Synthesis of Carbamic Ester by a Reaction of Carbon Dioxide, Tetrakis(dimethylamido)titanium(IV) and Epoxide

Yasuhiko Yoshida and Shohei Inoue

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Hongo, Tokyo 113

(Received July 11, 1977)

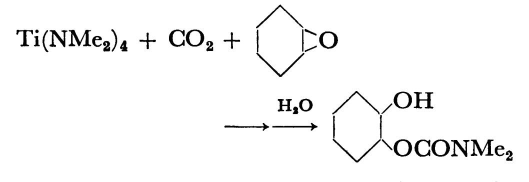
2-Hydroxycyclohexyl dimethylcarbamate was synthesized quantitatively by a reaction of carbon dioxide, tetrakis(dimethylamido)titanium(IV) and 1,2-epoxycyclohexane.

Carbon dioxide was inserted into the metal-nitrogen bond or the metal-oxygen bond to give metal carbamate or carbonate,[1] and the products were easily decomposed by water to regenerate carbon dioxide.

Since studies by Inoue *et al.*[2] suggested the possibility of the reaction of metal carbamate with epoxide to form carbamic ester resulting in the irreversible fixation of carbon dioxide, the reaction of tetrakis(dimethylamido)titanium(IV) ($Ti(NMe_2)_4$), carbon dioxide (CO_2) and 1,2-epoxycyclohexane was examined.

Results and Discussion

A reaction of $Ti(NMe_2)_4$, CO_2 and 1,2-epoxycyclohexane, followed by hydrolysis of the reaction mixture, was found to give 2-hydroxycyclohexyl dimethylcarbamate (**1**) in a high yield, thus



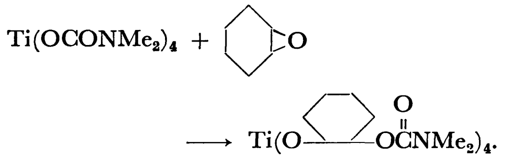
(1)

The carbamic ester (**1**) was confirmed to be in *trans*-form by comparison with an authentic sample prepared by a reaction of *trans*-1,2-cyclohexanediol with dimethylcarbamoyl chloride in the presence of pyridine. The main product of this reaction was carbamic ester (**1**), accompanied by small amounts of CO_2-epoxide copolymer (**2**), cyclic carbonate and a homopolymer of 1,2-epoxycyclohexane, depending upon the reaction conditions.

As shown in Table 1, the reactions were carried out under CO_2 pressure (50 kg/cm²), since the reaction did not occur at atmospheric pressure at room temperature. The reaction at 80 °C in a large excess of epoxide gave carbamic ester (**1**) in a quantitative yield (Run 7). Reactions carried out in benzene and THF (Runs 4 and 5) gave similar results. However, for the reaction carried out in dichloromethane, the yield of carbamic ester (**1**) was low and the by-products, such as CO_2-epoxide copolymer (**2**), cyclic carbonate and polyether were formed, although in small amounts. At 35 °C (Runs 1 and 2), carbamic ester (**1**) was obtained in a lower yield, but with no by-products. For the reaction of 1,2-epoxypropane, instead of 1,2-epoxycyclohexane, in THF at 80 °C over a period of 160 h, the carbamic ester yield was 58% and the amount of cyclic carbonate formed was 1/3 by weight of carbamic ester.

Since $Ti(NMe_2)_4$ has been reported to react rapidly with CO_2 to form $Ti(OCONMe_2)_4$,[3,4] the formation of carbamic ester is considered to proceed as follows:

$$Ti(NMe_2)_4 + CO_2 \longrightarrow Ti(OCONMe_2)_4 \quad (2)$$



(3)

This reaction is the first example of a metal carbamate and epoxide reaction resulting in the fixation of carbon dioxide.

$Ti(NMe_2)_4$ is considered to react preferentially with CO_2 even in the presence of epoxide, since $Ti(NMe_2)_4$ does not react with epoxyethane and 1,2-epoxypropane, as reported previously.[4] It was found that 1,2-epoxycyclohexane did not react with $Ti(NMe_2)_4$ at room temperature, but at 80 °C gave the polymer (poly-

Table 1. REACTION OF TETRAKIS(DIMETHYLAMIDO)TITANIUM, CARBON DIOXIDE AND 1,2-EPOXYCYCLOHEXANE[a]

Run	$Ti(NMe_2)_4$ (g)	Epoxide (g)	Solvent	Temp (°C)	Time (h)	Product (**1**)[b] (g)	Product (**1**)[b] (%)[c]	Product (**2**)[d] (g)
1	0.4	9.7	CH_2Cl_2	35	360	0.18	(13)	trace
2	1.0	9.7	THF	35	290	0.17	(5.0)	0
3	1.0	9.7	CH_2Cl_2	80	150	0.07	(2)	0.034
4	1.0	9.7	Benzene	80	210	1.7	(50)	0.027
5	1.0	9.7	THF	80	240	2.5	(74)	0.025
6	1.0	9.7	THF	80	23	0.30	(8.8)	0
7	1.0	39	—	80	220	3.4	(100)	0.007
8	1.8	3.1	THF	80	190	0.94	(15)	0

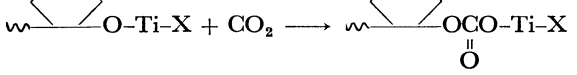
a) CO_2 50 kg/cm². Solvent 40 ml. b) 2-Hydroxycyclohexyl *N*,*N*-dimethylcarbamate. c) Yield based on four Ti–N bonds. d) Epoxide-CO_2 copolymer.

