Tetrahedron Letters,Vol.26,No.10,pp 1323-1324,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

CYCLOADDITION OF OXETANE AND CARBON DIOXIDE CATALYZED BY TETRAPHENYLSTIBONIUM IODIDE

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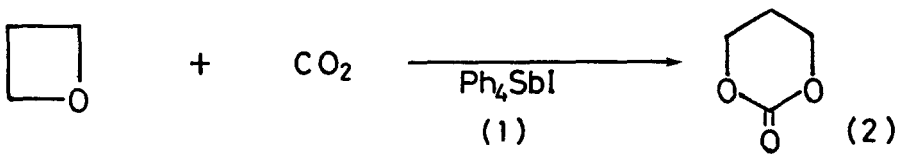
Abstract: Trimethylene carbonate was readily obtained in the reaction of oxetane and carbon dioxide in the presence of tetraphenylstibonium iodide.

Reactions of oxiranes and carbon dioxide (CO_2) have been ardently investigated and it is well known that the cycloaddition[1] and copolymerization[2] readily proceed by a variety of catalysts. We already reported that organoantimony- or organotin compounds excellently catalyze the cycloaddition.[3]

On the other hand, the reaction of oxetane with CO_2 has been scarcely reported because of the low reactivity.[4] To our knowledge, only one study[5] on the polymerization of oxetane and CO_2 was published except for our recent study,[6] in which organotin halide/base systems were found to cause the alternating copolymerization of them. However, in the tin-catalyst systems, only the polymerization occurred and no formation of trimethylene carbonate was observed.

Here, we wish to report a selective synthesis of trimethylene carbonate (2) from oxetane and CO_2 in the presence of tetraphenylstibonium iodide (1). This is probably the first example of the 1:1 cycloaddition of oxetane and CO_2.



All reactions were carried out as follows. A mixture of oxetane (20 mmol) and a catalyst (0.4 mmol) was placed in a 30 ml stainless steel autoclave. Then it was heated under CO_2-pressure (50 kg/cm^2). After the reaction, unreacted oxetane was removed under reduced pressure. The amounts of carbonate 2 and polymers were determined by GLC and ^{1}H-nmr, respectively. The reaction conditions and results are summarized in Table. It is obvious that 1 has characteristically a high activity for the formation of 2, since no reaction by other onium salts such as Ph_4PI and Bu_4NI (entry 2, 3). Moreover, neither Ph_3SbI_2 nor Ph_4SbBr could promote the cycloaddition under the similar conditions (entry 4, 5); these antimony halides are highly active in the reaction of oxiranes and CO_2.[3] In contrast to organotin halide/base systems which exclusively catalyzed the formation of polycarbonate, 1 gave 2 in a high yield.

The catalytic activity of 1 in benzene is higher than in polar solvents such as CH_3CN

and hexamethylphosphoric triamide (HMPA) (entry 8-10). The antimony-halogen bond has a covalent character, and a poor electrolytic property even in polar solvents has been reported.[7] Moreover, onium salts such as Ph_4PI and Bu_4NI were not effective at all. From these facts, it is suggested that a free I^- ion plays no important role in this antimony-catalyzed reaction. It is noteworthy that the iodide 1 is very effective for the formation of 2, but that 1 has no activity to the polymerization of 2 in spite of the readily polymerizable property[8]. No polymer was yielded even in the presence of a base (entry 11). Actually, 2 was not polymerized by 1 at all in similar conditions to those shown in Table.

Table. Reactions of Oxetane with Carbon Dioxide[a)]

entry	catalyst[b)]	solvent[c)]	conditions	yield(%) of 2	yield(%) of polymer
1	Ph_4SbI	-	100°C, 4h	96	0
2	Ph_4PI	-		0	0
3	Bu_4NI	-		0	0
4	Ph_3SbI_2	-		8	25[d)]
5	Ph_4SbBr	-		2	0
6	Ph_4SbI	-	120°C, 1h	84	0
7	Ph_4SbI	-	80°C, 24h	90	0
8	Ph_4SbI	benzene	100°C, 4h	90	0
9	Ph_4SbI	CH_3CN		79	0
10	Ph_4SbI	HMPA		69	0
11	Ph_4SbI-Ph_3P	-		75	0
12	Ph_3SnI-Bu_3P	-	100°C, 6h	0	100[e)]
13	Ph_3SnI	-		0	0

a) Oxetane 20 mmol, cat. 0.4 mmol, Pco_2= 50 kg/cm^2. b) Catalysts bearing no halogen such as Ph_3SbO and Ph_3Sb had no effect. c) Solvent = 2 ml (entry 8-10), no solvent (the others). d) Polymers contained both polyoxetane and polycarbonate. e) Polycarbonate. This result was reported in reference 6.

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(Received in Japan 24 November 1984)