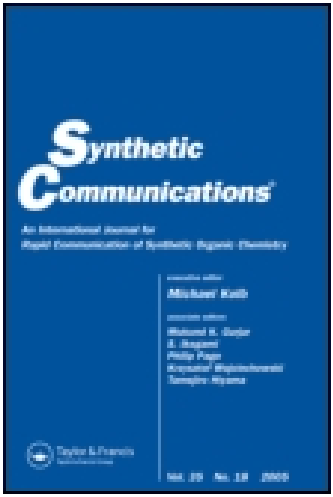

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Formation of 3-Hydroxyalkyl Carbamates from Carbon Dioxide, Amines and Oxetanes

Shigeru Ishii [a] , Ming Zhou [a] , Yasuhiko Yoshida [a] & Hiromichi Noguchi [a]

[a] Department of Applied Chemistry , Faculty of Engineering, Toyo University , Kujirai, Kawagoe, Saitama, 350-8585, Japan

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FORMATION OF 3-HYDROXYALKYL CARBAMATES FROM CARBON DIOXIDE, AMINES AND OXETANES

Shigeru Ishii, Ming Zhou, Yasuhiko Yoshida,* and Hiromichi Noguchi

Department of Applied Chemistry, Faculty of Engineering, Toyo University, Kujirai, Kawagoe, Saitama 350-8585, Japan

Abstract: The reactions of carbon dioxide, primary or secondary aliphatic amines and oxetanes at a CO_2 pressure of 40 atm at 100-120°C without any catalysts afforded new monocarbamates of 1,3-propanediols, with concomitant formation of amino alcohols from oxetanes and amines.

Production of useful chemicals by use of carbon dioxide as one of the starting materials is considered to be of great importance from the viewpoints of the reduction of the amount of CO_2 in the atmosphere to solve environmental problems and effective utilization of carbon resource. Thus, to date, a number of attempts have been made on the fixation of CO_2 into organic compounds in the presence of various catalysts. Specifically, organic carbamates, which are valuable synthetic intermediates and biologically active compounds,[1] have so far been prepared not

*To whom correspondence should be addressed; E mail: yoshida@eng.toyo.ac.jp

only by the use of phosgene via alkyl chloroformate, carbamoyl chloride or isocyanates,[1] which are all very toxic and more or less intractable, but also by the reactions using CO_2 as a direct raw material.[2-6] We have also disclosed that aliphatic amines and CO_2 react with epoxides to afford monocarbamates of the 1,2-ethanediols,[7] with vinyl ethers to yield 1-alkoxyalkyl carbamates,[8] and with alkyl halides[9] or ortho esters[10] to give alkyl carbamates. The present paper describes on an unprecedented synthesis of a series of 3-hydroxyalkyl carbamates from CO_2, aliphatic primary or secondary amines and oxetanes without any catalysts.

$$R^1R^2NH + CO_2 + \underset{1}{\square_O} \longrightarrow \underset{2}{R^1R^2NCO_2CH_2CH_2CH_2OH} \quad (1)$$

$$R^1R^2NH + \mathbf{1} \longrightarrow \underset{3}{R^1R^2NCH_2CH_2CH_2OH} \quad (2)$$

The reactions of oxetane (trimethylene oxide; **1**) with CO_2 and primary or secondary amines afforded monocarbamates of 1,3-propanediol (**2**; hydroxy carbamate) (eq. 1) with concomitant formation of aminoalcohols (**3**) from **1** and amines (eq. 2). Table 1 shows the effect of reaction temperature and time on the yields of 3-hydroxypropyl diethylcarbamate (**2a**) and 3-diethylamino-1-propanol (**3a**) in the reaction of CO_2, diethylamine and **1**. The yields of **2a** and **3a** became higher with a rise in reaction temperature (Runs 1, 2 and 5) and time (Runs 3, 4 and 5), reaching maximal yields of 30% and 43%, respectively, after 72 h at 120°C (Run 5). Besides, the yield of **3a** became increasingly greater than that of **2a** with increase in reaction temperature and time. These facts make it difficult to prepare **2a** in a yield over 40%.

Table 1. Reaction of CO_2, Diethylamine, and Oxetane[a]

Run	Temp. (°C)	Time (h)	Yield (%)[b] **2a** (R^1=R^2=Et)	**3a** (R^1=R^2=Et)
1	80	72	5	6
2	100	72	18	20
3	120	24	14	20
4	120	48	22	30
5	120	72	30	43

[a] Reaction conditions: CO_2, 40 atm; diethylamine, 80 mmol; oxetane, 40 mmol. [b] GLC yield based on oxetane.

