH_2$-), and 3.75 (2H, q, $CH_3CH_2$-O).

**Propyl Diethylcarbamate:** bp 58.6—59.0 °C/4.9 mmHg; IR (neat) 1700 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.7—1.4 (9H, m, ($CH_3CH_2$)$_2$N and $CH_3CH_2CH_2$-O), 1.6 (2H, m, $CH_3CH_2CH_2$-O), 3.27 (4H, q, ($CH_3CH_2$)$_2$N), and 3.98 (2H, t, $CH_3CH_2CH_2$-O); Found: C, 60.16; H, 10.81; N, 8.57%; $M^+$, 159. Calcd for $C_8H_{17}NO_2$: C, 60.34; H, 10.76; N, 8.79%; M, 159.

***N*-(Propyloxycarbonyl)piperidine:** bp 86.0—86.5 °C/4.4 mmHg; IR (neat) 1695 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.87 (3H, t, $CH_3CH_2CH_2$-O), 1.1—1.9 (8H, m, $CH_3CH_2$-$CH_2$-O and -($CH_2$)$_3$-), 3.27 (4H, m, -$CH_2NCH_2$-), and 3.94 (2H, t, $CH_3CH_2CH_2$-O); Found: C, 63.13; H, 10.11; N, 8.09%; $M^+$, 171. Calcd for $C_9H_{17}NO_2$: C, 63.12; H, 10.00; N, 8.17%; M, 171.

**Butyl Bis(1-methylethyl)carbamate:** bp 55.9—56.9 °C/2.0 mmHg; IR (neat) 1695 $cm^{-1}$ (ester C=O); $^1H$ NMR ($CDCl_3$) $\delta$=0.6—1.8 (13H, m, (($CH_3$)$_2$CH)$_2$N and $CH_3CH_2$-$CH_2CH_2$-O), 3.8 (2H, m, (($CH_3$)$_2$CH)$_2$N), and 4.00 (2H, t, $CH_3CH_2CH_2CH_2$-O); Found: C, 65.63; H, 11.55; N, 6.96%; $M^+$, 201. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.51; N, 6.95%; M, 201.

**Benzyl Diethylcarbamate:** bp 93.0—94.0 °C/2.0 mmHg; IR (neat) 1700 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.9 (6H, t, ($CH_3CH_2$)$_2$N), 3.07 (4H, q, ($CH_3CH_2$)$_2$N), 5.00 (2H, s, $C_6H_5CH_2$-O), and 7.13 (5H, s, $C_6H_5CH_2$-O); Found: C, 69.66; H, 8.35; N, 6.71%; $M^+$, 207. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.26; N, 6.76%; M, 207.

**1-Methylethyl Diethylcarbamate:** bp 44.8—45.4 °C/3.6 mmHg; IR (neat) 1700 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.6-1.5 (12H, m, ($CH_3CH_2$)$_2$N and ($CH_3$)$_2$CH-O), 3.13 (4H, q, ($CH_3CH_2$)$_2$N), and 4.73 (1H, m, ($CH_3$)$_2$CH-O); Found: C, 60.06; H, 10.75; N, 8.39%; $M^+$, 159. Calcd for $C_8H_{17}NO_2$: C, 60.34; H, 10.76; N, 8.79%; M, 159.

***N*-(1-Methylethoxycarbonyl)piperidine:** bp 61.2—61.4 °C/1.4 mmHg; IR (neat) 1695 $cm^{-1}$ (ester C=O); $^1H$ NMR ($CDCl_3$) $\delta$=0.8—1.8 (12H, m, ($CH_3$)$_2$CH-O and -($CH_2$)$_3$-), 3.27 (4H, m, -$CH_2NCH_2$-), and 4.76 (1H, m, ($CH_3$)$_2$CH-O); Found: C, 63.14; H, 9.98; N, 8.15%; $M^+$, 171. Calcd for $C_9H_{17}NO_2$: C, 63.12; H, 10.00; N, 8.17%; M, 171.

**Cyclohexyl Diethylcarbamate:** bp 83.1—83.7 °C/1.0 mmHg; IR (neat) 1710 $cm^{-1}$ (ester C=O); $^1H$ NMR($CDCl_3$) $\delta$=0.6—2.0 (16H, m, ($CH_3CH_2$)$_2$N and -($CH_2$)$_5$-), 3.14 (4H, q, ($CH_3CH_2$)$_2$N), and 4.50 (1H, m, CH-O); Found: C, 66.23; H, 10.80; N, 7.03%; $M^+$, 199. Calcd for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03%; M, 199.

**Methylene Bis(propylcarbamate):** mp 80.0—81.0 °C; IR (KBr pellet) 1695 $cm^{-1}$ (ester C=O); $^1H$ NMR ($CDCl_3$) $\delta$=0.85 (6H, m, ($CH_3CH_2CH_2NHCOO$)$_2$), 1.50 (4H, m, ($CH_3CH_2$-$CH_2NHCOO$)$_2$), 3.10 (4H, m, ($CH_3CH_2CH_2NHCOO$)$_2$), 5.40 (2H, s, ($CH_3CH_2CH_2NHCOO$)$_2$), and 5.6 (2H, s, O-$CH_2$-O); Found: C, 49.75; H, 8.52; N, 12.71%. Cacld for $C_9H_{18}N_2O_4$: C, 49.53; H, 8.31; N, 12.84%.

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