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A DIRECT SYNTHESIS OF MONOCARBAMIC ESTER OF 1,2-DIOL FROM CARBON DIOXIDE, EPOXIDE AND AMINE

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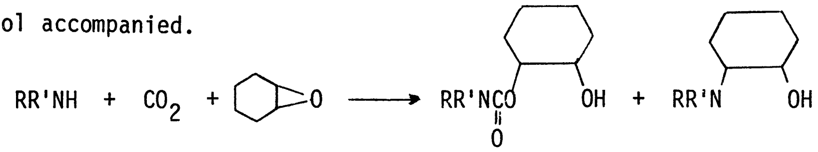
Monocarbamic ester of 1,2-diol derived from the corresponding 1,2-epoxide was obtained directly in a good yield by the reaction of epoxide, carbon dioxide, and primary or secondary amine.

Chemical fixation of carbon dioxide is of much interest in view of resource utilization as well as in connection with biochemical carbon dioxide fixation. In the course of our studies on the reaction of carbon dioxide and epoxide with organometallic catalyst systems,1) we have recently found that the reaction of tetrakis(dimethylamido)titanium (IV), carbon dioxide and epoxide gives dimethylcarbamic ester of 1,2-diol derived from the corresponding 1,2-epoxide in a quantitative yield.2) Further studies on this reaction have led to the finding that the carbamic ester is formed directly from carbon dioxide, epoxide and amine, together with amino alcohol as the by-product. The present communication describes this novel and simple method of the preparation of monocarbamic ester of 1,2-diol.

For example, a mixture of 1,2-epoxycyclohexane(ECH) and amine such as dimethylamine, diethylamine or propylamine was placed in an autoclave and stirred under pressure of carbon dioxide at 80°C for 22 hrs. The reaction mixture was subjected to distillation under reduced pressure to isolate the product and the product was recrystallized from petroleum ether to give the carbamic ester. (1, R =R'=CH_3; m.p. 52 - 53°C,2) 1, R=R'=C_2H_5; m.p. 34 - 35°C,3) 1, R=n-C_3H_7 , R'=H; m.p. 84 - 85°C3)). These compounds showed the infrared absorption of urethane carbonyl at 1700 cm^{-1}. As shown in Table 1, carbamic ester was formed selectively in a good yield by the reaction of carbon dioxide, ECH and diethylamine or propylamine. In the case of dimethylamine, the formation of a considerable amount of amino alcohol accompanied.



(1) (2)

Fig. 1 shows that the yield of carbamic ester (1) increased with temperature up to 80 - 90°C. In view of the fact that the yield of amino alcohol also increased with temperature, 80°C is preferable for the synthesis of the carbamic ester under the reaction conditions examined. Carbamic ester was obtained from other epoxides such as epoxyethane and 1,2-epoxypropane, but accompanied by a considerable amount of amino alcohol. In the case of epoxyethane the polymerization of the epoxide also took place. Since cyclic carbonate, which could be formed by the reaction of carbon dioxide and epoxide, was not detected in the reaction mixture of dialkylamine, carbon dioxide and ECH, the formation of carbamic ester by the reaction of amine and cyclic carbonate may be excluded. Therefore, the reaction between epoxide and either carbamic acid (3) or its ammonium salt (4) is considered as reasonable mechanism.

Table 1. The Reaction of Carbon Dioxide, Amine (RR'NH) and 1,2-Epoxycyclohexane[a)]

Run	R	R'	Yield (%)	
			Carbamic ester	Amino alcohol
1[b)]	Me	Me	42	40
2[c)]	Et	Et	62	5
3[c)]	n-Pr	H	54	5

a) CO_2 50 kg/cm^2, 80°C, 22 hrs.

b) Amine and epoxide 0.3 mol, respectively.

c) Amine and epoxide 0.2 mol, respectively.

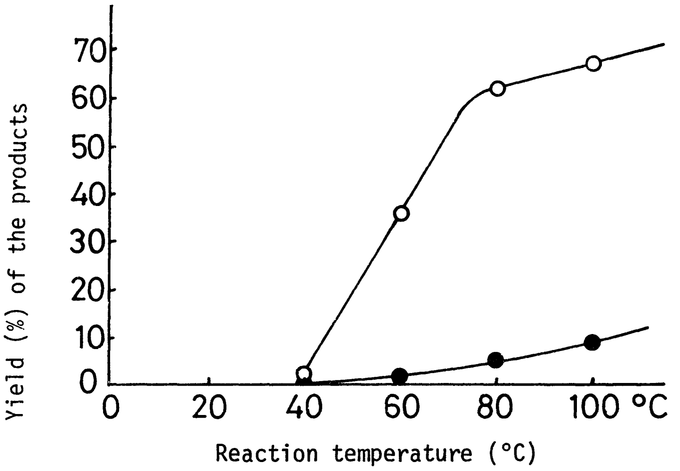
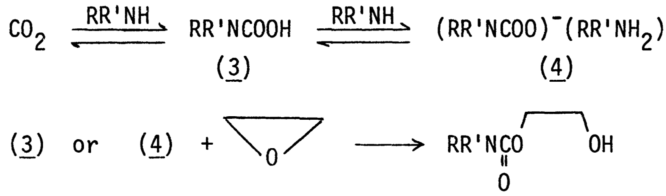


Fig. 1 Reaction of CO_2, Et_2NH and 1,2-Epoxycyclohexane.

CO_2; 50 kg/cm^2, 22 hrs.

○ Carbamate (1)

● Amino alcohol (2)



Recently, the formation of oxazolidone by the reaction of carbon dioxide with α-bromoacylophenones in the presence of aliphatic primary amine in methanol was reported.[4)] In this reaction, the attack of carbamic acid ammonium salt to the epoxide formed from the α-haloketone has been suggested. On the other hand, in the formation of carbamic ester from carbon dioxide, amine and vinyl ether,[5)] the structure of the product strongly indicates the mechanism involving the addition of carbamic acid (3) but not the salt (4). Further investigation is in progress.

References and Note

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