Reaction of Carbon Dioxide with 1-Phenylaziridine Catalyzed by Organo-antimony and -tin Compounds

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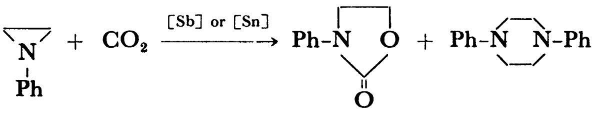
Synopsis. The reactions of carbon dioxide(CO_2) with 1-phenylaziridine(**1**) to afford 3-phenyl-2-oxazolidone(**2**) were carried out in the presence of organo-antimony and -tin compounds as catalysts. Tetraphenylstibonium bromide(Ph_4SbBr) and triphenyltin bromide(Ph_3SnBr) were found to be active catalysts. The use of a polar aprotic solvent, such as a HMPA, provided optimal reaction conditions.

In our previous papers,[1)] we reported that organometallic compounds of group IVA, VA, and VIA are effective catalysts for the cycloaddition reaction of CO_2 to oxiranes to afford the corresponding cyclic carbonates. However, little is known about the catalysts for the syntheses of 2-oxazolidones from the reactions of CO_2 with aziridines, except for the ammonium salts[2)] and iodine[3)] which are effective catalysts for the reactions of CO_2 with 1-substituted phenylaziridines and 2-methylaziridine, respectively. In this study, we found that Ph_4SbBr and Ph_3SnBr were also effective catalysts for the synthesis of **2** from the reaction of CO_2 with **1**.



1 **2** **3**

Results and Discussion

The reactions of CO_2 with **1** were carried out in the presence of organo-antimony and -tin compounds. As shown in Table 1, in the case of Ph_4SbBr, **2** and 1,4-diphenylpiperazine(**3**) were obtained in 86 and 9% yields, respectively, whereas other antimony compounds show low selectivity. On the other hands, with Ph_3SnBr, **3** was obtained as a main product. On the basis of the above results, the reactions catalyzed by Ph_4SbBr and Ph_3SnBr were carried out under various conditions to survey the optimal conditions.

The yield of **2** in the reaction catalyzed by Ph_4SbBr at 80 °C increases linearly with an increase in reaction time, whereas, that of **3** increases during the first 10 min and then does not increase. In the case of Ph_3SnBr, the yields of **2** and **3** increase with an increase in the reaction time. To check the effect of reaction temperature, the reactions were carried out at temperatures from 40 °C up to 120 °C. In the case of Ph_4SbBr, **2** was selectively obtained above 60 °C. On the other hand, Ph_3SnBr did not show catalytic activity up to 60 °C, but the yields of **2** and **3** increased at higher temperature above 80 °C. In order to improve the catalytic activity of Ph_4SbBr and Ph_3SnBr, the reactions were carried out in solvents of different polarities as shown in Table 2. The solvent effect is very clear. The use of polar aprotic solvents such as HMPA and DMSO gave **2** in high yields, whereas the nonpolar solvents such as benzene and hexane gave poorer results.

Table 1. Catalytic activities of the organometallic compounds in the reaction of CO_2 with **1**[a)]

Catalyst	Yield/%[b)]	
	2	**3**
Ph_4SbCl	7	19
Ph_4SbBr	86	9
Ph_3SbBr_2	63	30
Ph_3SbO	0	trace
Me_3SbCl_2	trace	8
Me_3SbBr_2	18	45
Me_3SbI_2	4	45
Ph_3SnCl	0	0
Ph_3SnBr	23	47
n-Bu_3SnBr	11	18
n-Bu_2SnBr_2	15	44
None	0	0

a) **1**: 30 mmol, CO_2: 50 kg/cm², Catalyst: 0.5 mmol, Temp: 80 °C, Time: 6 h. b) Yields are of isolated products obtained after column chromatography.

Table 2. Effect of solvent on the reactions of CO_2 with **1** in the presence of Ph_4SbBr and Ph_3SnBr at 80 °C[a)]

Catalyst	Solvent	μ(D)[d)]	Yield/%[e)]	
			2	**3**
Ph_4SbBr[b)]	HMPA	5.37	93	0
	DMSO	4.3	85	Trace
	DMF	3.82	75	Trace
	Acetonitrile	3.37	53	4
	THF	1.75	21	3
	Dioxane	0.45	20	0
	Hexane	0.085	20	6
	Benzene	0	17	2
Ph_3SnBr[c)]	HMPA		76	Trace
	DMF		25	15
	THF		0	Trace
	Hexane		0	Trace

a) **1**: 10 mmol, CO_2: 50 kg/cm², Catalyst: 0.5 mmol, Solvent: 2 ml. b) 1 h. c) 3 h. d) Ref. 9. e) Yields were determined by GC.