Table 2 presents the results of similar reactions of CO_2, various amines and oxetanes. Evidently, the reactions are greatly influenced by the structure of amines and oxetanes. Hydroxy carbamates were obtained in low or fair yields by the reaction of CO_2, aliphatic amines including piperidine and morpholine, and **1** (Runs from 5 to 9). In the reaction of CO_2 and **1** with an aromatic amine of low basicity, e. g. N-methylaniline, neither the expected hydroxy carbamate nor other products were obtained (Run 10) in agreement with the results in other monocarbamates syntheses.[7,9b,10]

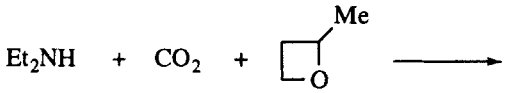
The reaction of CO_2, diethylamine and 2-methyloxetane (**4**) yielded two carbamates, i. e., 3-hydroxy-1-methylpropyl diethylcarbamate (**5**) and 3-hydroxybutyl diethylcarbamate (**6**) in a molar ratio of 5:95 (Run 9), as a result of the methine-oxygen and the methylene-oxygen bond scission, respectively (eq. 3). It would be reasonable to assume that the nucleophilic attack of carbamate anion, which is generated by the reaction of CO_2 with diethylamine,[11] on the α-methylene carbon of

Table 2. Reaction of CO_2, Various Amines, and Oxetanes[a]

Run	Amine	Oxetane	Hydroxy carbamate Yield (%)[b]
5	Et_2NH	Oxetane	**2a** 30[c]
6	Piperidine	Oxetane	**2b** 25
7	Morpholine	Oxetane	**2c** 10
8	$PrNH_2$	Oxetane	**2d** 9
9	Et_2NH	2-Methyloxetane	**5** / **6** 8[d]
10	PhMeNH	Oxetane	— 0

[a] Reaction conditions: CO_2, 40 atm; amines, 80 mmol; oxetanes, 40 mmol; 120°C, 72 h. [b] Isolated yield based on oxetanes. [c] GLC yield based on oxetane. [d] The product is a mixture of **5** and **6** in a molar ratio of 5:95.

4 predominates over that on the methyl-substituted α-methylene carbon, mainly owing to the steric hindrance exerted by the methyl group. The reactivity of **4** is much lower than that of **1** (cp. Run 9 with Run 5).



4

$$Et_2NCO_2CHMeCH_2CH_2OH + Et_2NCO_2CH_2CH_2CHMeOH \quad (3)$$

5 **6**

Further, though required, high reaction temperatures, the present reactions were totally free from the formation of oligomers or polymers of oxetanes, in contrast to

the corresponding reactions using epoxides.[7] Additionally, the formation of hydroxy carbamates in the reactions using tetrahydrofuran instead of oxetanes could be confirmed only by IR investigation, since their yields were extremely low. These results reflect the decreasing reactivity of cyclic ethers due to the decreasing strain in their rings with increase in their ring size.

In summary, the reactions of CO_2, primary or secondary alkylamines, and oxetanes were found to afford 3-hydroxyalkyl carbamates. Although the yields of the monocarbamates were not high, the present reactions have the merit of not using toxic and harmful reagents.

EXPERIMENTAL SECTION

All commercially available amines were dried and distilled before use. Carbon dioxide gas was introduced into an autoclave directly from a gas cylinder until the pressure reached 40 atm. Oxetane[12] and 2-methyloxetane[13] were prepared and purified according to the literature, and identified by IR and NMR.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were acquired on $CDCl_3$ solutions containing TMS as the internal standard using a JNM-EX400 FT-NMR spectrometer (JEOL Ltd.). IR spectra were measured on a JEOL JIR-7000 FT-IR spectrometer. Elemental analyses were carried out with use of a PE2400 Series II CHNS/O Analyzer (The Perkin-Elmer Corporation).

The general reaction procedure was as follows. A mixture of oxetane (40 mmol) and amine (80 mmol) placed in a 100 mL stainless steel autoclave under a pressure of CO_2 (40 atm; 4.1×10^6 Pa) was heated at a prescribed temperature. After a given

time the reaction mixture was quantitatively analyzed by GLC or subjected to vacuum distillation to isolate the products. They were unambiguously identified by IR, NMR as well as by elemental analysis. Assignments of the NMR data of isomers **5** and **6** were made by taking into consideration their molar ratio of 5:95 in the mixture product.