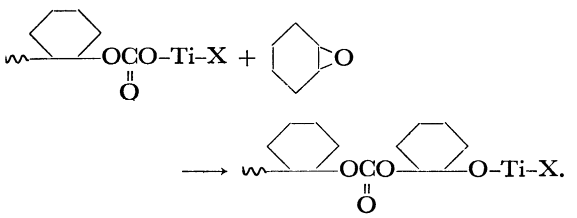
ether) in a 10% yield after 12 days. In the presence of CO_2, the homopolymerization of 1,2-epoxycyclohexane by $Ti(NMe_2)_4$ was not observed, except for the reaction in dichloromethane (Run 3).

It can be considered that the carbamic ester (**1**) is formed by the reaction of $Ti(NMe_2)_4$ with cyclic carbonate, the latter having been produced from CO_2 and epoxide. This mechanism, however, is believed to be negligible, since, in the reaction of 1,2-epoxycyclohexane under the present conditions, cyclic carbonate was hardly formed. Furthermore, the existence of unchanged $Ti(NMe_2)_4$ is most unlikely because of its extremely high reactivity with CO_2, which gives rise to $Ti(OCONMe_2)_4$.

An alternative mechanism for the formation of **1** would be the reaction of epoxide with carbamic acid, the latter being formed from carbon dioxide and amine which may be present in trace amounts. **1** would then react with titanium carbamate to regenerate carbamic acid. However, such a reaction requires the liberation of a stronger acid (carbamic acid) upon the reaction of the salt with a weaker acid (alcoholic group of **1**).

Concerning the formation of CO_2-epoxide copolymer as a by-product, the following mechanism can be considered, referring to the mechanism proposed for the formation of the CO_2-epoxide copolymer by an organozinc catalyst.[5,6)]


(4)


(5)

In accord with this mechanism, the reaction of 1,2-epoxycyclohexane and CO_2, with titanium isopropoxide as a catalyst, in THF at 80 °C for 210 h gave the copolymer (**2**), although in a low yield.

Experimental

Materials. Tetrakis(dimethylamido)titanium(IV) was synthesized from lithium dimethylamide and titanium tetrachloride in diethyl ether.[7)] After lithium chloride was filtered off and the solvent removed, distillation of the residual liquid afforded a yellow liquid product ($Ti(NMe_2)_4$), bp 75 °C/3 mmHg (lit,[7)] bp 44 °C/0.006 mmHg).

Commercially available epoxides, such as 1,2-epoxycyclohexane and 1,2-epoxypropane, and solvents, such as THF, benzene, and dichloromethane, were purified employing usual procedures and stored in a nitrogen atmosphere.

Commerical high-purity carbon dioxide gas was introduced into an autoclave directly from a gas cylinder without further purification.

Procedure. All reactions were carried out in a manner similar to that for Run 4, as follows.

A mixture of $Ti(NMe_2)_4$ (1 g, 4.5 mmol) and 1,2-epoxycyclohexane (10 ml, 99 mmol) in benzene (40 ml) was placed in a 200 ml autoclave and constantly stirred at 80 °C under CO_2 pressure (50 kg/cm^2). After 210 h of reaction, a few drops of water were added to the reaction mixture, the latter was filtered to remove insoluble materials, and the filtrate was concentrated under reduced pressure at room temperature. To the filtrate concentrate was added about 100 ml of petroleum ether with stirring. The mixture was seeded by a small amount of pure crystalline **1** and cooled in a refrigerator overnight, during which time white needles separated out. The crystals were filtered off and dried at room temperature *in vacuo*.

White needle-like crystals, *trans*-2-hydroxycyclohexyl dimethylcarbamate (**1**), mp 52—53 °C, (Found: C, 57.75; H, 9.31; N, 7.52; mol wt, 196 (V. P. O.), Calcd for $C_9H_{17}NO_3$: C, 57.71; H, 9.15; N, 7.48; mol wt, 187), was obtained in a 50% yield (1.7 g). NMR (chloroform-*d*): δ=1.2—2.2 (8H, m, cyclohexane-ring methylenes), 2.92 (6H, s, $N(CH_3)_2$), 3.41 (1H, s, OH), 3.56 (1H, m, hydroxyl-group methine), 4.48 (1H, m, carbamoyloxy-group methine). IR (KBr tablet method): 3500 cm^{-1} (O–H) and 1700 cm^{-1} (C=O).

After separation of the carbamic ester (**1**), the filtrate was concentrated and added to a large amount of methanol to give CO_2-epoxide copolymer, which was identified by IR spectrum,[5)] as a methanol insoluble fraction (27 mg).

We are grateful to Professor Teiji Tsuruta for valuable discussions.

References

1) S. Inoue, *Kagaku Zokan*, **63**, 33 (1974).

2) T. Tsuruta, K. Matsuura, and S. Inoue, *Makromol. Chem.*, **83**, 289 (1965); **103**, 118 (1967).

3) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **99**, 782; 792 (1977).

4) G. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Chem. Soc., A*, **1970**, 2550.

5) S. Inoue, *Prog. Polym. Sci. Jpn.*, **8**, 1 (1975).

6) S. Inoue, *Chemtech.*, **6**, 588 (1976).

7) A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *Eur. Polym. J.*, **7**, 289 (1971).