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REACTION OF CARBON DIOXIDE WITH EPOXIDES IN THE PRESENCE OF PENTAVALENT ORGANOANTIMONY COMPOUNDS

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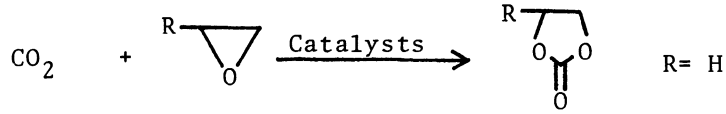
The reaction of carbon dioxide(CO_2) with epoxides in the presence of pentavalent organoantimony compounds gave corresponding cyclic carbonates as a product in almost quantitative yields even under mild conditions.

Recently, synthetic utilization of CO_2 has been extensively studied using various organometallic compounds as catalysts. We previously reported that methyltribromotin or butanestannoic acid have a catalytic activity for the reaction of CO_2 with ethylene oxide to give ethylene carbonate in 72 or 74% yields[1], respectively. In this communication, we describe the reaction between CO_2 and several epoxides catalyzed by pentavalent organoantimony compounds to give cyclic carbonates in almost quantitative yields even under mild conditions.



R= H, CH_3, CH_2Cl, and Ph.

The reaction was carried out in a 100 ml stainless steel autoclave in the range from 60 to 120°C. The time taken for heating up to the reaction temperature was 10 min , and then the reaction time was determined by measuring the time during which pressure in the autoclave fell to a constant value.

The results of the reactions are summarized in Table 1. In all reactions, corresponding cyclic carbonates were obtained in almost quantitative yields. Catalytic activity of organoantimony compounds seems to be superior to that of organotin compounds[1]. Especially, tetraphenylstibonium bromide and dibromotriphenylantimony showed notable catalytic activity, since cyclic carbonates were quantitatively obtained in short reaction time. Further, these antimony

compounds except pentaphenylantimony could be easily recovered from the reactions with propylene oxide. In the reactions with styrene oxide, poly(styrene oxide) was obtained as by-products in trace or ca. 10% yields. Judging from the reaction time, it seems that the reactivity of epoxides is in the following order; CH_3 > Ph > H > CH_2Cl.

Table 1 Reaction of CO_2 with epoxides catalyzed by pentavalent organoantimony compounds[a)]

Catalysts	Epoxides(R)	Temp.(°C)	Reaction time(min)	Yields(%) of cyclic carbonates[b)]
Ph_5Sb	H	120	330	82
	CH_3	120	130	87
Ph_4SbBr	H	120	12	96
	CH_3	120	8	92[c)]
		100	20	98[c)]
		60	120	93[c)]
	CH_2Cl	120	24	97
	Ph	120	16	91[d)]
Ph_3SbBr_2	H	120	38	95
	CH_3	120	16	97[c)]
		100	50	92[c)]
		60	390	97[c)]
	CH_2Cl	120	80	94
	Ph	120	24	82[e)]
Ph_3SbCl_2	H	120	180	99
		100	480	96
	CH_3	120	150	96[c)]
Me_3SbBr_2	H	120	15	72
		100	40	79
	CH_3	120	60	94[c)]
		100	150	91[c)]

a) Reaction conditions: Epoxides;0.1 mole , CO_2;0.2 mole (50kg/cm^2), Catalysts;0.001 mole. b) Based on epoxides. c) Catalysts were recovered. d) Trace of poly(styrene oxide) was obtained besides the carbonate. e) Poly(styrene oxide) was obtained in ca. 10% yield besides the carbonate.

Reference

1) H. Matsuda, A. Ninagawa, R. Nomura, and T. Tsuchida, Chem. Lett., 1979, 573.

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