3-Hydroxypropyl diethylcarbamate (2a): bp 85°C / 0.2 Torr; IR 3450, 1697, 1678 cm^{-1}; ^1H NMR δ 4.27 (t, 2H, OCH_2), 3.67 (t, 2H, CH_2OH), 3.28 (q, 4H, CH_3CH_2), 2.91 (s, 1H, *OH*), 1.85 (m, 2H, OCH_2CH_2), 1.12 (t, 6H, CH_3); ^{13}C NMR δ 156.9, 61.8, 58.8, 41.6, 32.8, 13.9. Anal. Calcd for $C_8H_{17}NO_3$: C, 54.84; H, 9.78; N, 7.99. Found: C, 54.50; H, 9.99; N, 7.64.

3-Hydroxypropyl 1-piperidinecarboxylate (2b): bp 117°C / 0.5 Torr; IR 3458, 1697, 1678 cm^{-1}; ^1H NMR δ 4.25 (t, 2H, OCH_2), 3.66 (t, 2H, CH_2OH), 3.41 (t, 4H, NCH_2), 2.90 (s, 1H, *OH*), 1.85 (m, 2H, OCH_2CH_2), 1.59 (m, 2H, $NCH_2CH_2CH_2$), 1.53 (br s, 4H, NCH_2CH_2); ^{13}C NMR δ 156.0, 61.7, 58.7, 44.8, 32.4, 25.6, 24.3. Anal. Calcd for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.39; H, 9.40; N, 7.39.

3-Hydroxypropyl 1-morpholinecarboxylate (2c): bp 124°C / 0.5 Torr; IR 3454, 1701, 1678 cm^{-1}; ^1H NMR δ 4.27 (t, 2H, $COOCH_2$), 3.65-3.67 (br s, 6H, OCH_2, CH_2OH), 3.47 (t, 4H, NCH_2), 2.70 (s, 1H, *OH*), 1.87 (m, 2H, OCH_2CH_2); ^{13}C NMR δ 155.9, 66.5, 62.2, 58.6, 43.9, 32.2. Anal. Calcd for $C_8H_{15}NO_4$: C, 50.78; H, 7.99; N, 7.40. Found: C, 50.68; H, 8.26; N, 7.40.

3-Hydroxypropyl propylcarbamate (2d): bp 110-118°C / 0.5 Torr; IR 3329, 1697 cm^{-1}; ^1H NMR δ 4.94 (s, 1H, *NH*), 4.22 (t, 2H, OCH_2), 3.66 (t, 2H, CH_2OH), 3.14 (q, 2H, $NHCH_2$), 2.85 (s, 1H, *OH*), 1.83 (m, 2H, OCH_2CH_2),

1.53 (m, 2H, CH_3CH_2), 0.92 (t, 3H, CH_3); ^{13}C NMR δ 157.2, 61.4, 58.6, 42.6, 32.3, 23.1, 11.1. Anal. Calcd for $C_7H_{15}NO_3$: C, 52.16; H, 9.38; N, 8.69. Found: C, 51.97; H, 9.67; N, 8.67.

3-Hydroxy-1-methylpropyl diethylcarbamate (5): bp 95-97°C / 1.2 Torr; IR 3450, 1697, 1678 cm^{-1}; ^1H NMR δ 5.10 (m, 1H, $CHCH_3$), 3.52-3.62 (m, 2H, CH_2OH), 3.28 (m, 4H, CH_3CH_2), 1.76-1.88 (m, 1H, $OCHCH_2$), 1.58-1.68 (m, 1H, $OCHCH_2$), 1.29 (d, 3H, $CHCH_3$), 1.12 (t, 6H, CH_3CH_2); ^{13}C NMR δ 156.38, 68.2, 58.4, 41.4, 40.0, 21.0, 13.5.

3-Hydroxybutyl diethylcarbamate (6): bp 95-97°C / 1.2 Torr; IR 3450, 1697, 1678 cm^{-1}; ^1H NMR δ 4.45-4.48 (m, 1H, OCH_2), 4.04-4.08 (m, 1H, OCH_2), 3.85 (m, 1H, $CHOH$), 3.28 (m, 4H, CH_3CH_2), 1.77-1.84 (m, 1H, OCH_2CH_2), 1.54-1.68 (m, 1H, OCH_2CH_2), 1.22 (d, 3H, $CHCH_3$), 1.12 (t, 6H, CH_3CH_2); ^{13}C NMR δ 156.44, 64.3, 62.0, 41.4, 39.1, 23.2, 13.5.

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