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A DIRECT SYNTHESIS OF CARBAMIC ESTER FROM CARBON DIOXIDE, VINYL ETHER AND AMINE

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1-Ethoxyethyl carbamate was obtained directly by the reaction of ethyl vinyl ether with carbon dioxide and amine such as dimethylamine and diethylamine.

Recent interest in the organic and bio-organic reactions of carbon dioxide has led to the development of syntheses of various compounds with carboxyl or carbonyl group, including high polymers.[1)] However, the reactions involving carbon dioxide and olefinic compounds so far reported are rather limited.[2,3,4,5)]

In the course of our studies[1)] on the reaction of carbon dioxide with cyclic compounds or unsaturated compounds, we found the formation of carbamic ester in the reaction system of carbon dioxide, vinyl ether and amine.

$$R_2NH \; + \; CO_2 \; + \; CH_2{=}CHOCH_2CH_3 \longrightarrow R_2NCOOCH(CH_3)OC_2H_5 \qquad (1)$$

(1)

A mixture of ethyl vinyl ether (EVE) and amine such as dimethylamine (Me_2NH) or diethylamine (Et_2NH) was placed in an autoclave and stirred under pressure of carbon dioxide at a temperature from 35 to 100°C for 70 hrs. The reaction mixture was subjected to distillation under reduced pressure to isolate the product, which was identified as the corresponding carbamic ester (1).

1-Ethoxyethyl diethylcarbamate (1, $R=C_2H_5$), b.p. 94°C/18 mmHg; Anal. Found: C, 57.00; H, 10.31; N, 7.51%. Calcd. for $C_9H_{19}NO_3$: C, 57.12; H, 10.12; N, 7.40%. 1-Ethoxyethyl dimethylcarbamate (1, $R=CH_3$), b.p. 82°C/20 mmHg; Anal. Found: C, 52.17; H, 9.52; N, 8.84%. Calcd. for $C_7H_{15}NO_3$: C, 52. 16; H, 9.38, N, 8.69%. IR: 1700 cm^{-1} (C=O), 1280 cm^{-1} (C-O-(C=O)-). In the ^1H NMR spectra of 1-ethoxyethyl dimethylcarbamate (Fig. 1), signals due to methyne (of 1-ethoxyethyl) and methyl (attached to the methyne) groups are found at 5.91 ppm (quartet) and 1.44 ppm (doublet), respectively, confirming the structure of (1).

As shown in Table 1, carbamic ester was obtained in 0.06 - 11% yield

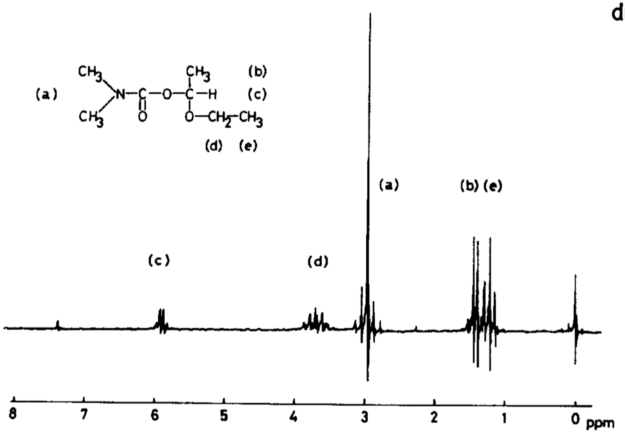


Figure 1. NMR spectrum of 1-ethoxyethyl dimethylcarbamate. (20% in $CDCl_3$)

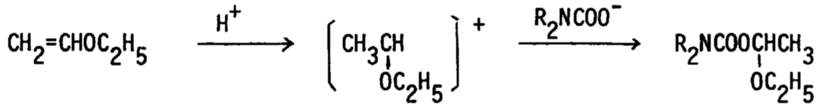
Table 1 The Formation of 1-Ethoxyethyl Carbamate (1) from Carbon Dioxide, Ethyl Vinyl Ether (EVE) and Amine[a)]

Amine	Amine/EVE mole ratio	Temp. (°C)	Yield of (1)[b)] (%)
Me_2NH	1	80	7.2
Et_2NH	1	80	3.7
Et_2NH	2	80	5.7
Et_2NH	10	80	11
Et_2NH	1	35	0.06
Et_2NH	1	100	11

a) CO_2; 50 kg/cm^2. Time; 70 hrs. b) On the basis of EVE.

depending upon the reaction conditions. The yield was higher at higher amine/EVE mole ratio and at elevated temperature. In these reactions, neither the regional isomer, 2-ethoxyethyl carbamate, nor the simple adduct of amine to vinyl ether was formed. The polymer of vinyl ether could not be detected either. Since the sole product is 1-ethoxyethyl carbamate, but not isomeric 2-ethoxyethyl ester, the reaction is considered to proceed by the electrophilic addition to vinyl ether of carbamic acid formed by the reversible reaction of carbon dioxide and amine, eq. (3) being the rate-determining step.

$$R_2NH + CO_2 \rightleftharpoons R_2NCOO^- + H^+ \qquad (2)$$



$$CH_2{=}CHOC_2H_5 \xrightarrow{H^+} \left[\begin{array}{l} CH_3CH \\ \quad | \\ \quad OC_2H_5 \end{array}\right]^+ \xrightarrow{R_2NCOO^-} \begin{array}{l} R_2NCOOCHCH_3 \\ \qquad\quad | \\ \qquad\quad OC_2H_5 \end{array} \qquad (3)$$

(1)

β-Substituted vinyl ether such as 2,3-dihydrofuran also gave carbamic ester in a 5.8% yield. This reaction is very interesting as a novel synthesis of carbamic ester[6)] by a direct fixation of carbon dioxide at moderate conditions.

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