Experimental

Materials. The organometallic compounds, Ph_3SbBr_2,[1c] Ph_4SbBr,[1c] Ph_4SbCl,[4] Me_3SbCl_2,[5] Me_3SbBr_2,[5] Me_3SbI_2,[5] Ph_3SbO,[6] Ph_3SnCl,[1d] Ph_3SnBr,[1d] *n*-Bu_3SnBr,[7] *n*-Bu_2SnBr_2[7] were prepared by the reported methods and checked by elemental analysis. 1-Phenylaziridine was prepared from 2-anilinoethanol.[8] The solvents were used after rectification.

Reaction Procedure. A mixture of 3.64 cm^3 (30 mmol) of **1** and 0.257 g (0.5 mmol) of Ph_3SbBr_2 was placed into a 50 cm^3 stainless steel autoclave. CO_2 was then introduced at a pressure of *ca.* 50 atmospheres (58.8 bar). The reaction was carried out for 6 h at 80 °C. After completion of the reaction, CO_2 was allowed to escape from the autoclave and the product was separated by column chromatography on silica gel (Wako-gel C-200; chloroform as an eluent). **3** was obtained from the first fraction and **2** from the second fraction. These were recrystallized from ethanol to give pure products. **2**; 2.7 g (yield 55%), mp 115—117 °C (lit,[9] 117—119 °C). **3**; 0.9 g (yield 25%), mp 166—169 °C (lit,[10] 163—164 °C).

Analytical gas chromatography(GC) was performed on a Shimadzu GC-3BT gas chromatograph by the use of Silicone OV-1 as packing.

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References

1) a) H. Matsuda, A. Ninagawa, R. Nomura, and T. Tsuchida, *Chem. Lett.*, **1979**, 573; b) H. Matsuda, A. Ninagawa, and R. Nomura, *ibid.*, **1979**, 1261; c) R. Nomura, A. Ninagawa, and H. Matsuda, *J. Org. Chem.*, **45**, 3735 (1980); d) R. Nomura, M. Kimura, S. Teshima, A. Ninagawa, and H. Matsuda, *Bull. Chem. Soc. Jpn.*, **55**, 3200 (1982).

2) A. P. Sineokov, F. N. Gladysheve, and V. S. Etlis, *Kim. Geterotsikl. Soedin.*, **1970**, 611: *Chem. Abstr.*, **73**, 66351d (1970).

3) a) K. Soga, S. Hosoda, H. Nakamura, and S. Ikeda, *J. Chem. Soc., Chem. Commun.*, **1976**, 617; b) K. Soga, S. Hosoda, and S. Ikeda, *Nippon Kagaku Kaishi*, **1978**, 246.

4) H. H. Willard, L. R. Perkins, and F. F. Blicke, *J. Am. Chem. Soc.*, **70**, 737 (1948).

5) H. Hibbert, *Ber. Deut. Chem. Ges.*, **39**, 160 (1906).

6) D. L. Venezky, C. W. Sink, B. A. Nevett, and W. F. Fortescue, *J. Organomet. Chem.*, **35**, 131 (1972).

7) H. Matsuda and S. Matsuda, *Kogyo Kagaku Zasshi*, **63**, 1960 (1960).

8) a) W. M. Pearlman, *J. Am. Chem. Soc.*, **70**, 871 (1948); b) H. W. Heine, B. L. Kapur, and C. S. Mitch, *ibid.*, **76**, 1173 (1954).

9) J. A. Riddick and W. B. Bunger, "Organic Solvents," in "Techniques of Chemistry," 3rd ed, ed by A. Weissberger, Wiley-Interscience, New York, (1970).

10) M. E. Dyen and D. Swern, *Chem. Rev.*, **67**, 197 (1967).

11) H. W. Heine, B. L. Kapur, and C. S. Mitch, *J. Am. Chem. Soc.*, **76**, 1173 (1954).